Self-assembly directed by NH⋯O hydrogen bonding: a neutron study of a trilayered supramolecular array formed between 1,2-diaminoethane and benzoic acid

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The supramolecular array formed by co-crystallisation of 1,2-diaminoethane and benzoic acid is investigated by neutron diffraction; the system self-assembles into an unusual layered structure composed of two-dimensional hydrogen-bonded networks sandwiched between layers of edge-to-face stacked aromatic systems; the number of hydrogen-bond donors and acceptors is balanced in the structure.

The self-assembly of two of more molecular components into well defined, solid-state supramolecular structures has been a topic of considerable recent interest.[1–3] Such 'crystal engineering' involves the attempted regulation of the subtle non-covalent interactions that dictate crystal packing in order to produce new materials showing unusual properties, including novel electrical and optical properties. Co-crystallisation of selected complementary molecules provides one means of generating new extended supramolecular frameworks of this type;[4] such an approach was employed in the study now reported.

Of the variety of intermolecular interactions commonly identified in solid-state supramolecular structures (hydrogen bonding, electrostatic, van der Waals, π–π stacking),[1,2,5–7] hydrogen bonds tend to have the highest strength and selectivity.[1,2]

Here, we report the single-crystal neutron structure of the 1 : 2 molecular assembly formed between 1,2-diaminoethane and benzoic acid.† Crystallisation of this adduct can be effected by slow evaporation of a stoichiometric mixture of the components dissolved in methanol. Large transparent crystals (*ca*. 0.4 × 0.8 × 0.8 cm, mp = 153.5 °C) grew rapidly overnight. The structure of the resulting supramolecular array (Fig. 1 and 2) is predominantly directed by π–π stacking and strong hydrogen-bond formation in which acid protons have transferred onto the amine nitrogens (analogous to 'intermolecular zwitterions') such that each amine in the structure is in its $-NH_3^+$ form. Polarised hydrogen-bond interactions of this type can be very strong[8] and, as often observed in related systems,[7,9,10] all the amine and acid protons within the structure take part in NH⋯O bonding. In the asymmetric unit as defined, the two independent benzoate moieties attached on opposite sides to a 1,2-diaminoethane moiety (*via* one strong hydrogen bond) lie approximately parallel [interplanar dihedral angle 3.1(2)°]. All hydrogen bonds in the array are very similar with N⋯O, N–H, H⋯O, N–H⋯O all very closely ranged [2.727(5)–2.764(6); 1.02(1)–1.09(1); 1.65(1)–1.78(1); 156(1)–172(1)°].

A two-dimensional planar layer is formed by parallel 'rows' of the acid/amine motifs being stacked side-by-side, each row being offset with respect to the next.

An edge-on projection of this layer is shown in Fig. 1; this illustrates that a pair of benzoate sheets effectively sandwich a sheet of 1,2-diaminoethane molecules parallel to the *ab* plane. The layer is 'stitched' together by hydrogen bonds between adjacent benzoic acids and 1,2-diaminoethanes of different motif units. Each benzoate participates in three strong hydrogen bonds, two to one oxygen in each case, with H⋯O⋯H 113.0(6), 112.6(6)°; C–O to that oxygen being slightly longer [1.264(5), 1.265(5) Å] than for those distances to the oxygens which have single hydrogen bonds [1.231(5), 1.241(5) Å]. It is noted that while each side adduct layer is very similar, they are not crystallographically equivalent, although the array has pseudo-symmetry.

Planar layers of acid/amine motifs are in turn stacked such that adjacent layers are bound together by edge-to-face (T-oriented) aromatic stacks in a herringbone arrangement (Fig. 1). The overall pattern of the layers can be expressed as . . .bab′bab′. . . where b and b′ are the non-identical benzoate layers and a is the amine layer. Owing to the proton transfer, a charge separation exists within the hydrogen-bonded layers, so that the amine layer is formally positively charged with the adjacent benzoate face being formally negatively charged.
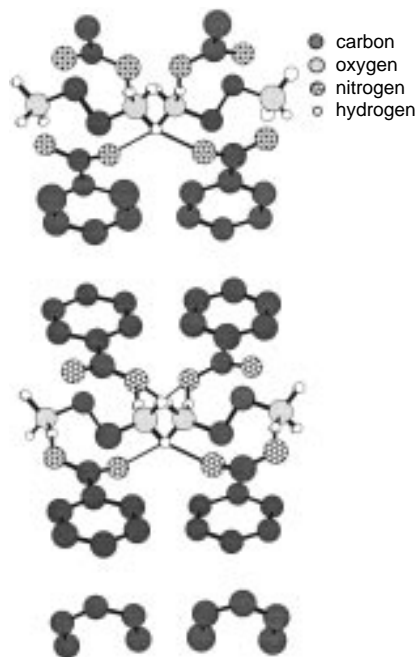

Fig. 1 The structure of the 1 : 2 adduct between 1,2-diaminoethane and benzoic acid; projection down *a* (*c* horizontal). Only hydrogens participating in NH⋯O hydrogen bonds are illustrated.

In an attempt to gain further insight into the nature of the proton transfer, hydrogen-bond geometry optimisations were performed on isolated 1:2 adducts using density functional theory (DFT) involving the G94 package.[10] At the SVWN5/6-31G* or B3LYP/6-31G* levels of theory[12,13] it is predicted that the protons in the (observed) NH⋯O bonds are transferred from the amine to the acid moieties, so that the hydrogen bond becomes N⋯HO in character. Calculations in the presence of a solvent reaction field (either H_2O, $CHCl_3$ or methanol) all follow this pattern.‡ This suggests that the proton-transfer (ionic) hydrogen bonds within the solid-state structure are stabilised by the extensive hydrogen-bonding array within the solid-state lattice. Supporting this proposition are the results of similar DFT[14] and semi-empirical[9] calculations on our previously reported cyclam:4-*tert*-butyl benzoic acid 1:2 adduct. In this system the network of NH⋯O hydrogen bonds is confined within a single adduct and proton transfer is predicted by DFT and semi-empirical calculations.

Finally, the B3LYP/6-31G* calculated dipole moment of a single 1,2-diaminoethane/benzoic acid motif is 6.41×10^{-30} C m; this moment, coupled with the non-centrosymmetric nature of the crystalline structure suggests this material may have interesting SHG (second harmonic generation) properties.

In summary, we have demonstrated that benzoic acid and 1,2-diaminoethane self-assemble to discrete 2:1 aggregates held together by extensive hydrogen bonding and π-stacking interactions. This study acts as a prototype for the synthesis of a range of other closely related carboxylic acid/diamine arrays, a class of new (charged-separated) assemblies of potential interest as new opto-electronic materials.
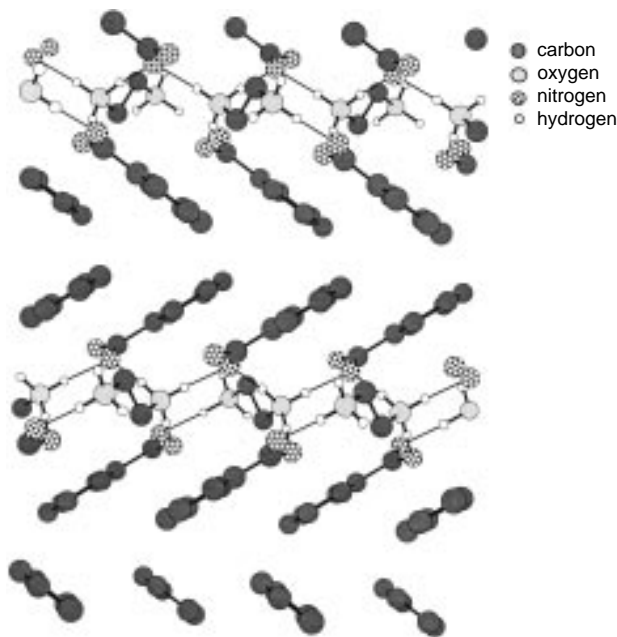

Fig. 2 The structure of the 1:2 adduct between 1,2-diaminoethane and benzoic acid; projection down *b* (*c* horizontal). Only hydrogens participating in NH⋯O hydrogens bonds are illustrated.

Footnotes

† *Crystallographic data*: $C_{16}H_{20}N_2O_4$, M = 304.4, orthorhombic, space group $Pca2_1$, a = 8.425(3), b = 9.144(3), c = 21.000(5) Å, U = 1618 Å^3, D_c (Z = 4) = 2.14_9 g cm^{-3}.

X-Ray study: N = 2942 unique diffractometer reflections [derived from a hemisphere to $2\theta_{max}$ = 65°; monochromatic Mo-Kα radiation, λ = 0.7107_3]; R_{int} = 0.017, N_0 [$I \geqslant 3\sigma(I)$] = 1625 'observed' refining to conventional R on $|F|$ = 0.041, R_w (statistical weights) = 0.034. Anisotropic thermal parameter forms for C, O, (x, y, z, U_{iso})$_H$ refined. (x, y, z) (C, O) resulting constrained in the refinement on neutron data. T *ca.* 295 K.

Neutron study: N = 1679 reflections [HIFAR reactor, 2TANA diffractometer, Lucas Heights, Australia; λ = 1.233(2) Å], N_0 = 981 refining to R = 0.046, R_w = 0.027. Anisotropic thermal parameter forms for C, O, (x, y, z, U_{iso})$_H$ refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/346.

‡ Similar results have been recorded in calculations on amino acid zwitterions where it has been found that proton transfers in such molecules are mediated by solvent molecules (J. H. Jensen and M. S. Gordon, *J. Am. Chem. Soc.*, 1995, **117**, 8159).

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