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ARTICLE

Turning Colour On and Off Using Molecular Disorder and Proton Transfer in Multi-Component Molecular Complexes

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Charlotte L. Jones,[a] Chick C. Wilson[a] and Lynne H. Thomas[a]*,

Six molecular complexes resulting from co-crystallisation experiments of 4-iodoaniline or the related 4-iodo-2-methylaniline with dinitrobenzoic acids are reported. The individual components are not coloured or very pale in colour, but when molecular complexes are formed combining the two, vividly red crystals are obtained when layered crystal structures prevail. Where proton transfer results in completely ionic co-components, colourless crystals are formed. Molecular disorder is also found to favour layered, coloured crystals. In the pair of thermochromic molecular complexes comprised of 4-iodo-2-methylaniline with 3,5-dinitrobenzoic acid, proton transfer from one molecule to the other is shown to result in a colour change from red to colourless.

Introduction

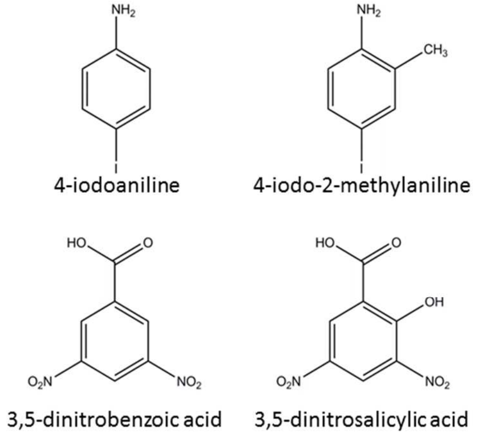
The principal goal of crystal engineering is the designed synthesis of functional solid-state materials, with the aim of controlling task-specific chemical and physical properties. One route to achieving this is through multi-component crystallisation, which targets the formation of molecular complexes containing more than one molecular species. The aim is, through a fundamental understanding of the association of molecules in the crystalline state, to control supramolecular assembly through intermolecular interactions.[1,2] Multi-component complexes include salts and co-crystals, as well as systems with proton disorder and mixed protonation states. The position of a proton can significantly impact the intermolecular interactions in the structure and consequently the properties displayed by the material. pKa values, whilst strictly applicable in the solution state, have been successfully applied to predict proton transfer in crystalline molecular complexes.[3,4] There are clear boundaries for ΔpKa values (the difference in pKa between the two components), which can reliably be used to predict whether a salt or co-crystal will form. However in the intermediate region between these boundaries a continuum exists and it is difficult to predict which will occur; mixed protonation states are also possible.[5]

Applications of molecular complexes formed using crystal engineering methods have to date been most widely found in pharmaceutical research, where complexes, either in salt or co-crystal form have been shown to improve the solubility of the active pharmaceutical ingredient (API) without compromising the pharmaceutical activity.[6,7] In more recent years, impact has also been seen in many other research fields, including energetic materials,[8–10] agrochemicals[11,12] and organic ferroelectrics.[13,14]

Multi-component molecular complexes have been used to modify some optical properties, but this has generally focused on non-linear optical[15,16] and luminescent properties.[17–20] There have been no systematic studies looking specifically at the modification of colour of organic, molecular materials by this method; there is, however, one report of a systematic co-crystallisation study targeting luminescent properties[17] rationalized by DFT calculations,[21] which also notes relatively small shifts in the colour of the complexes obtained.[17] Optical properties are not just a simple molecular property but also depend on the electronic intermolecular interactions resulting from the crystal packing; this has been clearly demonstrated in cases where polymorphism leads to different coloured crystals.[22–24] The introduction of co-molecules (molecular species introduced as the second component in the co-crystallisation process) will alter the crystal packing and therefore provides an alternative route to modify the optical properties of a solid. Despite this obvious potential to modify physical properties of pigments, not just in terms of the colour but also with respect to important materials properties such as fastness and solubility, we are only aware of one example of hydrogen-bond-based pigment co-crystals, which were formed using mechanochemical co-crystallisation to tune the colour of fluorescein.[25]

Some optical properties can be influenced by application of external stimuli such as a change in temperature, pressure or application of light. Where the stimulus is temperature this is known as thermochromism, and this effect can be observed in both the solution and solid states by a variety of mechanisms. In the case of thermochromic organic systems, the mechanism responsible for the colour change often involves an equilibrium between two species,[26] for example an intramolecular proton transfer. Intramolecular proton transfer is responsible for the thermochromic properties of a number of single-component crystal forms, including salicylideneanilines where the two molecular species are tautomers.[27] In multi-component materials, thermochromic transitions have been attributed to intermolecular proton transfer mechanisms in several cases, including the complex of 2-iodoaniline and picric acid[28] and the 1:1 adduct formed between squaric acid and 4,4'-bipyridine.[29,30]

Here we report the systematic study of a series of molecular complexes inspired by the previous observation of thermochromism in the 2-iodoaniline picric acid molecular complex. The molecules utilized in this study are shown in Scheme 1. In targeting this property, we demonstrate the value of molecular disorder as a design attribute for the first time.



Scheme 1. Molecular representations of the co-molecules used in molecular complexes **1-6**.

Experimental

Crystalline molecular complexes **1** (4-iodoanilinium 3,5-dinitrobenzoate) and **2** (4-iodoaniline 3,5-dinitrobenzoic acid methanol solvate 2:2:1) resulted from co-crystallisation experiments on 4-iodoaniline with 3,5-dinitrobenzoic acid. The starting materials were light purple and light yellow, respectively, leading to an orange solution on dissolution. **1** was grown from an equimolar solution of 4-iodoaniline and 3,5-dinitrobenzoic acid in acetonitrile at room temperature. Slow evaporation yielded colourless crystals. **2** was grown from an equimolar solution of 4-iodoaniline and 3,5-dinitrobenzoic acid in methanol. Slow evaporation at room temperature yielded red crystals.

3 (4-iodoanilinium 3,5-dinitrosalicylate) and **4** (4-iodoaniline, 4-iodoanilinium and 3,5-dinitrosalicylate 1:2:2) resulted from co-crystallisation experiments of 4-iodoaniline with 3,5-dinitrosalicylic acid. Both complexes were grown from a 2:1 stoichiometric solution of 4-iodoaniline and 3,5-dinitrosalicylic acid but the composition of the molecular complex formed was dependent on the crystallisation solvent and the temperature of evaporation; **3** was obtained from slow evaporation of acetonitrile at 40°C and **4** was obtained from slow evaporation of isopropyl alcohol at room temperature. The starting materials were light purple and light yellow, respectively leading to a pale orange solution on dissolution. Despite the stoichiometry of the solution, complex **3** crystallises in a 1:1 stoichiometric ratio resulting in pale yellow crystals. Molecular complex **4** crystallises in an effective 3:2 4-iodoaniline to 3,5-dinitrosalycilic acid ratio but with two of each species present in the ionic forms 4-iodoanilinium and 3,5-dinitrosalicylate; this resulted in dark orange crystals.

Crystals of **5** (4-iodo-2-methylanilinium 3,5-dinitrobenzoate) and **6** (4-iodo-2-methylaniline 3,5-dinitrobenzoic acid) were obtained from co-crystallisation of equimolar quantities of 4-iodo-2-methylaniline with 3,5-dinitrobenzoic acid and by slow evaporation of the solvents. **5** was obtained using ethanol as the solvent and by evaporation at 4°C. **6** was obtained using acetonitrile and allowing evaporation at room temperature. The starting materials were pale purple and pale yellow, respectively, leading to a pink/red solution on dissolution. **5** yielded colourless crystals and **6** gave bright red crystals.

Single-crystal X-ray diffraction data were collected on **1-6** using a Rigaku R-axis/RAPID image plate diffractometer equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å); all data were collected at 100 K. All structures were solved by direct methods using SHELXS-97[31] and refined using SHELXL-97[31] both within the WinGX program suite.[32]

In complexes **1**, **3**, **5** and **6**, all non-hydrogen positions and anisotropic displacement parameters were refined anisotropically.

In **2**, the two 4IA molecules are well-described and the positions and anisotropic displacement parameters for all heavy atoms were allowed to refine freely. When the positions and anisotropic displacement parameters of the two independent 3,5-DNBA molecules were allowed to refine freely, there was significant elongation of the anisotropic displacement parameters. A model was therefore adopted where the molecules could adopt two positions around the pivot nitro group but with the carboxylic acid or nitro groups flipped. Due to the close positions of these two orientations, significant constraints had to be applied for a chemically meaningful refinement. Details of these are given in the ESI. The close positions of the two meant that these atoms were only refined isotropically. The significant amount of molecular disorder meant it was not possible to accurately assign the protonation states of the molecules and therefore assign H-atoms to the carboxyl and amine groups. The H-atoms for these groups were therefore omitted from the model. All aromatic H-atoms and the H-atoms of the disordered methanol methyl groups were placed in calculated positions and refined as riding on the atoms to which they were bonded. It was not possible to identify the H-atoms of the methanol hydroxyl groups in a

Fourier difference map due to the disorder so these were also omitted from the model.

In complex **4**, one 4IA molecule is disordered with 50:50 occupancy over two positions. The atoms of the disordered 4IA ring were refined anisotropically, but due to overlapping regions of electron density the anisotropic displacement parameters for all carbon atoms in the ring were constrained to take the same value. In order to ensure chemically sensible bond lengths and angles were obtained, the benzene ring of this disordered molecule was constrained to take a standard geometry. Due to the close proximity of the I and N atoms the anisotropic displacement parameters were constrained to be equal. A series of constraints were also applied to ensure chemically sensible C-C-I/N angles and C-I/N distances. Details are given in the ESI.

In all complexes, with the exception of **2**, those H-atoms not involved in hydrogen bonds were placed on calculated positions and refined as riding on the atoms to which they were bonded. Those hydrogen atoms involved in hydrogen bonds were identified using Fourier difference maps and their positions and isotropic displacement parameters allowed to freely refine. Details of the hydrogen bond geometries are given in the ESI.

Powder X-ray diffraction data were collected on **5** and **6**, and a sample of **6** after heating to just above the transition temperature, using a Bruker D8 Advance diffractometer at ambient temperature (Cu-Kα radiation, 40 kV, 40 mA). Data were collected in the 2θ range 5 - 50°.

Differential Scanning Calorimetry (DSC) measurements were performed on complexes **5** and **6** using a TA Instruments Q20 DSC system. Crystals were gently ground and 2-5 mg weighed into a Tzero^{TM} aluminium pan and covered with a Tzero^{TM} aluminium lid. The samples were each loaded into the calorimeter and heated at a rate of 5°C/minute from 40°C to 125°C for complex **5**, and to 130°C and 90°C for the one- and two-cycle experiments on complex **6**, respectively. Melting points and transition temperatures were derived using the TA Universal Analysis software.

Hot stage microscopy analysis was conducted on complex **6** using a Mettler Toledo FP82 hot stage equipped with a Leica DM1000 microscope. A single crystal of the complex was placed in the sample chamber, and heated from ambient temperature to a final temperature of 130°C at a rate of 5°C/minute. The sample was cooled back to ambient temperature at the same controlled rate of 5°C/minute.

Infrared spectra were recorded for complexes **2** and **4** and on the single components, 4-iodoaniline, 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid, using a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a Universal ATR accessory for sampling.

Results and Discussion

Molecular Complexes of 4-Iodoaniline with 3,5-Dinitrobenzoic Acid

Crystallisation of 4-iodoaniline (4IA) with 3,5-dinitrobenzoic acid (3,5-DNBA) in a 1:1 ratio leads to two distinct molecular complexes, one colourless and one red in colour. The molecular complexes both contain a 1:1 stoichiometry of the two components but complex **2** incorporates an additional half methanol (solvent) molecule. This introduction of methanol has two effects; first, the colour of the crystal changes from colourless to red; secondly, the degree of proton transfer between the carboxylic acid group of the 3,5-DNBA molecule and the amine group of the 4IA molecule in the colourless complex (**1**) is partially turned off on incorporation of methanol (**2**).

Complex **1** contains two ionic species, 4-iodoanilinium and 3,5-dinitrobenzoate. Each of the three hydrogen atoms of the anilinium group is involved in a hydrogen bond to the carboxylate group of a 3,5-DNBA molecule; the two oxygen atoms of the carboxylate group show character between that of single and double bonds with approximately equidistant C-O distances consistent with a delocalisation of the charge across this group (1.266(3) and 1.248(3) Å). Whilst the 3,5-DNBA molecule is approximately planar, the hydrogen bonding involving the tetrahedral anilinium group is three-dimensional and results in a non-layered structure with no π···π stacking interactions and therefore colourless crystals (Figure 1, left). The iodine atoms also form short contacts with one of the carboxylate oxygen atoms with an I···O distance of 2.987(2) Å which is significantly shorter than the sum of the van der Waals radii of the two atoms (3.5 Å). The nitro groups form O···O and O···π interactions solely with other 3,5-DNBA molecules.

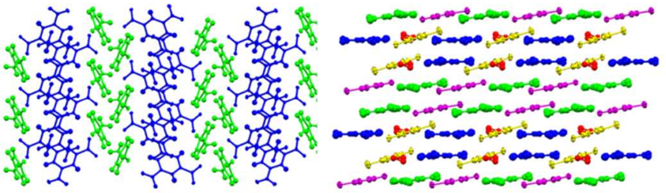


Figure 1. The crystal packing in the two molecular complexes of 4IA with 3,5-DNBA. Left, the 1:1 ionic complex, **1**, which shows no π stacking interactions; 3,5-DNBA in blue, 4IA in green. Right, the 2:2:1 methanol solvate, **2**, which has a layered structure and is red in colour; the two independent, disordered 3,5-DNBA chains are in green and blue, the two independent 4IA molecules in purple and yellow, methanol in red.

Complex **2** possesses a far more complex structure with significant molecular disorder and therefore some ambiguity in the protonation states of the two molecular species. The complex forms in a 2:2:1 4IA:3,5-DNBA:methanol ratio. The single crystal diffraction data show significant diffuse scattering indicating that this molecular disorder is characteristic of the material and not an indication of twinning or poor crystal quality. The global structure is layered, with π-stacking interactions (Figure 1, right), and the crystals are red in colour. The two 4IA molecules are generally well-described but show some elongation of the thermal parameters out of the plane of the benzene ring. The 3,5-DNBA molecules, however, show significant elongation of the anisotropic displacement parameters about a pivot of a single nitro group. This pivot group can clearly be assigned as a nitro group in each independent 3,5-DNBA molecule due to the N-O distances (1.21(1) and 1.21(1) Å; 1.20(1) and 1.23(1) Å). However, when the molecule is refined in a single position, the other two substituents have bond lengths which show character somewhere between that of a nitro group and a carboxylic acid or carboxylate group (Figure 2). The 3,5-DNBA molecules were therefore more appropriately modelled as approximately 50:50 disordered over two positions corresponding to a flipping of the carboxylic acid (or carboxylate group) and the nitro group.

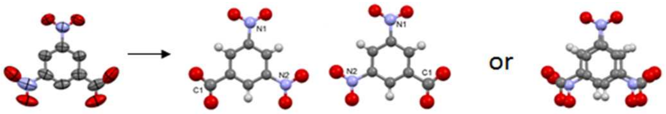


Figure 2. Disorder in the 3,5-dinitrobenzoic acid molecules in complex **1**. Left, the elongated anisotropic displacement parameters arising from a free refinement of a single position; middle the two possible orientations for the 3,5-dinitrobenzoic acid molecule and right, the model where the two positions are superimposed.

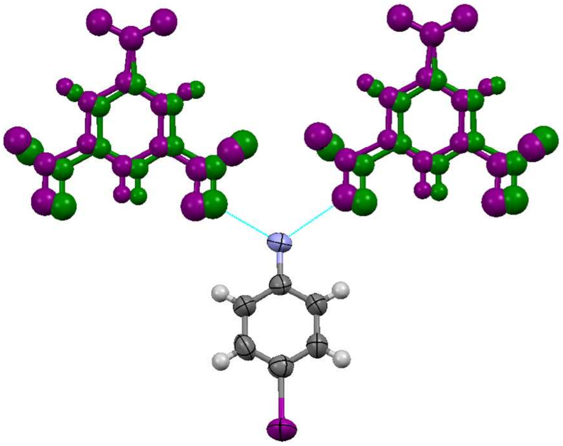


Figure 3. Chains which are formed between 3,5-DNBA molecules (purple and green represent the two orientations) and the 4IA molecule in **2**.

These 3,5-DNBA molecules are arranged into 1D chains along the a-axis (Figure 3); there are two independent chains of this type. The arrangement of these molecules in these chains is not consistent with either entirely deprotonated 3,5-DNBA molecules or entirely neutral molecules; neutral 3,5-DNBA molecules would tend to form hydrogen bonded carboxylic acid dimers. Without hydrogen atoms on the carboxylic acid groups, there would be no significant interactions holding these chains together. Therefore, it is most likely that there is approximately 50:50 disorder between a carboxylate group and a carboxyl group. Significant constraints have to be applied to ensure that approximately standard bond lengths are obtained for the carboxylic acid/carboxylate group and the nitro groups so it is important not to over-interpret the reliability of bond lengths involving these atoms. However, the O···O distance between neighbouring carboxylic acid/carboxylate groups is consistent with a short, strong, charge-assisted hydrogen bond between a carboxylic acid group and a carboxylate group (2.45(3) Å or 2.53(3) Å). The O···O distances between neighbouring carboxylic acid/carboxylate and nitro O atoms, or neighbouring nitro groups, are also consistent with either a moderate strength hydrogen bond or van der Waals interactions.

The methanol molecule sits between two independent 4IA molecules and is approximately 50:50 disordered over two positions (Figure 4). When the hydrogen atom is in the green position, it acts as a hydrogen bond donor to atom N1 and therefore N1 cannot be in its NH_3^+ protonated state and must be the neutral amine. In this case, N8 can be protonated and form a hydrogen bond to atom O15A; if N8 were also neutral, no additional hydrogen bond would be formed to the lone pairs of the O atom of the methanol molecule. The opposite is true when the methanol molecule is in the orange position; N8 must therefore be neutral and N1 is more likely to be in its protonated NH_3^+ state. This change in protonation state is likely to result in small changes in the position of the 4IA molecules in order to enhance the hydrogen bonding interactions; this is evident in the large size of the thermal parameters of these molecules.

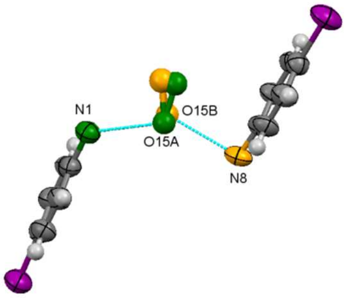


Figure 4. The disordered methanol molecule in **2** showing the two possible hydrogen bonds to the two independent 4IA molecules. When the methanol molecule is in the green orientation, it acts as a hydrogen bond donor to atom N1. When it is in the orange position, it acts as a hydrogen bond donor to atom N8. Methanol hydrogen atoms are omitted for clarity.

On a local, short-range level of a few molecules, it is likely that there are some shifts of the molecules depending on the protonation state, but this does not persist at longer length scales. Where the 4IA molecules are in their neutral states, the molecules may shift so that they are more co-planar with the 3,5-DNBA molecules and the NH_2 group is approximately co-planar with the rest of the 4IA molecule as would be expected (Figure 5). A hydrogen bond is accepted from the methanol molecule in this case. When the 4IA molecules are in their protonated states, the NH_3^+ group would be expected to take a tetrahedral shape and it would be expected to form three hydrogen bonds. In this case, the molecule may shift further out of the plane of the 3,5-DNBA molecules and act as a hydrogen bond donor to the methanol molecules (Figure 5). In the global crystal structure, there is a statistical averaging of these two cases resulting in slightly elongated thermal parameters out of the plane of the benzene ring for all of the atoms in the 4IA molecules.

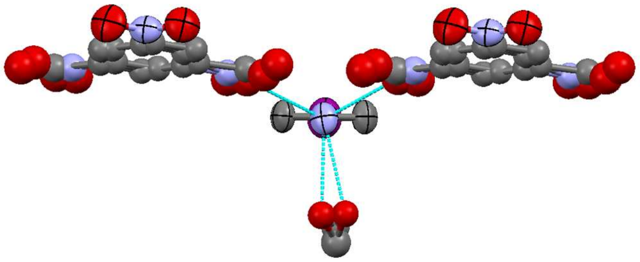


Figure 5. The intermolecular interactions of one of the amine groups of the 4IA molecule in **4**. A model is proposed where the aniline can be present in both its neutral, NH_2, and protonated, NH_3^+, states. Where it is present in its NH_2 state, the molecules may shift to become more co-planar with the 3,5-DNBA molecules such that the NH_2 group is co-planar with the rest of the 4IA molecule and the hydrogen bonds are still formed. When it is present in its NH_3^+ state, the molecule is shifted down and the NH_3^+ group is tetrahedral in shape and forms three hydrogen bonds, two to the 3,5-DNBA molecules and one to a methanol O atom. Hydrogen atoms are omitted for clarity.

Because of the high level of disorder, it is not possible to identify any of the hydrogen atoms involved in hydrogen bonds from the diffraction data. The IR spectrum of **2** shows changes in the N-H stretching region of the spectrum compared with pure 4IA including significant shifts in some of the peak positions and some splitting of peaks, indicating some changes in the amine group (see ESI). The peaks also do not entirely match those of complex **3** where the 4IA molecules are all present in their ionic form and show features somewhere intermediate between the two spectra; this is also consistent with the IR spectrum of **4** where the mixed ionization state of 4IA can be resolved. It is difficult to fully assign the peaks without further information but this may also support a model where the 4IA molecules are present in both neutral and ionic forms.

The overall crystal structure is comprised of layers of 3,5-DNBA chains connected by 4IA and methanol molecules. The layers are slightly puckered but due to the large amount of disorder in this complex, in localized regions, these are likely to flatten out. There are π···π interactions between nitro groups of parallel 3,5-DNBA molecules and staggered π···π interactions between 4IA and 3,5-DNBA molecules.

The I atom of one of the 4IA molecules forms weak I···O halogen interactions to the O atoms of carboxyl/carboxylate/nitro groups of two 3,5-DNBA molecules within the same plane (3.45(2) Å and 3.37(2) Å). The other I atom is not involved in any interaction, although due to the significant disorder, strong conclusions on these interactions should not be drawn as there is a dependence on the local structure rather than the average structure.

Molecular Complexes of 4-Iodoaniline with 3,5-Dinitrosalycilic Acid

Despite consistently crystallising 4-iodoaniline with 3,5-dinitrosalycilic acid (3,5-DNSA) in a 2:1 ratio of starting components, two molecular complexes in different stoichiometries have been obtained from different solvents. There are two possible functional groups on the 3,5-DNSA molecule with the potential for deprotonation, the hydroxyl group and the carboxylic acid group.

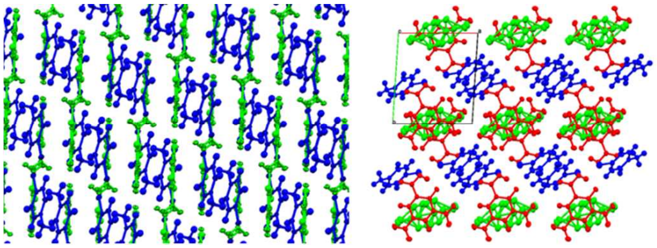


Figure 6. The contrasting packing in the two complexes of 4IA with 3,5-DNSA. Left, the 1:1 complex, **3**, containing only ionic species and with only pairwise π···π stacking of 3,5-DNSA molecules (green) and no stacking of 4IA molecules (blue); Right, columns of π···π stacked ionic 3,5-DNSA (red) and disordered neutral 4IA molecules (green), flanked by ionic 4IA molecules (blue).

3 is a 1:1 molecular complex with both species present in their ionic forms. In this case, an intramolecular hydrogen bond is formed between the hydroxyl group and the carboxylate group of the 3,5-DNSA. The hydrogen atom clearly resides on the hydroxyl group, identifiable in a Fourier difference map, but with a slightly elongated O-H distance (1.00(3) Å); this is supported by consideration of the C-O distances of both groups. In the carboxylate group, the C-O distance corresponding to the carbonyl oxygen atom clearly has a bond length consistent with that of a double bond (1.228(2) Å), but the other C-O distance is shorter than would be expected for an OH group (1.285(2) Å); the hydroxyl group, on the other hand, maintains a C-O distance consistent with a single C-O bond and no charge (1.321(2) Å). The NH_3^+ group forms two hydrogen bonds to the oxygen atoms of the carboxylate groups of two 3,5-DNSA molecules. A third hydrogen bond is formed to one of the nitro groups of a third 3,5-DNSA molecule. The iodine atom of the 4IA molecule is involved in two I···O interactions to the oxygen atoms of adjacent hydroxyl and nitro groups; the shorter of the two interactions is to the nitro group (3.267(1) and 3.388(1) Å). There is an additional nitro group O···O interaction to the carbonyl oxygen atom of a carboxylate group of a 3,5-DNSA molecule. Pairs of 3,5-DNSA molecules are stacked through staggered π···π interactions (layer spacing of ~3.24 Å, offset angle of ~26°, parallel displacement, ring centroid to ring centroid ~1.59 Å), but the 4IA molecules do not show any π interactions. Since these π stacking interactions are limited to only pairwise interactions, the crystal structure is not layered (Figure 6, left) and the resulting crystals are pale in colour.

Complex **4** contrasts with **3**, as it crystallises in a 3:2 4IA:3,5-DNSA ratio; both neutral and ionic 4IA molecules coexist but all 3,5-DNSA molecules are in their ionic form. The ionic 4IA and 3,5-DNSA molecules are well-behaved and ordered, but the neutral 4IA molecules are disordered over two positions through an inversion centre (Figure 7). The ordered components create a network in which disordered 4IA molecules are housed. These disordered molecules are isolated from one another. In contrast to **3**, the hydrogen atom in the intramolecular O-H···O hydrogen bond resides closer to the carboxylate O atom with a standard O-H bond length of

0.89(7) Å. Again, the carbonyl O atom of the carboxylic acid group is clearly identifiable (C-O 1.223(6) Å) and the hydroxyl group of the carboxylic acid group has a slightly longer C-O distance than that for the hydroxyl group (1.310(6) Å c.f. 1.291(5) Å). The NH_3^+ group of the 4IA molecule forms three hydrogen bonds, two to carbonyl O atoms of carboxylic acid groups and one to a deprotonated hydroxyl group O atom of a third 3,5-DNSA molecule. There are a number of C-H···O weak hydrogen bonds between aromatic C-H groups of 4IA molecules and nitro group O atoms of 3,5-DNSA molecules. The I atoms of the ordered 4IA molecules are also hydrogen bond acceptors for aromatic C-H groups of 3,5-DNSA molecules. These interactions create a framework in which isolated neutral 4IA molecules, which are 50:50 disordered over an inversion centre, are housed. There are no strong interactions involving the aniline group and the only interactions involving the I atom are weak I···π interactions to neighbouring, almost parallel 3,5-DNSA molecules on either side. The same type of interaction is formed regardless of the orientation of the disordered 4IA molecule, which may account for the statistical disorder. The disordered neutral 4IA molecules are π···π stacked with 3,5-DNSA, with each spaced by two stacked 3,5-DNSA molecules in channels along the c-axis (Figure 6, right) (layer spacing of ~3.558 Å, offset angle of ~25/20°, parallel displacement ~1.72/1.32 Å, ring centroid to ring centroid accounting for the two possibilities due to disorder). This continuous π-stacking is likely to be responsible for the orange colour of crystals of this complex.

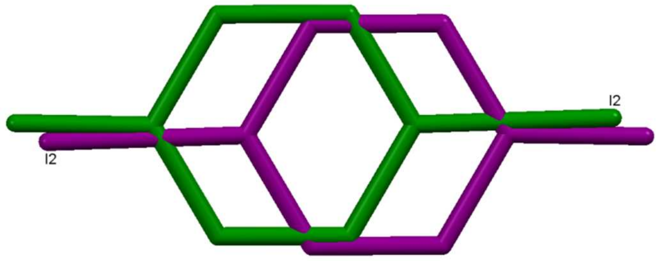


Figure 7. The disorder of the 4IA molecule over and inversion centre in complex **4**. Hydrogen atoms are omitted for clarity.

Molecular Complexes of 4-Iodo-2-methylaniline with 3,5-dinitrobenzoic Acid

Crystallisation of 4-iodo-2-methylaniline (4IMA) with 3,5-dinitrobenzoic acid in a 1:1 stoichiometric ratio results in two molecular complexes of the same 1:1 stoichiometry; one of these complexes is colourless and the other red depending on the solvent and temperature of crystallisation employed. The driving force between the different properties of the two complexes is location of the hydrogen atom of the acid group; the colourless complex (**5**) is comprised of the ionic species 4-iodo-2-methylanilinium and 3,5-dinitrobenzoate and a proton has been transferred from the 3,5-DNBA molecule to the 4IMA molecule; in the red molecular complex, **6**, in contrast, the two species are present in their native neutral forms.

In a similar manner to complex **1**, the three hydrogen atoms of the anilinium group in **5** form N-H···O hydrogen bonds to the carboxylate groups of three 3,5-DNBA molecules (N···O distances 2.720(3), 2.755(2), 2.770(2) Å); the shortest of these is supported by a C-H···O weak hydrogen bond from an aromatic C-H group adjacent to the anilinium group (C···O distance 3.307(3) Å). The C-O distances of the carboxylate group show character intermediate between single and double bonds (1.272(2) and 1.246(2) Å). The proton transfer and resultant 3-fold hydrogen bonding interactions of the anilinium group leads to a non-layered structure with no π···π stacking interactions which is consistent with the colourless property of the crystals (Figure 8, left). Short I···O halogen interactions are formed, this time to the O atom of one of the nitro groups (I···O = 3.203(1) Å) and is longer than that found in complex **1**. In addition, there are O···π and C-H···O interactions involving nitro group O atoms and π bonds and an aromatic C-H group of the 4IMA molecule.

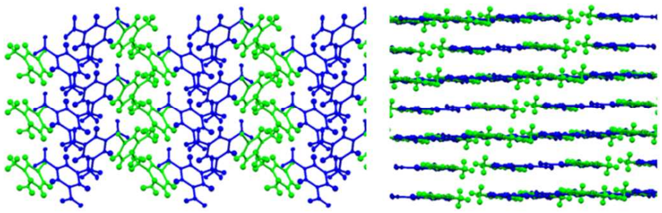


Figure 8. The crystal packing in the 1:1 molecular complexes of 4IMA and 3,5-DNBA. Left, the ionic, colourless complex, **5**, which is not layered; right the neutral complex, **6**, which is layered and red in colour. Green, 4IMA; blue 3,5-DNBA.

In complex **6**, the 3,5-DNBA molecules form hydrogen bonded homo-dimers forming $R^2_2(8)$ hydrogen bonded rings between the carboxylic acid groups. Both molecular species are planar in nature and this allows the formation of significant π-stacking interactions (Figure 8, right). The aniline group of the 4IMA molecules form hydrogen bonds to two nitro groups with N···O distances of 2.921(2) and 3.257(1) Å. The combination of these interactions and weak C-H···O hydrogen bonds from aromatic C-H groups of 3,5-DNBA molecules and the methyl group of the 4IMA molecules to nitro groups of the 3,5-DNBA molecules results in 2D planes. There is a weak C-H···O hydrogen bond connecting parallel planes from the methyl group of a 4IMA molecule in one plane and the carbonyl O atom of the carboxylic acid group of a 3,5-DNBA molecule in another plane. There are also offset π···π interactions between pairs of 3,5-DNBA molecules and 4IMA molecules (layer spacing of ~3.27 Å, offset angle of ~33°, parallel displacement ~2.14 Å) and some nitro·-·carboxylic acid π interactions between staggered 3,5-DNBA molecules in parallel planes. There are no I interactions.

Thermochromism

Complexes **1-4** do not show any evidence of temperature dependent thermochromism. Complexes **5** and **6** can, however, interconvert, with the colourless **5** the more stable of the two. Complex **6** is stable within the crystallization vessel, however, when the vessel is opened, it spontaneously converts to **5** over a period ranging from minutes to days. It was possible to keep samples of **6** sufficiently stable for characterisation via hot-stage microscopy (HSM) and differential scanning calorimetry (DSC); the survival of **6** could clearly be confirmed by the red colouration of the crystals which transformed to transparent and colourless on conversion to **5** (Figure 9). This could additionally be confirmed by powder diffraction (see ESI) of the coloured material which corresponded to the calculated powder pattern from single crystal diffraction data of **6**.

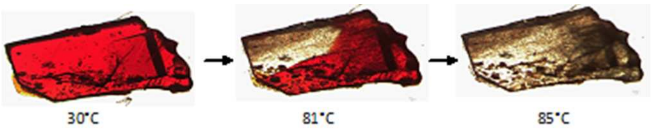


Figure 9. The thermochromism of **6** converting to **5**. The transition occurs as a wave across the crystal

HSM on a single crystal indicated a thermally induced colour change of **6** into colourless crystals in the temperature range 77-84°C (Figure 9). The transition clearly moves across the crystal in a wave. DSC measurements show a small endothermic event at temperatures between 43-63°C, presumably corresponding to the transformation of **6** into **5** and the associated colour change (Figure 10). There is a slight discrepancy between the DSC and HSM results and this may be a crystal size effect; the fact that the colour change appears as a wave over the crystal would suggest that the transition would take longer on the larger crystals used in the HSM measurements compared to the powdered samples in the DSC. This sample then melts at ~117°C; DSC measurements of **5** show a melt at the same temperature but with no endothermic transition at lower temperatures (see Figure S8 ESI). Powder diffraction data on crystals which had been heated to 80°C confirmed this colourless form to be the same as **5** (see ESI). This colour change transition is not reversible (see Figure S9 ESI).

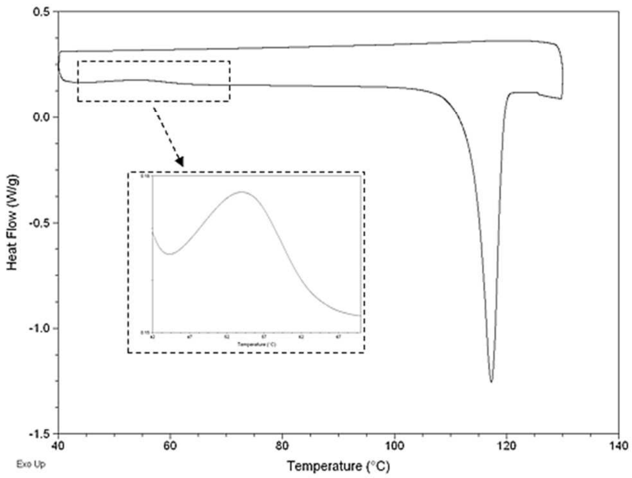


Figure 10. DSC of **6** showing a small exothermic event in the region of 43-65°C corresponding to the colour change observed in the HSM. A melt is then observed at ~117°C corresponding to that of **5** and the complex does not recrystallize on cooling.

The thermochromic phase transition of **6** to **5** results in a significant molecular rearrangement of the constituent molecules as a result of hydrogen transfer; the coloured, metastable form (**6**), is comprised of neutral co-molecules and the stable, colourless form (**5**) contains ionic species; hydrogen transfer, in this case, can only occur with this significant rearrangement of molecules and therefore explains the irreversibility of this transition.

The Role of Proton Transfer – Good or Bad?

Three pairs of molecular complexes have been reported here. Only two complexes, **5** and **6** contain the same chemical composition but quite different optical properties. Complex **6** contains solely neutral species, whereas **5** exhibits proton transfer from one molecule to the other resulting in solely ionic species. This simple proton transfer between species is sufficient to initiate molecular rearrangement from the metastable form **6** which is layered and red in colour, to the more stable **5** which is not layered and colourless. The other two colourless complexes, **1** and **3**, both form in 1:1 stoichiometries of the co-components and are ionic in nature. All three coloured complexes contain at least some neutral molecules even when they co-exist with the ionic forms and therefore do not have 1:1 stoichiometric ratios. Where there are mixed protonation states, the most influential molecule appears to be the 4IA, as complex **4** contains only the ionic co-component 3,5-DNSA molecules but both neutral and ionic 4IA molecules; this can be rationalized by the change in shape of the NH_2 group to the NH_3^+ ion moving from co-planar with the rest of the 4IA molecule to tetrahedral whereas the 3,5-DNSA (or 3,5-DNBA) molecules are approximately planar regardless of the protonation state. The hydrogen bonds from the NH_3^+ group might be expected to be stronger than those from the NH_2 group due to their charged nature in the former and thus direct the hydrogen bonding into a more three-dimensional form, resulting in non-layered crystal packing arrangements. In these systems where proton transfer changes the dimensionality of the hydrogen bonding network, it is clear that proton transfer is undesirable for colour properties. However, it should be noted that elimination of proton transfer does not preclude adoption of colour properties in all materials, for example colour has been observed in zwitterionic molecular complexes.[33]

The Role of Molecular Disorder

Two of the three coloured molecular complexes show whole molecule disorder of one or more of the components. The presence of this disorder, therefore, can be considered to be a favourable attribute, increasing the likelihood of layered crystal structures and therefore π···π interactions which may give rise to colour. There are several approaches that can be adopted to increase the likelihood of obtaining disordered molecular complexes like these. Symmetric molecules are able to adopt more than one molecular configuration and introducing a mis-match of hydrogen bond donors and acceptors or competing interactions of similar affinities can increase the likelihood of incorporating molecular disorder.

In these systems, 3,5-DNBA and 3,5-DNSA were selected, as in their neutral forms it might be expected that the strongest hydrogen bond donors and acceptors would be the hydroxyl and carbonyl groups of the carboxylic acid group. Homo-dimers might therefore be expected to form as in complex **6**. In contrast, when in their ionic states, O-H···O charge assisted hydrogen bonds, where available, would be the preferential intermolecular interactions. This interaction is available through an intramolecular hydrogen bond in 3,5-DNSA. In 3,5-DNBA, this is only likely to be satisfied if other, neutral 3,5-DNBA molecules co-exist. The saturation of interactions involving the carboxylic acid group leaves only weaker hydrogen bond acceptors on the 3,5-DNBA molecule in the form of nitro groups for the co-molecule to interact with. In this scenario, there may be some competition between the relatively weaker hydrogen bond donor, the NH_2 group of the 4IA and the I atom which can form I···O interactions to the nitro group O atoms. The weakness of the NH_2 group as a hydrogen bond donor is indicated in complex **6** where the only hydrogen bonds involving this group are to the weak hydrogen bond acceptor O atoms of the nitro groups with N···O distances more characteristic of moderate to weak hydrogen bonds.

This competition is apparent in **4** where the 4IA molecule can adopt two positions and there are no interactions involving the NH_2 group and only weak I···π interactions. The presence of both neutral and charged 4IA molecules in this complex and a stoichiometric ratio with 4IA in excess also contributes to the presence of disorder with the NH_2 group competing with the significantly more basic NH_3^+ group for the strongest hydrogen bond acceptor atoms.

In complex **2**, the 3,5-DNBA and 4IA molecules are present in the same relative stoichiometry, but the incorporation of methanol into the structure, providing another strong hydrogen bond donor O-H group, is enough to switch from an ionic crystal (**1**) to a mixed ionization species with both neutral and charged species of each co-existing (**2**). The symmetry of the 3,5-DNBA molecule and the similar sizes of carboxylic acid/carboxylate and nitro groups in this case allows the possibility of positional disorder in the 3,5-DNBA molecules and more subtle disorder of the 4IA molecules apparent only in the elongated thermal parameters of these molecules.

The use of 4IMA reduces the symmetry of the 4IA molecule and adds increased steric bulk to the molecule (**5** and **6**). The methyl group is also capable of forming weak hydrogen bonds and it is these effects that remove the ability of the 4IMA molecule and 3,5-DNBA molecules to exhibit disorder.

Conclusions

Six molecular complexes combining 4-iodoaniline and 4-iodo-2-methylaniline with 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid have been synthesized by evaporative crystallisation. All starting components are colourless or pale coloured in nature; co-crystallisation has resulted in three vividly red molecular complexes and three colourless molecular complexes. The 3,5-DNBA and 3,5-DNSA molecules both have the potential to act as proton donors and the aniline group of the co-molecules is able to act as a proton acceptor. Therefore, it is possible to obtain molecular complexes comprised of both neutral and ionic co-molecules. The complexes reported show a diverse composition with varying stoichiometries. Where all molecules are in their ionic states (**1**, **3**, and **5**) the resulting complexes are not layered and the crystals are colourless. Where at least some of the 4IA or 4IMA molecules are in their neutral form, coloured complexes are obtained and in the case of 4IA, disorder is also observed. Disorder, therefore appears to be a favourable attribute in encouraging the formation of layered structures with π···π interactions between molecules of differing type. An understanding of the subtle influences on the inter-layer electronic effects requires further work.

Complexes **1** and **2** contain the same relative stoichiometry of the co-components but **2** also contains methanol. The incorporation of the methanol molecule in this case is sufficient to induce switching from an ionic complex to a mixed ionization state complex with both charged and neutral species and from colourless to red crystals, respectively.

The pair of 4IMA and 3,5-DNBA complexes (**5** and **6**) show thermochromism with red crystals converting to colourless crystals at elevated temperatures. The colour change takes the form of a wave across the crystals and corresponds to the transfer of a hydrogen atom from the 3,5-DNBA molecule to the 4IMA molecule; this results in a significant structural rearrangement and the transition is not reversible.

When designing other molecular complexes using similar molecules with colour properties, it is apparent that hydrogen transfer is undesirable in these types of system where proton transfer results in a change of hydrogen bonding environment from two-dimensional to three-dimensional networks (NH_2 taking a planar geometry vs NH_3 which is tetrahedral) but disorder is a desirable attribute for molecular complexes leading to the layered crystal packing necessary for efficient charge-transfer between molecules. There are a number of strategies that can be adopted for encouraging disorder and we are in the process of deliberately designing disorder into similar molecular complexes. A detailed understanding of the disorder and the role that this plays in the optical properties is also important; to this end, we are utilizing the diffuse scattering present in the diffraction patterns of these disordered materials and this will form the basis of future publications on these and other materials.

Acknowledgements

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Table 1. Summary of the crystallographic data for **1**-**6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$(C_6NIH_7)^+$, $(C_7N_2O_6H_3)^-$	$2(C_6NIH_6)$, $2(C_7N_2O_6H_4)$, (CH_3OH)	$(C_6NIH_7)^+$, $(C_7N_2O_7H_3)^-$	(C_6NIH_6), $2(C_6NIH_7)^+$, $2(C_7N_2O_7H_3)^-$	$(C_7NIH_9)^+$, $(C_7N_2O_6H_3)^-$	(C_7NIH_8), $(C_7N_2O_6H_4)$
M/g mol^{-1}	431.14	894.32	447.14	1113.30	445.17	445.17
T/K	100	100	100	100	100	100
Space Group	$P2_12_12_1$	P-1	P-1	P-1	$P2_1$	P-1
a/Å	6.0536(7)	9.947(7)	7.3806(15)	9.0879(11)	10.756(9)	8.534(2)
b/Å	10.5285(16)	12.823(9)	9.3433(18)	9.9637(12)	5.790(4)	8.769(2)
c/Å	24.444(3)	13.020(10)	11.754(2)	10.5749(12)	13.363(9)	11.882(8)
α	90	94.249(16)	80.602(5)	94.099(4)	90	111.035(8)
β	90	91.739(16)	71.795(5)	103.810(4)	107.859(8)	101.327(7)
γ	90	90.493(19)	79.460(5)	92.568(4)	90	95.273(7)
V/Å	1558.0(4)	1655(2)	752.1(3)	925.59(19)	792.1(10)	800.9(6)
Z	4	2	2	1	2	2
ρ_{cal}/ g cm^{-3}	1.838	1.730	1.974	1.997	1.886	1.846
μ/mm^{-1}	2.090	1.967	2.173	2.611	2.058	2.036
θ Range/°	3.16-27.47	2.99-27.48	3.05-27.48	2.99-27.49	3.20-27.47	3.21-27.48
Ref Collected	10999	38785	18894	22287	18081	18691
Independent	3552	7522	3419	4221	3620	3661
Observed>2σ	3349	4315	3209	3036	3583	3500
Rint	0.0299	0.0586	0.0327	0.0356	0.0206	0.0189
Completeness %	99.7	99.2	99.3	99.6	99.8	99.4
Parameters	220	344	233	257	230	218
Flack parameter	-0.02(2)	-	-	-	-0.010(9)	-
GooF	1.154	1.075	1.087	1.194	1.088	1.132
R_1 (obs)	0.0211	0.0791	0.0191	0.0392	0.0131	0.0180
R_1 (all)	0.0249	0.1317	0.0211	0.0657	0.0133	0.0190
wR2 (all)	0.0449	0.1856	0.0474	0.1110	0.0332	0.475
$\rho_{max,min}$/e Å^{-3}	0.560, -0.357	1.831, -0.695	0.508, -0.266	1.209, -1.434	0.412, -0.246	0.516, -0.347

Notes and references

[a] Department of Chemistry, University of Bath, Bath, BA2 7AY, UK. Email: L.H.Thomas@bath.ac.uk

Electronic Supplementary Information (ESI) available: cifs for **1**-**6** CCDC numbers 984155-984160; photographs of crystals of **1**-**6**; IR Spectra for 4IA, 3,5-DNBA, 3,5-DNSA, and **2**-**4**; powder X-ray diffraction patterns for **5**, **6**, and **6** which has converted to **5** on heating; DSC traces of **5** and a cycle of **6** showing the irreversibility of the thermochromic phase transition. See DOI: 10.1039/b000000x/

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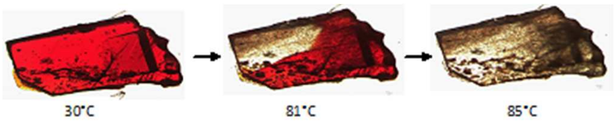
Grahical abstract



Three pairs of molecular complexes based around 4-iodoaniline and 3,5-dinitrobenzoic acid are reported. Within each pair, one complex is colourless and one red; the influences on the colour are discussed including the role of molecular disorder and proton transfer.