Organic Salts of L-Tartaric Acid: Materials for Second Harmonic Generation with a Crystal Structure Governed by an Anionic Hydrogen-bonded Network

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Twelve hydrogen-bonded hydrogen-L-tartrate salts, capable of second harmonic generation (SHG), have been synthesized {the crystal structure of piperazinium(2+) bis-hydrogen-L-tartrate, $[H_2NC_4H_8NH_2][C_4H_5O_6]_2$, is reported}; the structural significance of hydrogen bonding and its use as a tool in crystal engineering is discussed.

The influence of hydrogen bonding on the geometry and crystal packing of organic molecular solids is well known,[1,2] and it is possible to utilize regiospecific hydrogen bonds to control the way in which molecular units form aggregate structures.[3,4] Previous work[5] has shown that hydrogen bonding plays an important structural role in a series of SHG-active organic salts of dihydrogenphosphate, and subsequent calculations showed that hydrogen bonding provided a significant contribution (>20–25%) to the lattice energy of such salts.[6] We now present results illustrating that hydrogen bonding plays an instrumental role in the structure of a novel class of SHG-active salts, hydrogen-L-tartrates, [AH][L-tartH] (where tartH$_2$ = L-tartaric acid,† and A = amine).

L-Tartaric acid was chosen as the starting point for this study as its chirality guarantees a nonlinear response in its salts (SHG is only possible in a noncentrosymmetric medium).[7]

Table 1 SHG-activities and melting points of salts of hydrogen-L-tartrate,[a] [AH][L-tartH]

[AH]$^+$	Melting point/°C	SHG-activity/ α-SiO$_2$[c]
Piperidinium	109–110	0.3
Pyridinium	143–145	0.6
Piperazinium(1+)	250 (decomp.)	2.9
Piperazinium(2+)[b]	230 (decomp.)	1.6
Benzylammonium	170–172	1.8
3-Hydroxy-6-methylpyridinium	162–164	0.4
1-Methylimidazolium	50–53	0.3
2-Aminopyrimidinium	172–174	2.0
1-Methylpropylammonium	122–123	1.4
(S)-1-Phenylethylammonium	193–195	1.1
3-Hydroxypyridinium	137–139	13.7
Dimethylammonium	132–134	0.6

[a] All salts detailed in Table 1 gave satisfactory microanalyses. [b] The salt is $[C_4H_{12}N_2][L\text{-tartH}]_2$. [c] Data are correct to ±10%.

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† (2R,3R)-(+)-tartaric acid.

Table 2 Geometry of the hydrogen bonds in $[C_4H_{12}N_2][\text{L-tartH}]_2{}^a$

D–H$\cdots$A	r(D–H)/nm	r(H$\cdots$A)/nm	r(D$\cdots$A)/nm	(D–H$\cdots$A)/°
N–H(NA)$\cdots$O(1)	0.088(4)	0.197(4)	0.2817(3)	161(4)
N–H(NB)$\cdots$O(4)′	0.089(4)	0.198(4)	0.2819(3)	156(4)
O(2)–H(O2)$\cdots$O(5)″	0.091(4)	0.157(4)	0.2484(3)	174(4)
O(3)–H(O3)$\cdots$O(6)‴	0.078(4)	0.198(4)	0.2719(3)	158(4)

^{a} Symmetry code: (′) $\frac{1}{2} - y$, $-\frac{1}{2} + x$, $\frac{1}{4} + z$; (″) $1 + x$, y, z; (‴) $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $1\frac{1}{4} - z$.

Twelve salts were prepared by neutralizing the acid with equimolar amounts of the relevant base, and their SHG-activities were measured relative to α-quartz, using the standard powder technique.[8] The samples (particle size *ca.* 80–120 μm) were irradiated at 1064 nm using a pulsed Nd-YAG laser, and the intensity of the second harmonic (532 nm) was measured in the forward direction, $\theta = 0°$, Table 1.

Every [L-tartH]⁻ salt does, as expected, exhibit some SHG-activity. There is a large variation in the magnitude of the nonlinear response from different salts, which suggests that it is possible to improve the SHG-activity by a suitable choice of cation. The materials listed in Table 1 display a number of favourable properties: they are colourless, transparent and soluble, and have, in general, good mechanical properties, including relatively high melting points. Such thermal stability is crucial if SHG-active materials are to be successfully incorporated into working optoelectronic devices.[9] In addition, the simplicity of the synthetic route makes it easy to generate a range of materials with a variation in a specific property, *e.g.* refractive index. Materials with diverse refractive indices can be utilized to achieve a good refractive index match with a polymeric host in the preparation of SHG-active composites.[10]

An X-ray single-crystal study‡§ of piperazinium(2+) bis-hydrogen-L-tartrate reveals the presence of extensive hydrogen bonding. Adjacent anions form infinite chains through a 'head-to-tail' arrangement *via* a short hydrogen bond, $r[\text{O}(2)\cdots\text{O}(5)''] $ 0.2484(3) nm, Table 2. The hydrogen-bonded chains are then crosslinked in the *a–b* plane *via* O(3)$\cdots$O(6)‴, to form layered structures.

Each cation is surrounded by four [L-tartH]⁻ anions, Fig. 1, and the piperazinium cations form layers at $z = 0$, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$,

‡ *Crystal data:* $C_{12}H_{22}N_2O_{12}$, $M = 386.3$, tetragonal, space group $P4_12_12$, $a = b = 0.7541(1)$, $c = 2.7638(3)$ nm, $U = 1.5718$ nm³, $Z = 4$, $D_c = 1.63$ g cm⁻³, $F(000) = 816$. Monochromated Mo-Kα radiation, $\lambda = 0.071069$ nm, $\mu = 1.4$ cm⁻¹. Data were collected on a crystal (0.15 × 0.15 × 0.15 mm), using an Enraf–Nonius CAD4 diffractometer in the θ–2θ mode, with $\Delta\theta = \{0.8 + 0.35 \tan(\theta)\}°$ and a maximum scan time of one minute. A total of 1643 reflections were measured for $2 < \theta < 25°$ and $+h+k+l$, and after averaging ($R_{\text{avg}} = 0.026$), 913 unique reflections remained of which 588 with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$. 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 analysis. Hydrogen atoms were located on a difference map. The hydrogen atom vibrational parameters were fixed such that $B_{\text{iso}} = 1.3\,B_{\text{eq}}$ for the atom to which they are bonded, but their positional parameters were allowed to refine freely. The weighting scheme was $\omega = 1/\sigma^2(F)$ and the final residuals were $R = 0.029$, $R' = 0.037$. 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 crystal was representative of the bulk material, the X-ray powder diffraction pattern was simulated from the single crystal data (using the CERIUS 2.3 package) and compared with the experimental X-ray powder pattern, recorded on the bulk sample. The match between simulated and experimental pattern demonstrated that only one structural form of $[C_4H_{12}N_2]$-$[\text{L-tartH}]_2$ was present.[12]
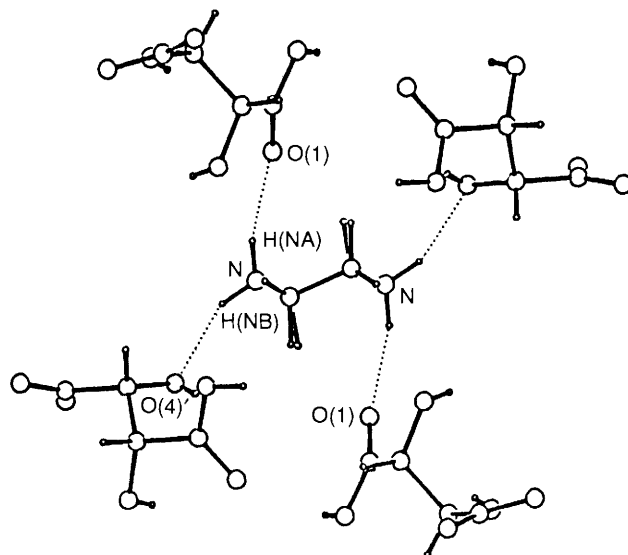

Fig. 1 The environment of one cation in piperazinium(2+) bis-hydrogen-L-tartrate, which cross-links two layers of anions (layers viewed edge on)

half-way between the anion layers. Each cation is hydrogen bonded to two oxygen atoms in the layer above, N–H(NA)$\cdots$O(1) and N–H(NB)$\cdots$O(4)′, and by symmetry related hydrogen bonds to two oxygen atoms in the anion layer below. The compact packing of ions throughout the structure is reflected by the high density, $D_c = 1.63$ g cm⁻³, and decomposition point, 230 °C, of the material.

Clearly, hydrogen bonding plays a prominent part in determining the structure of piperazinium(2+) bis-hydrogen-L-tartrate, notably by creating a strongly bonded network of anions. In order to establish the possible existence of preferred hydrogen-bond patterns in other organic salts of hydrogentartrates, the hydrogen-bond interactions in three such structures {piperazinium(2+) bis-hydrogen-L-tartrate, (*S*)-1-phenylethylammonium hydrogen-L-tartrate[11,12] and (*S*)-1-phenylethylammonium hydrogen-*meso*-tartrate[13]}, were analysed using a method developed by Etter.[4,14] This method was originally devised for analysing molecular solids, but is here used (for the first time) as a means of recognizing and comparing hydrogen-bonded aggregate structures within organic *salts*.¶ Because the cations only contain hydrogen bond donor sites and, hence, will not generate extended interactions, this examination has been restricted to the anionic network within each salt, Table 3.

¶ A graph set is specified using the pattern designator (*G*), its degree (*r*) and the number of donors (*d*) and acceptors (*a*); G^a_d (*r*). *G*, the descriptor referring to the pattern of hydrogen bonding, can be either *I* (intramolecular bond), *C* (infinite chain), *R* (intermolecular ring), or *D* (noncyclic dimers and other finite structures) and the parameter *r* 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 first-order motifs (a hydrogen-bonded set constructed by only one type of hydrogen bond), and then to first-order networks (a combination of all the relevant motifs, *e.g.* if the array contains four different hydrogen bond types, then the first-order network is a combination of four motifs). Higher order motifs are assigned to sets generated by several different hydrogen bond types.[4,14]
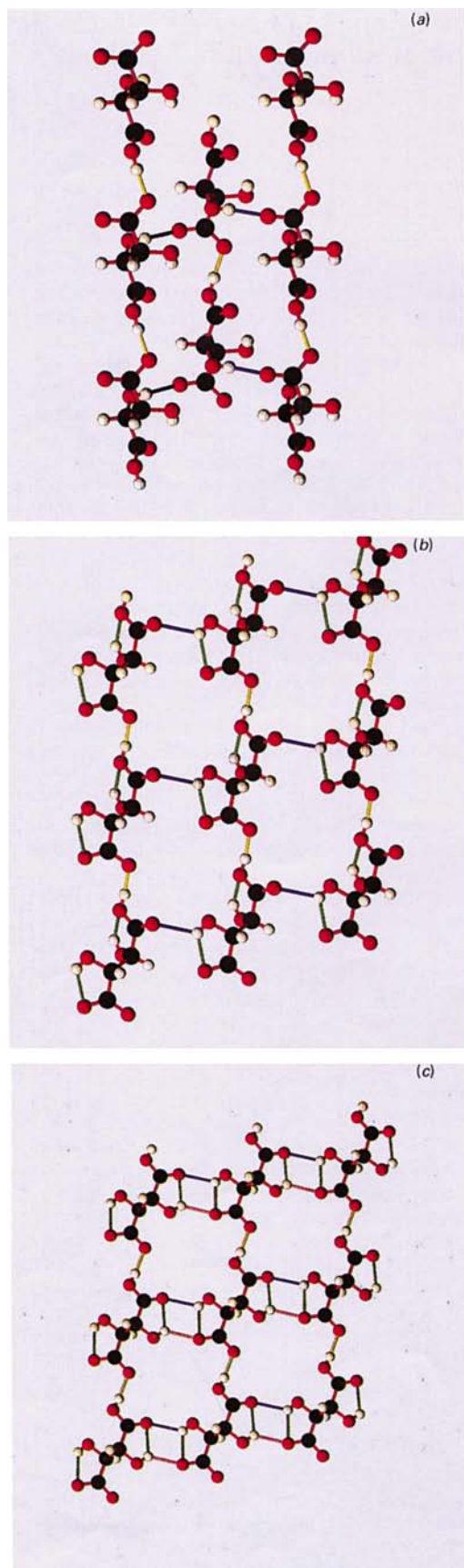
Table 3 First-order graph-set analysis of three organic hydrogentartrates

Compound	First-order network
Piperazinium(2+) bis-hydrogen-L-tartrate	$N_1 = C_1^1(7)C_1^1(6)$
(S)-1-phenylethylammonium hydrogen-L-tartrate	$N_1 = C_1^1(7)C_1^1(6)2I_1^1(5)$
(S)-1-phenylethylammonium hydrogen-*meso*-tartrate	$N_1 = C_1^1(7)2C_1^1(6)2I_1^1(5)$

The encoding of first-order networks shows that the hydrogen-bonded networks present exhibit a remarkable consistency, Fig. 2. All three structures contain the seven-membered chain $\{C_1^1(7)\}$ which is responsible for a head-to-tail link between adjacent anions. Each structure also comprises a six-membered chain $\{C_1^1(6)\}$ which provides a crosslinking between adjacent infinite chains of anions. In the case of (S)-1-phenylethylammonium hydrogen-*meso*-tartrate, Fig. 2(c), there are two such crosslinks plus two intramolecular hydrogen bonds $\{2I_1^1(5)\}$, whereas in (S)-1-phenylethylammonium hydrogen-L-tartrate, Fig. 2(b), there is one cross-link and two intramolecular bonds. This clearly demonstrates the effect that minor stereochemical changes may have upon a complex hydrogen-bonded network.

Although the number of structures reported here is limited, fifteen extant organic hydrogentartrate structures (extracted from the Cambridge Crystallographic Data Centre), have been examined. The anions prefer specific aggregate structures, essentially independent of the charge and size of the cation, indicating that it may be possible to utilize such ions as building units for crystal engineering. The strength and directionality of the hydrogen bond, in combination with the pattern preference displayed by certain ions, *e.g.* dihydrogenphosphate or hydrogentartrate, creates a tool with which it may be possible to design ionic materials with specific, and controllable, structural features. Since the properties of a solid are critically dependent upon its structure, it is feasible to design materials with desired characteristics by incorporating specific properties into the subunits.

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