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The Effect of Local Crystalline Environment on Hydrogen Atom Behavior in Molecular Complexes of a Proton Sponge

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Local Crystalline Environment.

Abstract

Proton behavior within the hydrogen bond (HB) networks of five molecular complexes of the proton sponge DMAN and different organic acids is investigated by single crystal neutron diffraction. The complexes form with either 2:1 (acid:DMAN) or 1:1 stoichiometric ratios and contain common structural motifs. All show proton transfer from an acid to DMAN forming a DMANH^+ moiety and hydrogen bonded acid dimers; complexes with halobenzoic acids have acid molecules linked by short, strong, charge-assisted HBs, while all complexes contain a short, strong, intramolecular $\text{N-H}\cdots\text{N}$ HB in DMANH^+ . The hydrogen atom behavior within the short, strong HBs, accurately described from the neutron data, is rationalized in terms of weak interactions in the local crystal environment, with the position of the proton within both sets of short, strong HBs affected by a combination of the weak interactions in the vicinity of the HBs. A correlation is also found between the thermal motion of the bound proton in the $\text{N-H}\cdots\text{N}$ HB of DMANH^+ and nearby oxygen atoms when they are sufficiently close to one another. This work shows that all interactions in the local environment combine to determine the behavior of protons within short, strong HBs and that by taking these interactions into account further control over the crystal structure and properties may be achievable.

Introduction

Intermolecular interactions form the basis upon which crystal engineering is used to attempt the design and control of materials in the solid-state.¹⁻⁴ The most commonly used interaction is the hydrogen bond (HB);⁵ these range from very short HBs where the electron of the hydrogen atom is shared almost equally between the donor and acceptor atoms, similar to a covalent bond,⁶ through bifurcated HBs involving multiple donors/acceptors⁷ to long range, weak HBs involving, for example, π electron clouds as acceptors.⁸ Rules for the formation of HBs have long been known⁹

and HBs now underpin many of the supramolecular synthons used to form robust and reproducible structural motifs, allowing an element of control to be exerted over solid-state architectures.^{10,11} To control further the assembly of molecules in the solid-state, much research has been carried out to attempt the design of specific types of HBs; for example, studies have been conducted on the utility of pK_a matching¹² or the use of Hammett substitution constants.¹³ These types of studies are important, not only in terms of building reproducible structural motifs which can be predicted, but also because certain types of HB may display interesting and potentially desirable characteristics such as solid-state proton migration¹⁴ in strong HBs or proton disorder¹⁵ in moderate HBs; such characteristics could lead to the generation of valuable solid-state physical properties such as, for example, thermochromism.¹⁶

While the HBs act as the main driving force behind assembly in the solid-state and govern the general crystallographic structure, to fully understand the behavior of the hydrogen atoms within HBs, particularly in systems which may display features such as proton migration or disorder, a more complete picture of the interactions in the local crystalline environment is required. A recent study has shown that weaker interactions in the local environment of HBs may play a role in the presence (or absence) of proton disorder within 3,5-dinitrobenzoic acid dimers, potentially enabling tuning of the temperature at which the disorder manifests,¹⁵ while a further study investigated the degree of proton transfer in multi-component complexes of 4-phenylpyridine and found that the local environment also played a role here.¹⁷

In this work, we investigate the effects of the local crystalline environment on the behavior of hydrogen atoms within different types of HBs in complexes of the proton sponge, N,N,N',N'-tetramethyl-1,8-naphthalenediamine (DMAN) (Figure 1). DMAN acts as a strong base which readily accepts a proton when complexed with an acid, hence the term proton sponge.^{18,19} DMAN-acid complexes always contain a strong, intramolecular N-H···N HB containing the bound

proton within a protonated DMANH^+ moiety and the consequent deprotonation of the acid often forms, as in the case of complexes of DMAN with halobenzoic acids, strong, charge-assisted $\text{O-H}\cdots\text{O}$ HBs within acid dimer units.²⁰ Therefore, DMAN-acid complexes present an excellent family of compounds to use in the investigation of local environment effects on proton behavior within strong HBs as they present two distinct types of strong HBs. Moreover, high resolution X-ray diffraction studies have already shown the potential for the local environment to exert a significant influence on the electronic behavior of the hydrogen atom within the $\text{N-H}\cdots\text{N}$ HB of a protonated DMANH^+ moiety;²¹ a more in-depth study of a larger number of complexes is necessary to further understand the role of the local environment on proton behavior. DMAN-acid complexes also usually have an acid oxygen atom interacting with the methyl groups of the protonated DMAN and close to the intramolecular $\text{N-H}\cdots\text{N}$ HB; by studying a series of DMAN-acid complexes it may therefore be possible to monitor the effect of "tuning" the length of this interaction while still maintaining the same robust structural motif so that direct comparisons can be made.

In another recent X-ray diffraction study, DMAN was crystallized with several organic acids revealing the presence of the same structural motifs containing strong HBs described above.²⁰ In this X-ray study, it was not possible to accurately locate or describe the behavior of the hydrogen atoms within the short, strong HBs due to the weak scattering from hydrogen. Therefore, to investigate the behavior of these hydrogen atoms, we have conducted single crystal neutron diffraction studies on several of these DMAN complexes; neutron diffraction enables precise and unambiguous hydrogen atom location while also allowing for the refinement of hydrogen atom anisotropic displacement parameters. Structural data of five DMAN molecular complexes with organic acids are presented: the previously investigated 1:2 (DMAN:acid) complexes with 2-fluorobenzoic acid (2-FBA), 2-iodobenzoic acid (2-IBA) and 4-iodobenzoic acid (4-IBA)²⁰ and two new 1:1 complexes with chloranilic acid (CLA) and 2,3-dihydroxybenzoic acid (2,3-OHBA)

(Figure 1), which display similar structural motifs to the previously described complexes. X-ray data are also presented for the previously unknown complexes with CLA and 2,3-OHBA.

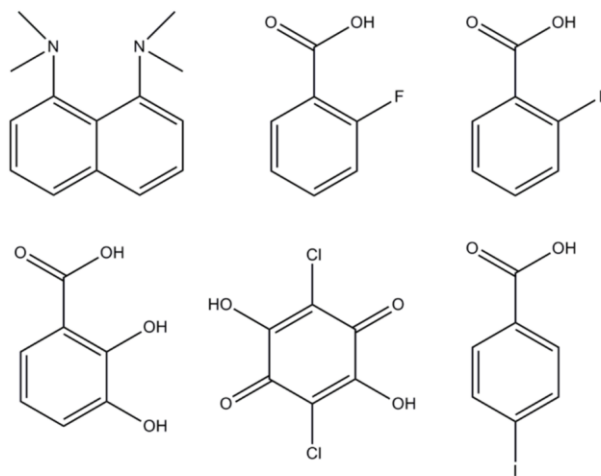


Figure 1. Clockwise from top left: molecular structure diagrams of DMAN, 2-fluorobenzoic acid, 2-iodobenzoic acid, 4-iodobenzoic acid, chloranilic acid and 2,3-dihydroxybenzoic acid.

Experimental

Crystals of the 1:2 complexes of DMAN with 2-FBA (**1**) and DMAN with 4-IBA (**3**) were obtained by slow evaporation from acetonitrile solutions at 50 °C and room temperature (RT), respectively. Crystals of the 1:2 complex of DMAN with 2-IBA (**2**) were obtained by slow evaporation from an acetone solution at RT. Crystals of the 1:1 complexes of DMAN with CLA (**4**) and DMAN with 2,3-OHBA (**5**) were obtained by slow evaporation from methanol solutions at 4 °C and RT, respectively.

X-ray data for complexes **4** and **5** were collected on a Bruker Nonius Kappa diffractometer equipped with a CCD area detector and an Oxford Cryosystems N₂ low temperature device²² using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Reflections were processed using the DENZO / SCALEPACK programs²³ and an absorption correction applied using the SADABS program.²⁴ Data were collected at 100 K for complex **4** and at 100, 200 and 300 K for complex **5**. The structures were

solved by direct methods using SHELXS-97²⁵ and refined with anisotropic displacement parameters for all non-H atoms using SHELXL-97²⁵ within WINGX.²⁶ Hydrogen atoms were located using Fourier difference methods and refined isotropically.

Neutron data for complex **2** have been reported previously.²⁰ Neutron data for the four remaining complexes were collected on the Very Intense Vertical Axis Laue Diffractometer (VIVALDI)²⁷ at the Institut Laue-Langevin reactor source in Grenoble, France. Data were collected at 200 K for all complexes, with the temperature maintained by a He-flow cryostat. No absorption corrections were deemed necessary due to the small sizes of the crystals used. Orientation matrices were determined using the program LAUEGEN.²⁸ Unit cell parameters were assumed to be the same as those determined from X-ray data as the Laue method at a continuous neutron source only allows relative linear cell dimensions to be determined precisely. Reflections were integrated using ARGONNE_BOXES²⁹ and normalized to a common wavelength, scaled and merged with LAUE4.³⁰ The final refinement for all neutron data sets was completed using SHELXL-97²⁵ within the program WINGX²⁶ with initial atomic coordinates taken from the X-ray structures. All hydrogen positional and anisotropic displacement parameters have been fully refined for each neutron structure.

Results and Discussion

Crystal Structures

The complexes of DMAN with halobenzoic acids (**1-3**) form in a 1:2 (DMAN:acid) ratio, while the complexes of DMAN with CLA and 2,3-OHBA (**4-5**) form in a 1:1 ratio. The X-ray structural determinations of complexes **1-3** have been previously reported, along with the neutron structural determination of complex **2**,²⁰ in the present work the other neutron determined structures are reported and compared. For complexes **4** and **5**, both the X-ray and neutron determined structures

are reported here. All structural determinations were carried out at 200 K and all values reported in the text were derived from the neutron data, unless otherwise stated.

The structures of the five molecular complexes are similar and share several common features and strong interactions. In all complexes, a proton has transferred from an acid molecule to a DMAN molecule, where it is bound in a strong, intramolecular N-H \cdots N HB, and a hydrogen bonded acid dimer forms. The N-H \cdots N HBs containing the bound proton are all asymmetric, with the hydrogen atom not centered within the HB. In all cases, a DMANH⁺ moiety is created and an acid molecule is deprotonated. In the case of the halobenzoic acid complexes **1-3**, this deprotonated acid coexists with a neutral acid molecule, but in complexes **4-5**, only charged species are present. In each case a hydrogen bonded dimer is formed between two acid molecules; this is singly charged for **1-3** and will be denoted DIMER⁻, or doubly charged in the case of **4-5**, denoted DIMER²⁻. In all complexes, an acid molecule is located above the N-H \cdots N HB of DMANH⁺ where either one (in **1-3**) or two (in **4-5**) oxygen atoms from an acid molecule interact with the bound proton and methyl hydrogen atoms of DMANH⁺.

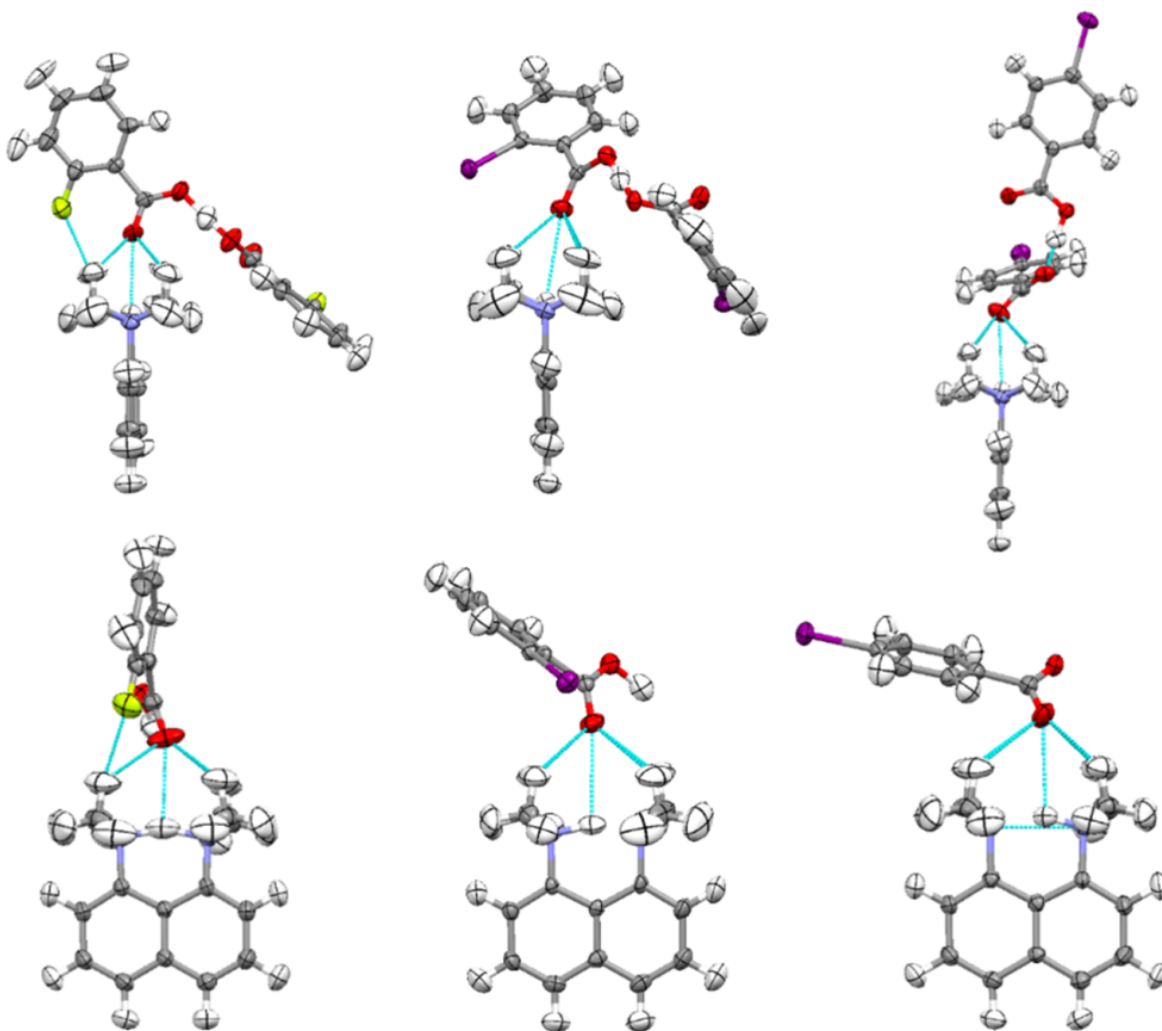


Figure 2. Crystal structures of the 1:2 molecular complexes of DMAN with 2-FBA (**1**; top and bottom, left), 2-IBA (**2**; top and bottom, center) and 4-IBA (**3**; top and bottom, right). The top images show the orientation of DIMER⁻ moieties relative to DMANH⁺; in each structure one acid oxygen atom is located above the N-H···N HB of DMANH⁺ containing the bound proton. The bottom images show the interactions between acid molecules and bound protons and methyl hydrogens of DMANH⁺ more clearly, with an acid molecule of the DIMER⁻ omitted in each for clarity.

The crystal structures of **1-3** determined by X-ray diffraction have been reported previously.²⁰ The structures of these three complexes differ in the precise location of the DIMER⁻ above the

DMANH⁺ moiety and in the weaker interactions in which both the DMANH⁺ and DIMER⁻ are involved; all structures contain one DMANH⁺ and one DIMER⁻ in the asymmetric unit. A short, strong, charge-assisted O-H \cdots O HB is present in each of the three complexes and links the two molecules in the DIMER⁻, the hydrogen atoms within these HBs are not centered (Figure 2). Dimers are twisted or bent around the charge-assisted HB so that the molecules in the DIMER⁻ are not coplanar, torsion angles of ~ 86.7 and 114.0° around the charge-assisted HB are observed in **1** and **2**, respectively, while in **3** the dimer is bent with an angle of $\sim 74.3^\circ$ between the planes of the two aromatic rings of the molecules in the DIMER⁻ (Figure 2). The three complexes each have one oxygen atom of the DIMER⁻ interacting with the bound proton (for distances see Table 1) and methyl groups of DMANH⁺ (C \cdots O distances range from 3.230(5) Å in **1** to 3.646(5) Å in **2**).

The two 1:1 molecular complexes (**4-5**) also form HBs between acid molecules. In contrast to the 2:1 complexes, a dimer of acid molecules connects two DMANH⁺ molecules creating a four molecule supramolecular unit rather than the three molecule unit found in the 2:1 complexes. This difference in stoichiometry and supramolecular connectivity is a consequence of the increased number of HB donors and acceptors on the two acid molecules allowing a more extended hydrogen bonded structure (and also for the protonation of the two DMAN molecules in these complexes).

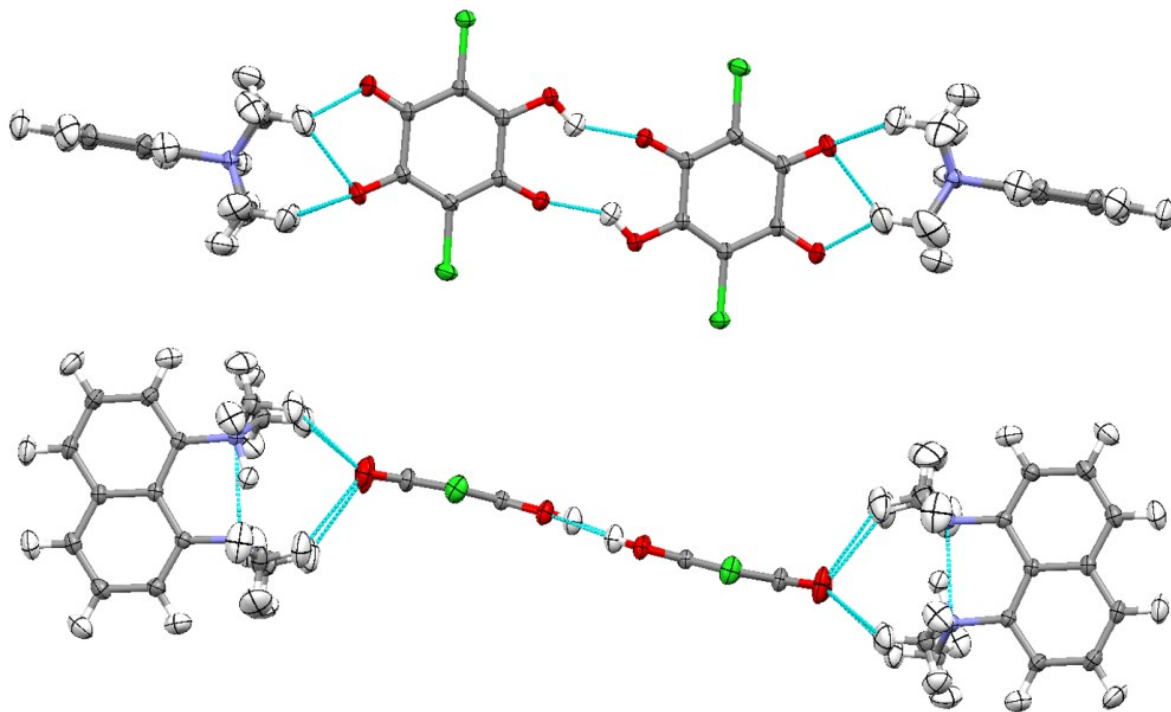


Figure 3. Crystal structure of the 1:1 CLA complex (**4**) showing two DMANH^+ moieties containing bound protons linked by a DIMER^{2-} unit; two acid oxygen atoms are located above the DMANH^+ $\text{N-H}\cdots\text{N}$ intramolecular HBs containing bound protons. The top image shows the HBs of the DIMER^{2-} while the bottom image shows the same unit in a different orientation where the interactions between acid oxygen atoms and hydrogen atoms of DMANH^+ are visible.

The 1:1 CLA complex (**4**) crystallizes with one DMANH^+ and one CLA^- molecule in the asymmetric unit (Figure 3). It contains a DIMER^{2-} formed by two singly deprotonated CLA^- molecules. The acid molecules of the dimer are linked by two symmetry equivalent $\text{O-H}\cdots\text{O}$ HBs, forming a $R_2^2(10)$ hydrogen bonded ring in a similar manner to that found in other molecular complexes containing singly deprotonated CLA^- molecules.³¹ These $\text{O-H}\cdots\text{O}$ HBs are only moderate in strength, with an $\text{O}\cdots\text{O}$ distance of 2.681(5) Å; this is shorter than the HB observed in the neutral, pure CLA structure where the $\text{O}\cdots\text{O}$ distance of the HB is 2.752 Å.³² Also compared with pure CLA, where the electron density is distributed equally on each side of the molecule as it

is located on an inversion center,³² the electron density on the CLA⁻ molecule in **4** is skewed towards the side of the molecule nearer the DMANH⁺ moiety and away from the side of the molecule involved in the HB of the dimer; this can be inferred by the C-O bond distances which are shortest on the side pointing towards DMANH⁺ (1.213(2) and 1.236(2) Å) and longer on the side involved in the dimer HB (1.323(2) Å for the protonated oxygen and 1.252(2) Å for the other oxygen). The fact that the C-O bond distance involving the non-protonated oxygen of the dimer HB is intermediate between a single and double bond shows that the dimer HB is also charge-assisted. The molecules of the dimer are approximately coplanar and each acid molecule is above the N-H \cdots N intramolecular HB of DMANH⁺ containing the bound proton, with two acid oxygen atoms interacting with the bound proton (distances in Table 1) and methyl group hydrogens (C \cdots O distances range from 3.219(2) to 3.737(2) Å). There are several weak interactions between the DIMER²⁻ molecules and nearby DMANH⁺ molecules, while the DMANH⁺ molecules are also involved in parallel slipped π - π stacking with other, inverted DMANH⁺ molecules.

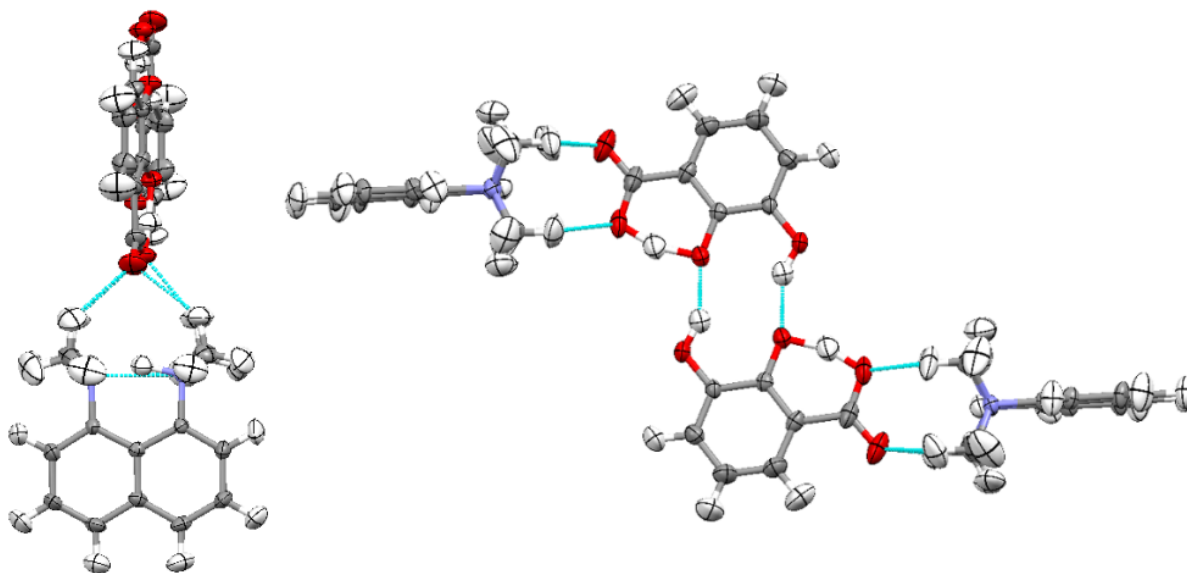


Figure 4. Crystal structure of the 1:1 2,3-OHBA complex (**5**) showing the location of one 2,3-OHBA⁻ molecule above the N-H \cdots N intramolecular HB of DMANH⁺ containing the bound proton

(left) and the hydrogen bonded DIMER²⁻ with the two acid oxygen atoms interacting with the DMANH⁺ units clearly visible (right).

The 1:1 2,3-OHBA complex (**5**) contains one DMANH⁺ and one 2,3-OHBA⁻ molecule in the asymmetric unit (Figure 4). A DIMER²⁻ forms, made up of two singly deprotonated 2,3-OHBA⁻ molecules linked by two symmetry equivalent O-H \cdots O HBs, forming a $R_2^2(10)$ hydrogen bonded ring; each 2,3-OHBA⁻ molecule also contains an intramolecular O-H \cdots O HB. The intermolecular O-H \cdots O HB of the dimer is moderate in strength while the intramolecular O-H \cdots O HB is strong, with O \cdots O distances of 2.681(5) and 2.427(5) Å, respectively; the intramolecular HB length is shorter than those observed in pure 2,3-OHBA (2.597 Å in both the triclinic and monoclinic polymorphs).³³ The proton within the strong intramolecular HB is not centered and lies closer to the oxygen atom interacting with the DMANH⁺; this behavior is not investigated in detail in this work as it is the only HB of this type in the complex series and therefore systematic comparisons cannot be made. As in the previous structures, an acid molecule sits above the intramolecular N-H \cdots N HB of DMANH⁺ containing the bound proton; two acid oxygen atoms interact with the bound proton (distances in Table 1) and methyl hydrogens of DMANH⁺ (C \cdots O distances range from 3.293(6) to 3.561(7) Å). There are again several weak interactions between the DIMER²⁻ and nearby DMANH⁺ molecules and the DMANH⁺ molecules again π - π stack in a head-to-tail conformation.

Interactions between Acid Molecules and the Bound Proton of DMANH⁺

The five complexes presented in this work all contain the common structural motif of an acid molecule located above the intramolecular N-H \cdots N HB of a protonated DMANH⁺ molecule, with interactions between one or two acid oxygen atoms and the bound proton of DMANH⁺. The effect of such interactions in DMAN molecular complexes has been highlighted previously³⁴ and here we

attempt to more accurately quantify the effects with neutron diffraction data. These interactions in the five systems occur over different distances depending on the complex: O \cdots H distances range from 2.666(6) Å in complex **1** to 3.716(3) Å in complex **4** (Table 1). With the location and anisotropic displacement parameters of the hydrogen atoms determined precisely and unambiguously by neutron diffraction, this series of molecular complexes presents an opportunity to investigate any effect of the nearby oxygen atoms on the behavior of the bound protons and how this changes over distance.

Theoretical studies of the potential energy surfaces in which the bound protons of a proton sponge reside suggest that for an N-H \cdots N HB with a short N \cdots N distance (such as those presented in this work), the potential is either a flat, single minimum or a double-well potential with a very low energy barrier between the two positions; the energy barrier increases in height as the N \cdots N distance increases.³⁵ In both of these scenarios the proton can readily move along the bond with minimal energy requirement. The N \cdots N distances in the five DMAN complexes presented here are very short for N-H \cdots N HBs, with distances ranging from 2.570(3) to 2.6209(10) Å (Table 2). As these structures have been determined at 200 K, thermal displacement parameters of the bound protons (representative of the possible movement) should be well defined and an expected elongation of the density along the N \cdots N direction of the HB due to the flat potential well may be observed; from the data a range of values are observed for the size of the thermal ellipsoids and of the corresponding anisotropic displacement parameters of the bound protons (Table 1 and Figure 5).

Table 1. Distances between the bound proton in DMANH⁺ and acid oxygen atoms above the N-H \cdots N HB in the five complexes listed in ascending order. Listed alongside is the largest principal

thermal parameter of the bound proton. The two values for the interaction distance in complexes **4-5** correspond to the two oxygen atoms which interact with the bound proton in these complexes.

Complex	O \cdots H / Å	U_{\max} Hydrogen / Å ²
2-FBA (1)	2.666(6)	0.1087
4-IBA (3)	2.809(6)	0.0477
2-IBA (2)	2.912(5)	0.0647
CLA (4)	2.985(3)	0.0388
	3.716(3)	-
2,3-OHBA (5)	3.053(8)	0.0467
	3.355(9)	-

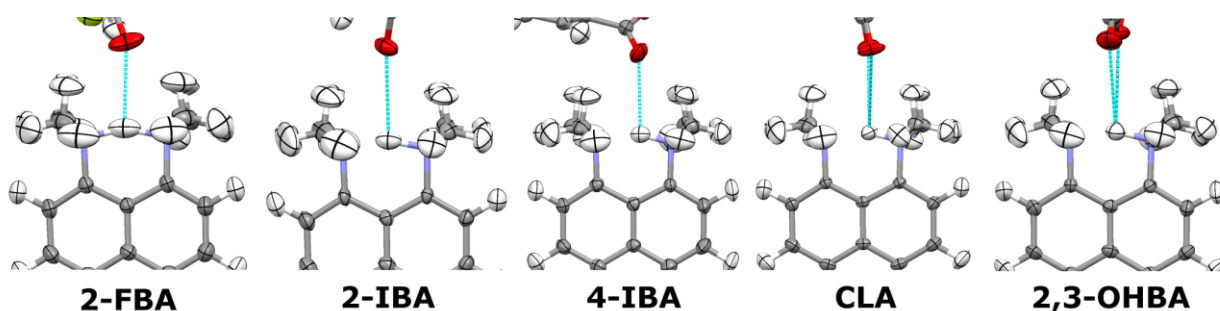


Figure 5. Interactions between the bound protons in the intramolecular N-H \cdots N HB of DMANH⁺ and the nearest acid oxygen atoms for the five complexes.

Of the five complexes, that with 2-FBA (**1**) has the largest anisotropic displacement parameter for the bound proton; this complex also has the shortest O \cdots H distance and the oxygen also has a large anisotropic displacement parameter along the N \cdots N direction of the intramolecular HB containing the bound proton (Table 1 and Figure 5). It appears that the relatively short distance between the oxygen and hydrogen leads to an interaction and a correlated movement along the direction of the N-H \cdots N HB. It is not possible from this example alone to determine if the

movement of the proton within the flat potential causes the oxygen atom to also have a larger thermal motion or *vice versa*, though it is clear that the behaviors are correlated.

The next closest interaction is found in the complex with 4-IBA (**3**); here the displacement parameters of the bound proton are much smaller and the equivalent parameters of the acid oxygen, whilst still significantly elongated, are no longer along the direction of the N-H \cdots N HB. This would suggest that in **1**, the movement of the bound proton is perhaps more a consequence of the movement of the oxygen atom than the other way around, with the oxygen atom acting to encourage movement of the proton within the flat potential well. A similar observation is made in the complex with 2-IBA (**2**) which has the next shortest interaction. The oxygen atom displacement ellipsoid is still significantly elongated, though again not along the direction of the N-H \cdots N HB, and the thermal motion of the bound proton is again reduced compared to **1** (though elongated along the N \cdots N direction and larger than in **3**). It may be that the longer distance between the bound proton and acid oxygen atoms in **2** and **3** is now too large for the oxygen atom to have a significant influence on the behavior of the bound proton; the distance limit within which the oxygen atom can influence the behavior of a proton with a flat potential well in complexes such as these would then be concluded to lie in the region of $\sim 2.67 - 2.81$ Å. Alternatively or in addition, it may be that the shape of the potential well in which the bound proton resides means that it is only when the displacement parameters of the oxygen atom are elongated along the direction of the N-H \cdots N HB that a correlation is observed.

Complexes **4** and **5** present a slightly different situation due to the presence of the second acid oxygen atom interacting with DMANH⁺. In both complexes, the bound proton has smaller anisotropic displacement parameters compared with the other three complexes; however, the displacement parameters of the oxygen atoms are still elongated approximately along the direction of the N-H \cdots N HB. The smaller anisotropic displacement parameters of the bound proton could

potentially be the result of the additional interaction acting to stabilize the position of the proton; however, as these contacts are at a greater distance than those in the other complexes, the distance may be too great for the oxygen atom to have a significant effect on the behavior of the bound proton even if the oxygen atom displacement parameters are elongated along the direction of the N-H \cdots N HB. Therefore, the effect of an oxygen atom on the bound proton behavior appears to be dependent on both the distance between the two atoms and also the thermal behavior of the oxygen atom itself whilst the flat-bottomed potential well of the N-H \cdots N HB means that the proton is free to move when the interaction to an oxygen is sufficiently short and the oxygen moves along the direction of the HB within which the bound proton resides.

Position of the DMANH⁺ Bound Proton

In the X-ray determinations of the complexes presented in this work, locating the position of the bound proton within the intramolecular N-H \cdots N HB of DMANH⁺ proved difficult.²⁰ With neutron data now available and the hydrogen atoms accurately located (see Figure 6 and the Fourier difference maps in Supporting Information), the N-H \cdots N HBs are clearly found to be asymmetric with the hydrogen atoms within them not centered (Table 2). In an isolated DMANH⁺ molecule, it would be expected that the hydrogen atom within this HB would be located centrally;³⁵ however, a close to centered proton is only found in complex **1**. Therefore, other interactions must be playing a role in determining the lowest energy position of the proton within the N-H \cdots N HB.

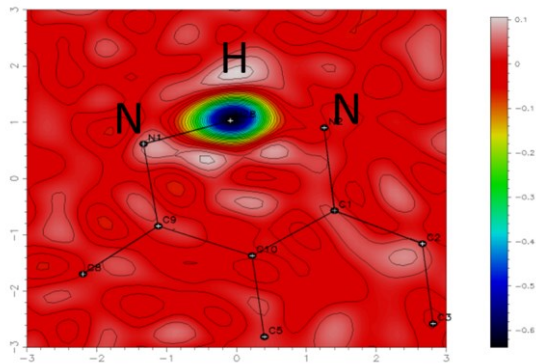


Figure 6. A Fourier difference map of the intramolecular N-H \cdots N HB in the DMANH $^+$ molecule of the 2-FBA complex (**1**) generated from the 200 K neutron diffraction data. The hydrogen atom is removed from the structural model and the difference in the nuclear density between the experimental data and the structural model is displayed. A cut of the nuclear density through the HB shows the negative density (as hydrogen has a negative scattering length for neutrons) where the hydrogen atom should be. The refined atomic positions from the structural model are overlaid showing the agreement with the measured nuclear density. Similar Fourier difference maps for the other complexes are presented in the Supporting Information.

Table 2. Hydrogen bond distances of the intramolecular N-H \cdots N HB in the DMANH $^+$ molecule of the five complexes.

Complex	N-H / Å	H \cdots N / Å	N-H \cdots N / Å	\angle NHN / $^\circ$
2-FBA (1)	1.310(6)	1.342(6)	2.595(2)	156.2(5)
2-IBA (2)	1.200(7)	1.417(6)	2.570(3)	158.1(4)
4-IBA (3)	1.102(6)	1.562(6)	2.602(3)	154.9(5)
CLA (4)	1.115(7)	1.565(2)	2.6209(10)	155.5(2)
2,3-OHBA (5)	1.172(6)	1.485(6)	2.600(3)	155.9(5)

The most obvious interaction which may affect the position of the hydrogen atom in the N-H \cdots N HB is that with the oxygen atoms of the acid as discussed above, however, while these oxygen atoms are located above the HB, they are not located centrally. To estimate how centrally the oxygen atoms are located above the HB, the distance between the DMANH⁺ nitrogen atoms and the oxygen atoms can be measured. In complex **1**, where the proton is close to the center of the HB, the distances between the nitrogen atoms and the acid oxygen are 3.164(4) and 3.258(4) Å; the hydrogen atom is located closer to the nitrogen furthest from the oxygen. It could be expected that the hydrogen would be located closer to the nitrogen atom nearest the oxygen due to the attractive interaction to the oxygen affecting the shape of the potential energy surface of the N-H \cdots N HB and therefore the location of the hydrogen atom, but this is not the case in **1**, and contributions from other weak interactions may also play a part. In particular, the weak interactions (e.g. C-H \cdots O, π - π , C-H $\cdots\pi$) to each of the fused rings of DMANH⁺ are asymmetric and this could lead to one side of the N-H \cdots N HB being favored over the other.

This asymmetry of weak interactions to either side of the DMANH⁺ molecule is a feature of all five complexes. While these weak interactions could play a role in determining the position of the bound proton, the interaction to the acid oxygen atoms above the N-H \cdots N HB also plays a part; evidenced by the fact that in the four other complexes (apart from **1**), the hydrogen atom is located closer to the nitrogen atom closest to the oxygen above. The position of the bound proton therefore seems to depend on a combination of factors influenced by the local environment of the N-H \cdots N HB and the DMANH⁺ molecules, so that many interactions must be taken into account to be able to account fully for the hydrogen atom behavior.

Proton Position in Charge-Assisted HBs

In the 1:2 DMAN complexes with halobenzoic acids (**1-3**), another type of short, strong HB is present: the charge-assisted HB linking the molecules in the DIMER⁻ units. As in the case of the

proton in the N-H \cdots N HBs of DMANH⁺, it is not possible to accurately locate these hydrogens from the X-ray structural determinations; the hydrogen atoms could be identified in Fourier difference maps but the electron density was often smeared out and the clearest indication of the position of the proton was elucidated from the C-O and C=O bond distances of the acid groups where two bond distances which are close in length would indicate the presence of a delocalized negative charge and hence less bonding with the hydrogen atom.²⁰ From the neutron data presented in this work, an assessment of the effect of the local crystal environment on the proton position within the charge-assisted HBs can now be made.

The formation of the charge-assisted HB, along with other weaker interactions such as those between acid molecules and the methyl hydrogens and bound proton of DMANH⁺, acts to stabilize the negative charge on the acid dimer. In the absence of other interactions to the DIMER⁻, the hydrogen atom of the charge-assisted HB would be centered within the HB and shared equally between the two molecules of the dimer to give the greatest stabilization, in effect having half a negative charge on each molecule. However, as in the case of the N-H \cdots N HB of DMANH⁺, the hydrogen atom is not shared equally between the two molecules of the dimer according to the neutron data and therefore other interactions must play a role in determining the position that it adopts (Table 3).

Table 3. Hydrogen bond distances for the short, strong, charge-assisted O-H \cdots O HBs in the halobenzoic acid dimer; (a) represents the oxygen atom of the acid molecule interacting with the bound proton of DMANH $^+$ while (b) is the other acid molecule of the dimer which is not positioned above the DMANH $^+$ molecule.

Complex	O \cdots H / Å (a)	O \cdots H / Å (b)	O-H \cdots O / Å
2-FBA (1)	1.290(7)	1.170(7)	2.453(5)
2-IBA (2)	1.201(5)	1.265(6)	2.465(4)
4-IBA (3)	1.360(5)	1.108(6)	2.465(4)

The acid molecule of the DIMER $^-$ located above the DMANH $^+$ and interacting with the bound proton can be denoted as acid **A**, while the other acid molecule of the dimer which does not interact directly with the bound proton can be denoted as acid **B**. In both the 2-FBA (**1**) and 4-IBA (**3**) complexes, the hydrogen in the charge-assisted HB is found to lie closer to acid **B**. In these two complexes, both acid molecules in the dimer take part in a similar number and type of weaker interactions when excluding the interactions to the DMANH $^+$ bound proton and methyl groups, therefore suggesting the two molecules benefit from the same level of stabilization from these interactions. Once the interactions to the DMANH $^+$ bound proton and methyl groups are taken into account, it is clear that acid **A** benefits from increased stabilization compared with acid **B** and this therefore explains the hydrogen of the charge-assisted HB being located closer to acid **B** in these two complexes (Table 3).

In contrast to the situation in **1** and **3** above, in the complex with 2-IBA (**2**) the hydrogen atom of the charge-assisted HB is located closer to acid **A**. As in **1** and **3**, the two molecules of the DIMER $^-$ are involved in a similar type and number of weaker interactions when excluding those to the bound proton and methyl hydrogens of DMANH $^+$. Therefore, when these interactions are

accounted for it may be expected that the hydrogen would reside closer to acid **B**, but this is not the case. The reason for this may be that the distance between the acid **A** and the DMANH^+ in **2** is longer than in the other two complexes ($\text{O}\cdots\text{H}$ distances between the bound proton and acid **A** are listed in Table 1). This again shows that it is a combination of weaker interactions in the local crystal environment which determine the hydrogen atom position in the strong HBs studied here.

Conclusions

We have presented a neutron diffraction study of five molecular complexes of the proton sponge DMAN with various organic acids. All the structures show one proton transferred to the DMAN molecule and contained within an intramolecular short, strong $\text{N-H}\cdots\text{N}$ HB and a structural motif of an acid oxygen atom interacting with this bound proton. The thermal motion of the bound proton is found to be correlated with that of the nearby oxygen atoms when the distance between them is sufficiently short (less than $\sim 2.8 \text{ \AA}$) and the thermal parameters of the oxygen atom are elongated along the direction of the $\text{N-H}\cdots\text{N}$ HB. At longer distances or where the oxygen displacement parameters are elongated in different directions, no obvious correlation in behavior is apparent. The asymmetry of the $\text{N-H}\cdots\text{N}$ HBs, manifest in the non-centering of the proton in the HB, is found to be affected by local crystal environment. Asymmetric weak interactions to each side of the DMANH^+ molecule play a role, in combination with the interaction with the nearby acid oxygen atoms. Finally, the position of the proton in the charge-assisted HBs in the DIMER^- of the complexes with halobenzoic acids is also found to be affected by a combination of the weak interactions in the local environment of the HB.

This study takes advantage of the benefits of neutron diffraction in accurately defining hydrogen atom parameters, the unique opportunity presented by these complexes in terms of the number and type of short, strong HBs present, and the similarity of structures which allows systematic comparisons to be made. While the number of complexes studied is limited, this study represents

one of the most comprehensive neutron diffraction studies of proton sponges to date, and it is clear from these data that the proton behavior can be rationalized by taking the weak interactions in the local crystal environment into account. Studies such as this allow for a greater understanding of how weaker interactions may play a subtle role in affecting the behavior of hydrogen atoms within HBs. This effect is likely to be greater in materials containing short, strong HBs as the potential of the HB is flatter and the proton within more easily manipulated. Therefore, these results may aid in the design of materials with desirable features such as solid-state proton migration which is only observed in short, strong HBs.

ASSOCIATED CONTENT

Supporting Information. Summary of the crystallographic data; Fourier difference maps imaging the hydrogen atoms in the N-H \cdots N hydrogens bonds of DMANH⁺ in complexes **2-5**; Crystallographic Information Files (cifs). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The structures of five complexes containing the proton sponge DMAN and an organic acid have been determined by neutron diffraction. The hydrogen atom behavior within the short, strong hydrogen bonds is strongly influenced by the local crystalline environment and in particular, weak intermolecular interactions. This shows the importance of taking into account all interactions in the local environment to understand the hydrogen atom behavior.

