Crystal Engineering: Hydrogen-bonded Salts of Hydroxybenzoic Acids for Second Harmonic Generation

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Hydrogen bonding between ions has been used to engineer specific structural features into two novel crystalline materials with nonlinear optical properties, (*S*)-1-phenylethylammonium 3-hydroxybenzoate and (*S*)-1-phenylethylammonium 4-hydroxybenzoate; their crystal structures are reported and the importance of their hydrogen-bonded networks is discussed.

One of the most elusive, and desirable, targets for chemical research concerns the ability to design a material with predictable chemical and physical properties. In recent years, a new field has emerged which involves the design of crystals with specific solid state properties: crystal engineering.[1,2] The interplay between molecules and ions is governed by a range of intermolecular forces,[3] and the interaction which, arguably, has attracted most interest is hydrogen bonding.[4]

Our previous studies on hydrogen-bonded salts[5,6] have shown that hydrogen bonds between ions are, energetically,

Table 1 Geometry of the hydrogen bonds in [(*S*)-MeCHPhNH$_3$][3-HOC$_6$H$_4$CO$_2$][a]

D–H···A	*r*(D–H)/nm	*r*(H···A)/nm	*r*(D···A)/nm	∠(DH···A)/°
O(3)–H(O3)···O(2′)	0.094(5)	0.187(5)	0.2739(4)	152(5)
N–H(N)···O(2′)	0.098(5)	0.179(5)	0.2774(4)	173(4)
N–H(N)···O(1″)	0.101(5)	0.178(5)	0.2767(4)	166(4)
N–H(N)···O(1‴)	0.088(5)	0.198(5)	0.2846(4)	167(4)

[a] Symmetry elements: (′) $-1 + x, y, z$; (″) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (‴) x, y, z.

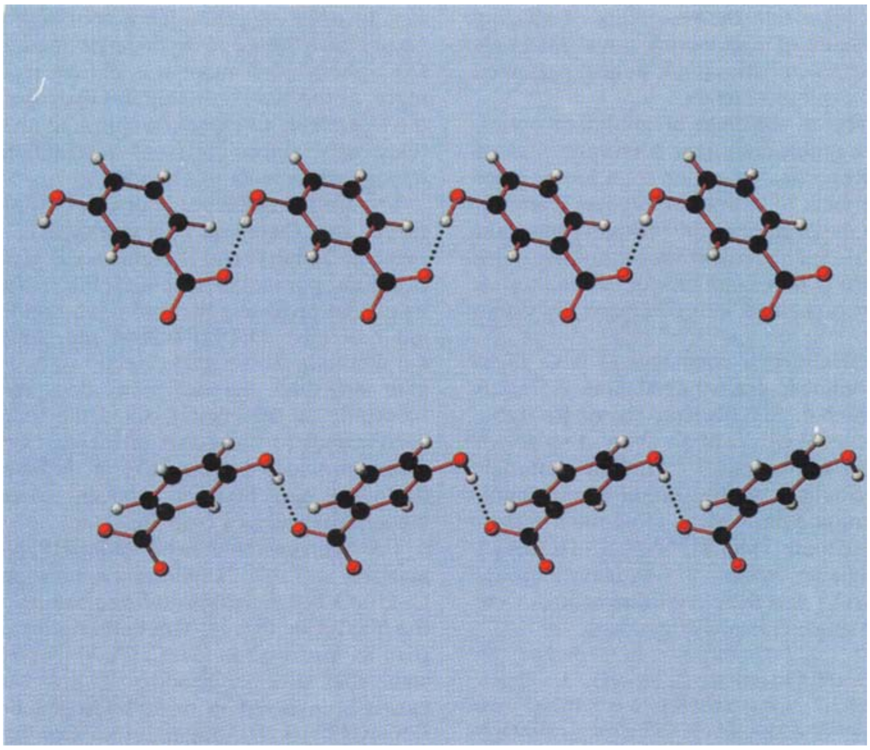

Fig. 1 [MeCHPhNH$_3$][3-HOBA]: infinite chains of anions parallel to the *a*-axis, with hydrogen bonds displayed as dotted lines, viewed down *b*

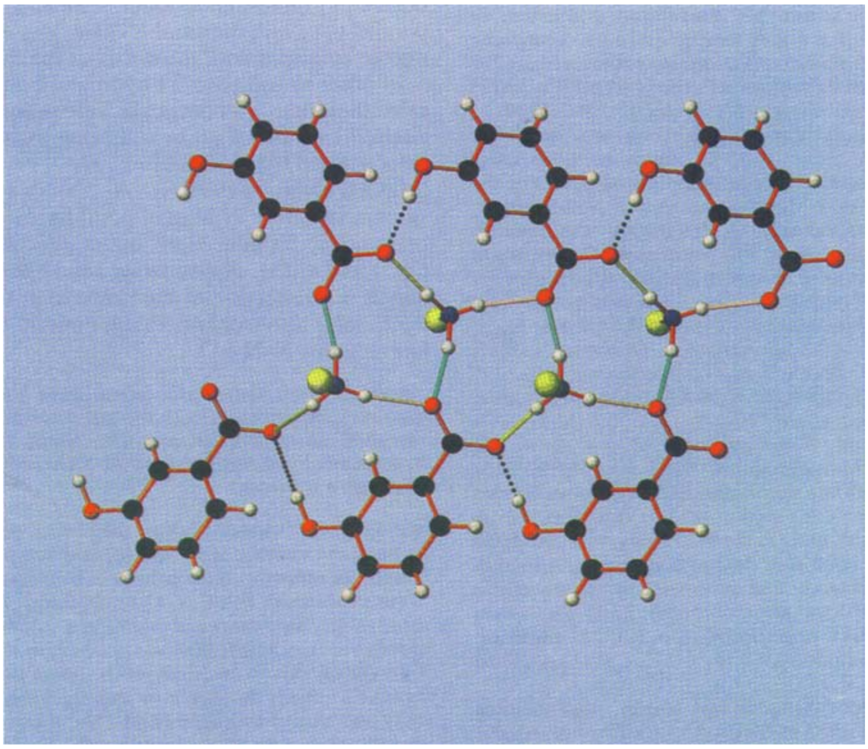

Fig. 2 [MeCHPhNH$_3$][3-HOBA]: cations crosslinking infinite chains of anions in the *a*–*c* plane, viewed down *b*. Symmetry related N···O hydrogen bonds are indicated by their colour: yellow, pink and green. O···O hydrogen bonds are displayed as dotted lines. The MeCHPh group of the cations has been replaced by a single atom (yellow) for clarity.

strong enough to play a significant role in the structural organization and packing of ions within a crystalline material.[7] Moreover, we demonstrated that it is possible to use the organic cations to carry the high optical polarizability and the hydrogen-bonding inorganic[5] (or organic[6]) anions to provide thermal and structural stability, a technique recently adopted by Zyss and coworkers[8] for the design of novel materials for nonlinear optics; the resulting crystalline salt, 2-amino-5-nitropyridinium dihydrogenphosphate, shows significant second harmonic generation (SHG) activity.[8] Consequently, with the success of this approach, the possibility of utilizing hydrogen bonds as a means of engineering novel materials with desired structural characteristics (and, hence, preferred properties), needs to be explored further.

So far, synthetic efforts in the field of nonlinear optics, notably second harmonic generation, have been concentrated on tuning molecular properties in order to achieve more pronounced nonlinear effects.[9,10] Considerably less attention has been focused on the importance of the physical properties displayed by the material. Such considerations, however, are of paramount importance if new nonlinear optical materials are to be successfully incorporated into commercially viable devices.

Recently developed SHG-active composites[11] have highlighted the need for nonlinear optical crystalline materials which are colourless, soluble, SHG-active, thermally stable and with a needle-like crystal habit. In an attempt to design salts to meet these criteria, two novel crystalline materials were synthesized (by acid–base neutralization in methanol, followed by recrystallization from water): (*S*)-1-phenylethylammonium 3-hydroxybenzoate [MeCHPhNH$_3$][3-HOBA],[†] and (*S*)-1-phenylethylammonium 4-hydroxybenzoate [MeCHPhNH$_3$][4-HOBA],[†] and their crystal structures were determined using X-ray single crystal diffraction.[‡]

In order to create a needle-like crystal, it was assumed that a structure dominated by a strongly hydrogen-bonded chain would manifest itself in the solid state as an elongated crystal. In order to achieve this, 3-hydroxybenzoic acid and 4-hydroxybenzoic acid were selected as starting points. By deprotonating these acids, the formation of a head-to-tail hydrogen bond between the hydroxylic proton and one of the charged carboxylate oxygens would be encouraged. Such an interaction would create an infinite chain of anions which could dominate, and control, the orientation of the counterion. In order to guarantee a nonlinear response (SHG only occurs in a noncentrosymmetric medium), a chiral amine, (*S*)-1-phenylethylamine was chosen as counterion. Furthermore, as this base only contains hydrogen-bond donors, N–H, it was unlikely to cause disruption to an anionic infinite chain (especially since O–H···O interactions are energetically stronger than N–H···O bonds).

The single-crystal study of [MeCHPhNH$_3$][3-HOBA] confirmed that there was only one type of O–H···O interaction present, Table 1, and that this bond generates infinite chains of anions, parallel to the *a*-axis, Fig. 1. This chain is reinforced by cations providing two hydrogen-bonds, r[N···O(2′)] 0.2774 nm and r[N···O(1‴)] 0.2846 nm, linking adjacent anions parallel to *a*. This highly directional hydrogen-bonded aggregate structure, parallel to *a*, does manifest itself macroscopically in the crystal, since the long axis of the needle corresponds to the *a*-axis of the unit cell. In addition, each cation provides a cross-link, in the *a*–*c* plane, r[N···O(1″)] 0.2767(4) nm, between adjacent chains, creating infinite ladders parallel to *a* (see Fig. 2).

The hydrogen bonding in [MeCHPhNH$_3$][4-HOBA], summarized in Table 2, follows a similar pattern, with the only O–H···O bond creating infinite chains of anions, parallel to the *b*-axis (see Fig. 3). This bond is shorter and closer to linear than its analogue in [MeCHPhNH$_3$][3-HOBA], suggesting a somewhat stronger head-to-tail link between anions. Each cation is involved in three hydrogen bonds, two of which, r[N···O(2″)] 0.2807 nm and r[N···O(1‴)] 0.2816(4), provide a cross-link, parallel to *a*, between adjacent chains of anions. The final hydrogen bond r[N···O(1′)] 0.2768(4) nm, Table 2, creates a three-dimensional structure by making a link, parallel to *c*, with the anionic chain, Fig. 4. The long axis of the needle coincides with the *a*-axis of the unit cell.

In order to compare the hydrogen-bond patterns in the two salts, their first-level networks were assigned using the method devised by Etter.[12][§] The following assignments were made: [MeCHPhNH$_3$][3-HOBA], $N_1 = C_1^1(7)3D$ and [MeCHPhNH$_3$][4-HOBA], $N_1 = C_1^1(8)3D$. This encoding summarizes the hydrogen bonding in a simple, yet comprehensive, fashion. Both materials contain infinite chains, $C_1^1(7)$ and $C_1^1(8)$, respectively, where the difference in chain length is a reflection of the position of the –OH substituent. Both salts also contain three dimeric (*D*) hydrogen bond interactions, N–H···O.

[†] *Crystal data* for [MeCHPhNH$_3$][3-HOBA]: $C_{15}H_{17}NO_3$, $M = 259.3$, orthorhombic, space group $P2_12_12_1$, $a = 0.6358(1)$, $b = 1.1620(5)$, $c = 1.8310(9)$ nm, $U = 1.3527$ nm^3, $Z = 4$, $D_c = 1.27$ g cm^{-3}, $F(000) = 552$. Monochromated Mo-Kα radiation, $\lambda = 0.071069$ nm, $\mu = 0.8$ cm^{-1}, $T = 173$ K. Data were collected on a crystal (0.2 × 0.2 × 0.05 mm), cut from a needle, using an Enraf-Nonius CAD4 diffractometer fitted with a cold dinitrogen stream, low temperature attachment, in the θ–2θ mode, with $\Delta\theta = [0.8 + 0.35 \tan(\theta)]^\circ$ and a maximum scan time of one minute. A total of 1426 reflections were measured for $2 < \theta < 25^\circ$ and $+h +k +l$, and 981 unique reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{\frac{1}{2}}/Lp$. There was no crystal decay and no correction was made for absorption. The structure was solved by direct methods using SHELXS-86. All remaining calculations were carried out using the SDP-Plus program system on a MicroVax computer. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were located on a difference map. The hydrogen atom vibrational parameters were fixed such that $B_{\text{iso}} = 1.3B_{\text{eq}}$ for the atom to which they are bonded, but positional parameters were allowed to refine freely. Final parameters were $R = 0.041$, $R_w = 0.046$, $\omega = 1/\sigma^2(F)$, $s = 1.4$, 223 variables, $(\Delta/\sigma)\text{max} = 0.17$, $(\Delta\rho)\text{max,min} = +0.19, -0.19$ e Å^{-3} on a final difference map.

Crystal data for [MeCHPhNH$_3$][4-HOBA]: $C_{15}H_{17}NO_3$, $M = 259.3$, orthorhombic, space group, $P2_12_12_1$, $a = 0.6520(1)$, $b = 1.1918(2)$, $c = 1.7922(3)$ nm, $U = 1.3927$ nm^3, $Z = 4$, $D_c = 1.24$ g cm^{-3}, $F(000) = 552$. Monochromated Mo-Kα radiation, $\lambda = 0.071069$ nm, $\mu = 0.8$ cm^{-1}. Data were collected, using a piece 0.5 mm long, cut from a needle of cross-section 0.15 × 0.10 mm, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode, with $\Delta\theta = [0.8 + 0.35 \tan(\theta)]^\circ$ and a maximum scan time of one minute. A total of 1460 reflections were measured and processed as in the above structure determination (901 unique reflections). Final parameters were $R = 0.040$, $R_w = 0.043$, $\omega = 1/\sigma^2(F)$, $s = 1.4$, 223 variables, $(\Delta/\sigma)\text{max} = 0.33$, $(\Delta\rho)\text{max,min} = +0.14, -0.13$ e Å^{-3} on a final difference map.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] In order to verify that the chosen single crystals were representative of the bulk material, the X-ray powder diffraction patterns were simulated from the single crystal data (using the CERIUS 2.3 package) and compared with the experimental X-ray powder pattern, recorded on a bulk sample. The match between simulated and experimental patterns demonstrated that only one structural form of each salt was present.

[§] A graph set is specified using the pattern designator (*G*), its degree (*n*) and the number of donors (*d*) and acceptors (*a*); $G_d^a(n)$. *G*, the descriptor referring to the pattern of hydrogen bonding, can be either *S* (intramolecular bond), *C* (infinite chain), *R* (intermolecular ring), or *D* (noncyclic dimers and other finite structures) and the parameter *n* refers to the number of atoms in a ring, or the repeat unit of a chain. The set of ions to be analysed is called an array. Graph sets are assigned initially to motifs (a hydrogen-bonded set constructed by only one type of hydrogen bond), and then to first-level networks (a combination of all the relevant motifs, *e.g.* if the array contains four different hydrogen bond types, then the first-level network is a combination of four motifs). Higher level motifs are assigned to sets generated by combinations of hydrogen bond types.

Table 2 Geometry of the hydrogen bonds in [(*S*)-$MeCHPhNH_3$][4-$HOC_6H_4CO_2$][a]

D–H···A	*r*(D–H)/nm	*r*(H···A)/nm	*r*(D···A)/NM	∠(D–H···A)/°
O(3)–H(O3)···O(2′)	0.083(4)	0.185(4)	0.2674(4)	172(4)
N–H(N)···O(1″)	0.106(4)	0.172(4)	0.2768(4)	168(4)
N–H(N)···O(2‴)	0.087(4)	0.194(4)	0.2807(4)	176(4)
N–H(N)···O(1⁗)	0.092(4)	0.190(4)	0.2816(4)	175(4)

[a] Symmetry elements: (′) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (″) x, y, z; (‴) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (⁗) $- \frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

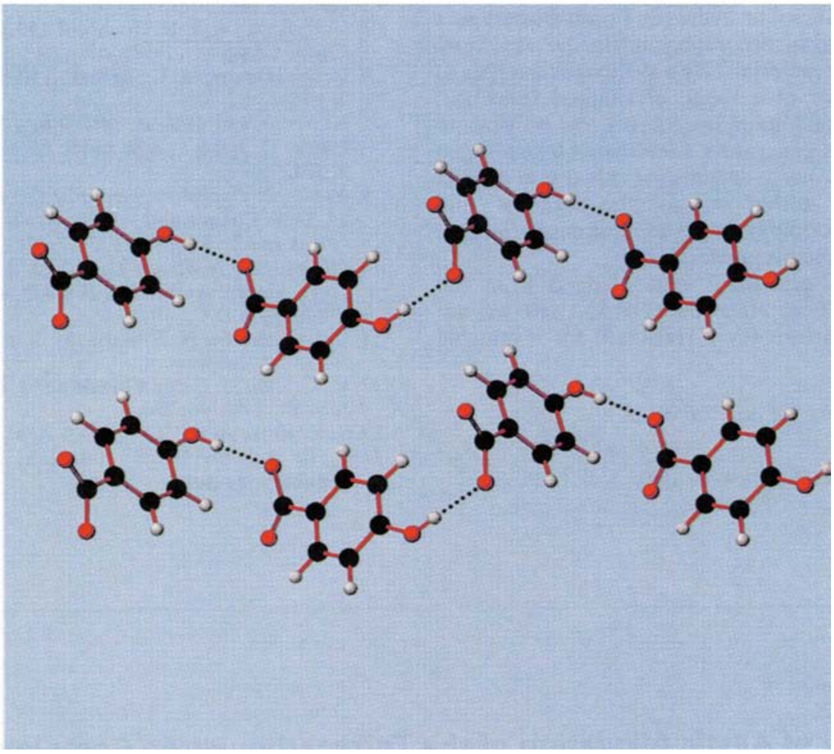

Fig. 3 [$MeCHPhNH_3$][4-HOBA]: infinite chains of anions parallel to the *b*-axis, with hydrogen bonds displayed as dotted lines, viewed down *c*

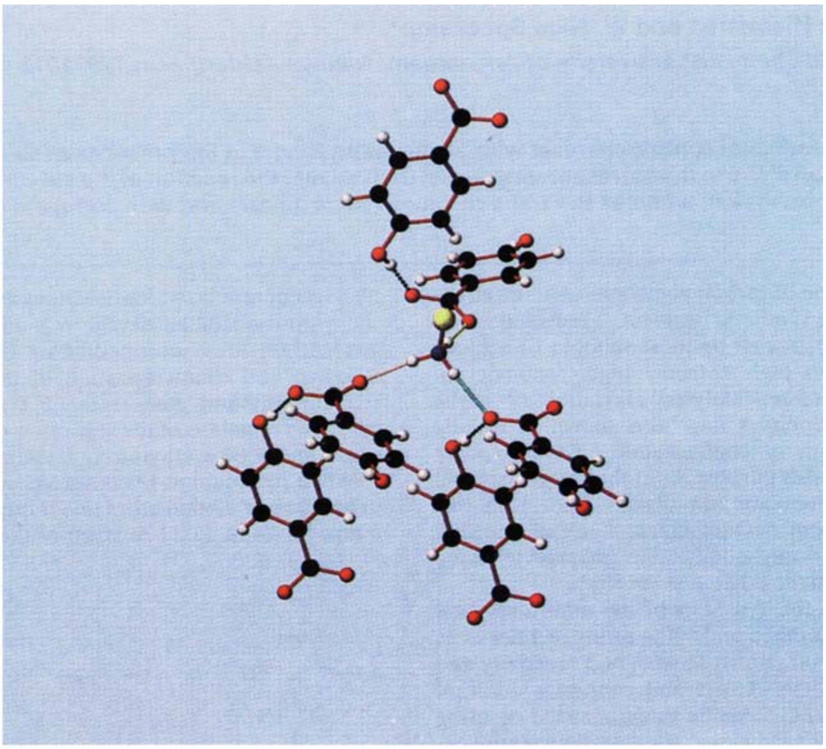

Fig. 4 [$MeCHPhNH_3$][4-HOBA]: the geometry around one cation showing the crosslinking, parallel to *a*, of adjacent anionic chains, plus the hydrogen-bonded link, parallel to *c*, to an infinite anionic chain. Symmetry related N···O hydrogen bonds are indicated by their colour: yellow, pink and green. O···O hydrogen bonds are displayed as dotted lines. The MeCHPh group of the cations has been replaced by a single atom (yellow) for clarity.

Preliminary powder measurements[13] of the SHG activities of these materials show that they are, as expected, SHG-active: [MeCHPhNH$_3$][3-HOBA] is comparable to K[H$_2$PO$_4$] and [MeCHPhNH$_3$][4-HOBA] is comparable to urea.[14] Furthermore, both salts are colourless, transparent, and very water soluble with relatively high melting points (173–175 and 208–210 °C, respectively). In addition, they both exhibit a needle-like morphology which is an essential requirement for the successful incorporation into SHG-active composites.

This study clearly illustrates the potential of using the strength and regiospecificity of hydrogen bonds in salts as a means of designing, and incorporating, distinctive structural features into crystalline materials. By a systematic analysis of the structural behaviour of a range of charged functional groups, both organic and inorganic, it will be possible to identify a set of 'pattern generators' (dominated by hydrogen bonds), which can be used as building blocks in crystal engineering. This will further increase the potential, and flexibility, of this methodology as a means of designing new materials with predictable properties.

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