Table 6. *Selected geometric parameters* (Å, °) *for* (2*c*)

Cl—C1	1.689 (4)	N2—C18	1.480 (4)
O1—C8	1.224 (5)	N2—C14	1.484 (4)
O2—C12	1.405 (4)	C8—C9	1.496 (6)
N1—C8	1.343 (4)	C9—C10	1.529 (5)
N1—C7	1.447 (5)	C10—C11	1.537 (5)
N1—C11	1.462 (4)	C11—C12	1.521 (4)
N2—C13	1.459 (4)	C12—C13	1.532 (5)
C8—N1—C7	121.9 (3)	N1—C8—C9	108.2 (3)
C8—N1—C11	113.7 (3)	C8—C9—C10	104.3 (3)
C7—N1—C11	124.4 (3)	C9—C10—C11	103.2 (3)
C13—N2—C18	112.4 (3)	N1—C11—C12	112.8 (3)
C13—N2—C14	115.7 (3)	N1—C11—C10	102.1 (2)
C18—N2—C14	116.6 (3)	C12—C11—C10	112.7 (3)
C6—C1—Cl	120.2 (3)	O2—C12—C11	109.0 (3)
C2—C1—Cl	118.0 (4)	O2—C12—C13	108.7 (3)
N1—C7—C6	113.6 (3)	C11—C12—C13	111.8 (3)
O1—C8—N1	125.1 (4)	N2—C13—C12	110.3 (3)
O1—C8—C9	126.7 (4)		

Table 7. *Relevant geometry* (Å, °) *of hydrogen bonds in the crystals of the* (2*a*), (2*b*) *and* (2*c*) *stereoisomers*

	D	H	*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
(2*a*)	O	H2	O1^{i}	0.82	2.71 (1)	1.90	167
(2*b*)	O2	H2	O1^{ii}	0.82	2.748 (6)	1.94	169
(2*c*)	O2	H2	N2	0.82	2.698 (4)	2.22	118
(2*c*)	C7	H7*B*	O2	0.97	3.013 (4)	2.36	124

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, -y, z-\frac{1}{2}$.

The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure.

The structures were solved by direct methods and refined by anisotropic full-matrix least squares. Compounds (2*b*) and (2*c*) crystallize in polar space groups; the origin of the coordinate system for each of them was fixed automatically by the *SHELXL*93 program (Sheldrick, 1993) by using the algorithm of Flack & Schwarzenbach (1988). All the H atoms were placed in calculated positions and refined isotropically riding on the attached atoms. Their *U* values were: for (2*a*), 1.5 × U_{eq} of the parent atom for all H atoms; for (2*b*), 1.2 × U_{eq} of the parent atom for 20 H atoms, the remainder being refined singly; for (2*c*), a common *U* value, refined for each of three groups of H atoms.

The poor quality of the crystals of (2*a*) is the reason why its analysis is of lower accuracy than those of (2*b*) and (2*c*). Nevertheless, the results are good enough to support the discussion presented above. As shown by the atomic ellipsoids of Fig. 1, the *sec*-butyl residues are affected by high thermal motion or disorder in all three analyses.

The absolute configurations, deduced from the values of the Flack (1983) index [−0.03 (7), −0.02 (4) and 0.12 (3) for (2*a*), (2*b*) and (2*c*), respectively] are in agreement with those expected on the basis of the chirality of the reagents used in the syntheses.

The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma), and on a COMPAQ-486c portable computer.

For all compounds, data collection: local programs; cell refinement: *LQPARM* (Nardelli & Mangia, 1984); data reduction: local programs; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965), *PLUTO* (Motherwell & Clegg, 1978); software used to prepare material for publication: *PARST* (Nardelli, 1983), *PARSTCIF* (Nardelli, 1991); software used to perform non-bonded energy calculations: *ROTENER* (Nardelli, 1988).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Influence of Hydrogen Bonding on the Structure of 1-Methylimidazolium D-Tartrate

Joan Fuller

The Frank J. Seiler Research Laboratory, 2354 Vandenberg Drive, Suite 2A35, United States Air Force Academy, Colorado 80840, USA

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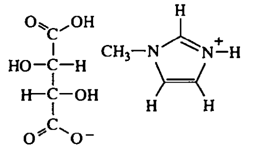
Abstract

The title compound, 1-methylimidazolium D-tartrate, $C_4H_7N_2^+.C_4H_5O_6^-$, consists of a tightly interwoven tartrate network that is hydrogen bonded to the imidazolium

cations. There is a broad range of hydrogen-bond interactions within this structure. The interactions between the anions and cations are believed to influence the alignment of the cations and thereby contribute to the nonlinear optical activity of the salt.

Comment

The development of nonlinear optical materials capable of second harmonic generation (SHG) is a rapidly growing area because of the commercial importance of these materials in the fields of optical communication, signal processing, sensing, and instrumentation (Eaton, 1992). The requirement of non-centrosymmetry for SHG activity has generated the need to design materials that will crystallize in non-centrosymmetric space groups. As a response to this need, enantiomeric salts are being investigated for nonlinear optical applications. Enantiomeric tartrate salts have been shown to have SHG activity comparable to α-quartz and in some cases urea (Aakeröy, Hitchcock & Seddon, 1992; Aakeröy, Seddon & Leslie, 1992). In these salts, the tartrate anions form complex hydrogen-bonded networks that dominate the structure. It has been proposed that the strength and directability of the anionic networks may allow for the possibility of designing materials with enhanced nonlinear optical activity if the appropriate cation is chosen (Aakeröy, Hitchcock & Seddon, 1992; Aakeröy, Seddon & Leslie, 1992). In addition to the influence of the anionic hydrogen-bond network, previous work has suggested that the SHG activity of tartrate salts is due in part to the nonlinear electronic polarizability of the hydrogen bonds between the cation and anion (Delfino, Jacco, Gentile & Bray, 1977). If this is indeed the case, then the title compound, (I), shown in Fig. 1, can be expected to have enhanced nonlinear optical activity as it incorporates both the anionic network and the cation-to-anion hydrogen bonds.



(I)

Nonlinear optical measurements previously reported by Aakeröy, Seddon & Leslie (1992) and Aakeröy, Hitchcock & Seddon (1992) indicate that the 1-methylimidazolium tartrate salt has less than half of the SHG activity of α-quartz. Subsequent measurements performed in this laboratory on the particle-sized recrystallized salt indicate a higher SHG efficiency ($5 \times \alpha$-quartz). This difference in measured SHG activity could be due to particle sizing or the purity of the salt (Kurtz & Perry, 1968). In addition to higher SHG values, we also recorded a higher melting point for the salt than was previously reported: 374 *versus* 323 K (Aakeröy, Hitchcock & Seddon, 1992; Aakeröy, Seddon & Leslie, 1992).

H atoms were placed in idealized riding positions and were not refined further. Because not all the H-atom positions were located, the criterion used to identify hydrogen bonds in the structure is that the $X\cdots Y$ distance in X—H$\cdots Y$ must be smaller than the sum of the van der Waals radii of X and Y (Huheey, 1983). Hydrogen-bonding contact details are given in Table 3,

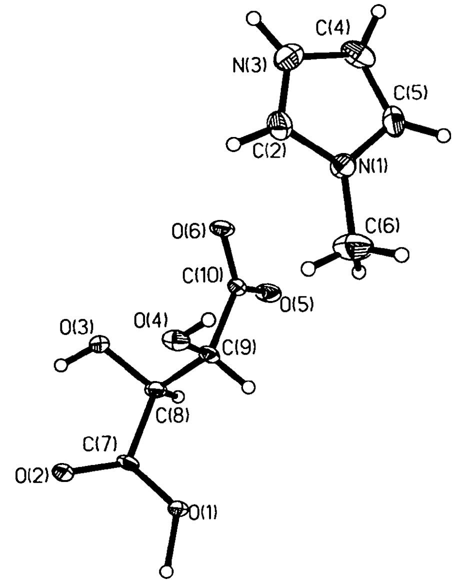


Fig. 1. Salt structure showing 50% probability displacement ellipsoids.

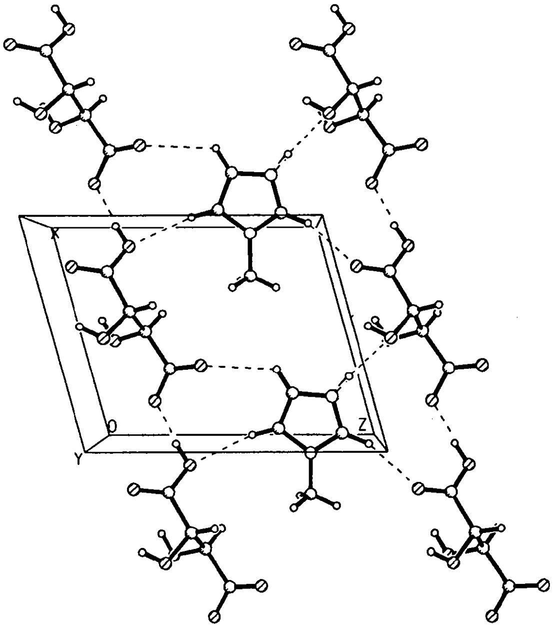


Fig. 2. View down the *b* axis showing the cation-to-anion hydrogen bonds. Some molecules have been omitted for clarity.

where only the $X\cdots Y$ distances are reported. The $X\cdots Y$ distance is used in the discussion below.

Analysis of the structure shows that 1-methylimidazolium cation interacts with the tartrate anionic network through short N—H···OH and C—H···COOH hydrogen bonds (2.89 and 3.14 Å, respectively). In addition, the two less acidic C atoms, C4 and C5, are hydrogen bonded to the tartrate chain through the carboxylate groups, with hydrogen bonds of 3.20 and 3.27 Å, respectively. It appears that the hydrogen bonds in this structure help to align the cationic aromatic rings parallel to the tartrate chains, which run along the *a* axis. The tartrate anions form a head-to-tail chain arrangement through the carboxylate groups, forming short O—H···O linkages of 2.48 Å. Two additional hydrogen bonds, O—H···OH and COO···OH, both of 2.89 Å, interlink the anions, thus completing a three-dimensional network. The extent of anion–cation interaction can be seen in Figs. 2 and 3.

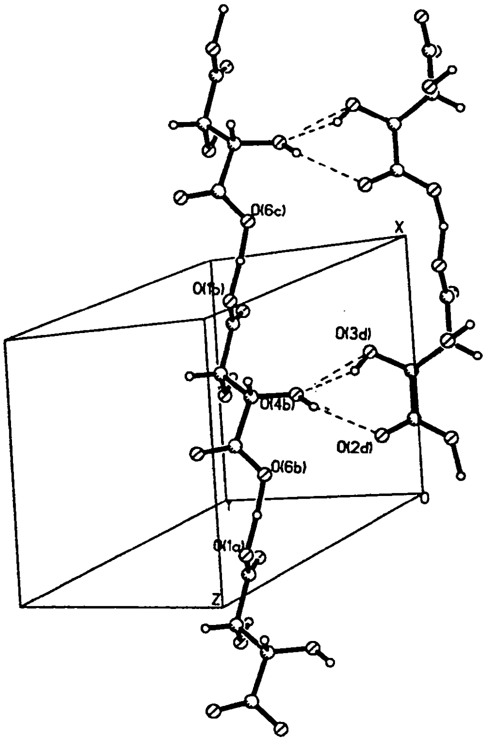


Fig. 3. Tartrate-anion interactions. Cations have been omitted for clarity.

Experimental

The salt was prepared by mixing stoichiometric amounts of 1-methylimidazole (Aldrich 99+%) and D-tartaric acid (Aldrich 99%) in warm water. After dissolving the D-tartaric acid, the solution was rotatory evaporated to dryness and the resulting white solid was dried overnight under vacuum at 348 K. The white solid was hydroscopic and proved to be very difficult to recrystallize. Crystals suitable for X-ray diffraction were obtained from a saturated acetonitrile solution, which was placed in a sand bath with a thermal gradient of approximately 293–373 K. Crystals grew up to 0.4 × 0.4 × 0.6 mm within 5 h. After examination, the larger crystals appeared to be twinned and, therefore, a smaller crystal was chosen for the X-ray measurement. Because the crystals were not air stable for long periods of time, a single crystal was mounted and sealed in a thin walled glass capillary. The melting point was visually determined to be 371–374 K. The crystal density D_m was measured by flotation.

Crystal data

$C_4H_7N_2^+.C_4H_5O_6^-$
$M_r = 232.20$
Monoclinic
$P2_1$
$a = 7.609\ (2)$ Å
$b = 7.587\ (2)$ Å
$c = 9.414\ (2)$ Å
$\beta = 105.24\ (3)°$
$V = 524.4\ (2)$ Å^3
$Z = 2$
$D_x = 1.478$ Mg m^{-3}
$D_m = 1.469$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 5–25°$
$\mu = 0.128$ mm^{-1}
$T = 293\ (2)$ K
Transparent plate
0.5 × 0.4 × 0.3 mm
Colorless

Data collection

Siemens *P*4/*RA* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1410 measured reflections
1143 independent reflections
974 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0239$
$\theta_{\rm max} = 25°$
$h = -8 \rightarrow 1$
$k = -9 \rightarrow 1$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0435$
$wR(F^2) = 0.1095$
$S = 1.091$
1140 reflections
144 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2 + 0.1518P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.253$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.258$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O4	0.4595 (3)	0.4559	0.1395 (3)	0.0456 (8)
O3	0.4742 (3)	0.8311 (6)	0.1322 (3)	0.0463 (8)
O1	0.8912 (3)	0.6060 (6)	0.2962 (2)	0.0474 (9)
O5	0.3476 (3)	0.6767 (7)	0.4379 (3)	0.0577 (10)
O6	0.1821 (3)	0.5516 (7)	0.2310 (3)	0.0502 (8)
O2	0.7938 (3)	0.7569 (7)	0.0864 (3)	0.0551 (9)
C7	0.7738 (4)	0.6971 (8)	0.2008 (3)	0.0386 (10)
C10	0.3306 (4)	0.6012 (7)	0.3212 (4)	0.0387 (10)
C9	0.5022 (4)	0.5595 (7)	0.2692 (3)	0.0358 (9)
C8	0.5953 (4)	0.7302 (8)	0.2436 (3)	0.0372 (10)

N1	0.0529 (4)	0.1289 (8)	0.2565 (3)	0.0471 (9)
N3	−0.2099 (5)	0.2000 (8)	0.1254 (4)	0.0645 (12)
C2	−0.0414 (6)	0.1763 (9)	0.1259 (4)	0.0561 (13)
C4	−0.2274 (6)	0.1734 (9)	0.2606 (5)	0.0635 (13)
C5	−0.0632 (7)	0.1277 (9)	0.3474 (4)	0.0632 (13)
C6	0.2480 (6)	0.0948 (11)	0.3034 (6)	0.089 (2)

Table 2. *Selected geometric parameters* (Å, °)

O4—C9	1.415 (4)	C9—C8	1.523 (6)
O3—C8	1.421 (5)	N1—C2	1.299 (5)
O1—C7	1.287 (5)	N1—C5	1.379 (5)
O5—C10	1.214 (4)	N1—C6	1.453 (6)
O6—C10	1.277 (4)	N3—C2	1.291 (6)
O2—C7	1.213 (4)	N3—C4	1.327 (6)
C7—C8	1.532 (5)	C4—C5	1.344 (7)
C10—C9	1.539 (5)		
O2—C7—O1	126.4 (3)	O3—C8—C7	109.9 (3)
O2—C7—C8	119.8 (3)	C9—C8—C7	112.5 (3)
O1—C7—C8	113.8 (3)	C2—N1—C5	107.7 (3)
O5—C10—O6	127.2 (3)	C2—N1—C6	127.0 (4)
O5—C10—C9	119.0 (3)	C5—N1—C6	125.2 (4)
O6—C10—C9	113.7 (3)	C2—N3—C4	108.9 (4)
O4—C9—C8	110.2 (3)	N3—C2—N1	110.0 (4)
O4—C9—C10	111.5 (3)	N3—C4—C5	108.1 (4)
C8—C9—C10	110.0 (3)	C4—C5—N1	105.3 (3)
O3—C8—C9	109.6 (3)		

Table 3. *Contact distances* (Å)

$O(1)\cdots O(6^{i})$	2.48 (1)	$C(5)\cdots O(1^{iv})$	3.27 (1)
$O(3)\cdots O(4^{ii})$	2.89 (1)	$C(4)\cdots O(5^{v})$	3.20 (1)
$O(4)\cdots O(2^{iii})$	2.89 (1)	$N(3)\cdots O(3^{vi})$	2.89 (1)
$C(2)\cdots O(2^{iii})$	3.14 (1)		

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, \frac{1}{2}+y, -z$; (iii) $1-x, y-\frac{1}{2}, -z$; (iv) $1-x, y-\frac{1}{2}, 1-z$; (v) $-x, y-\frac{1}{2}, 1-z$; (vi) $-x, y-\frac{1}{2}, -z$.

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1056). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Mono- and Diprotonated 1,4-Dihydrazinophthalazine: $C_8H_{11}N_6^+.Cl^-$ and $C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$

Olivero Carugo, Carla Bisi Castellani and Angelo Perotti

Dipartimento de Chimica Generale, Università di Pavia, via Taramelli 12, I-27100-Pavia, Italy

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Abstract

The crystal structures of 1,4-dihydrazinophthalazine monohydrochloride, $C_8H_{11}N_6^+.Cl^-$, and 1,4-dihydrazinophthalazine dihydrochloride dihydrate, $C_8H_{12}N_6^{2+}.2Cl^-.2H_2O$, have been determined. The protonation sites on the 1,4-dihydrazinophthalazine molecule were identified (*i.e.* 1,4-dihydrazinophthalazin-2-ium chloride and 4-hydrazinio-1-hydrazinophthalazin-2-ium dichloride dihydrate). A potentiometric study showed that in aqueous solution 1,4-dihydrazinophthalazine behaves as a diprotic base with $pK_{a1} = 4.24$ and $pK_{a2} = 8.13$.

Comment

1,4-Dihydrazinophthalazine, $C_8H_{10}N_6$, (I), derivatives have been studied because of their potential pharmaceutical applications as antihypertensive agents (Durey & Tripod, 1967). In addition, they have applications in coordination chemistry as binucleating ligands (Andrew, Ball & Blake, 1969; Andrew & Blake, 1969; Ball & Blake, 1969, 1974; Rosen, 1971; Sullivan & Palenik, 1977; Robichaud & Thompson, 1984; Attanasio, Dessy & Fares, 1985; Attanasio, Fares & Imperatori, 1986; Thompson, Mandal, Gabe & Charland, 1986; Wen, Thompson, Lee & Gabe, 1988; Thompson, Lee & Gabe, 1988; Bontchev *et al.*, 1989; Mandal, Thompson, Newlands, Charland & Gabe, 1990). Several such studies have shown the acidic H atoms of these molecules to be quite mobile, allowing tautomeric equilibria. For example, a detailed ^1H NMR analysis (Thompson & Woon, 1986) of some hydrazone derivatives of 1,4-dihydrazinophthalazine showed that these molecules are present in solution as forms (II) and (III). It also revealed that the equilibrium between these tautomers is affected by complexation to metal ions, in particular diamagnetic copper(I). With regard to solid-state structures, Stadnicka & Lebioda (1979) and Herrnstadt, Mootz, Wunderlich & Mohrle (1979) reported the structure of the 1,4-dihydrazinophthalazine.H_2SO_4 salt in which the 1,4-dihydrazinophthalazine molecule is diprotonated, one proton being bonded to N2 and the other to N4. The crystal structure of 1-hydrazinophthalazine