Anilinium monohydrogen DL-malate

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Crystals of the title salt, $[(C_6H_5NH_3)]^+ \cdot [(HOOC(CH_2)-CH(OH)COO)]^-$ or $C_6H_8N^+ \cdot C_4H_5O_5{}^-$, are built up from protonated anilinium residues and monodissociated DL-malate ions. The $NH_3{}^+$ group of the anilinium cation is ordered at room temperature. Rotation of the $NH_3{}^+$ group along the $C(aromatic)-Nsp^3$ bond (often observed at room temperature in other anilinium salts) is prevented by $N-H\cdots O$ hydrogen bonds between the $NH_3{}^+$ group and the malate anions. The anions are connected by four $O-H\cdots O$ hydrogen bonds into two-dimensional sheets parallel to the (001) plane. The charged moieties, i.e. the anilinium cations and the sheets of hydrogen-bonded malate anions, form two-dimensional layers in which the phenyl rings of the anilinium residues lie perpendicular to the malate-ion sheets. The conformation of the monodissociated malate ion in the crystal is compared with that obtained from ab initio molecular-orbital calculations.

Comment

Crystals of organic and inorganic anilinium salts exhibit structural phase transitions induced by order/disorder transformations of the protonated amine group, $NH_3{}^+$. The potential energy barrier for rotation of the $NH_3{}^+$ group along the $C(aromatic)-Nsp^3$ single bond is small if the H atoms interact weakly with neighbouring ions or molecules. In this case, the $NH_3{}^+$ group exhibits rotation at room temperature, but this rotation is inhibited at lower temperatures. Investigation of the title compound, (I), has its origin in our interest in the characterization of compounds that form multiple and different hydrogen-bonding systems (Janczak & Perpétuo, 2003, and references therein; Perpétuo & Janczak, 2003). Additionally, the geometry and conformation of (I) have been compared with the ab initio fully optimized parameters calculated at the B3LYP/6-31G(d,p) level (Frisch et al., 1995). The ab initio molecular orbital calculations were carried out on isolated ions, i.e. the anilinium cation and the monodissociated DL-malate anion, and the results are illustrated in Fig. 1.

Our X-ray study of (I) shows that the $NH_3{}^+$ group in the anilinium cation is ordered at room temperature. The relatively high anisotropic displacement parameters of the C atoms of the malate anion indicated that this ion could be disordered. Nevertheless, some of the disorder models that have been tested for the malate anion show no disorder, and thus the relatively high displacement parameters can be taken to indicate large molecular motion. Additionally, the powder diffraction data collected between room temperature and 90 K did not show evidence for any structural phase transition. The benzene ring of the anilinium cation (Fig. 2) (like that of other anilinium compounds) has a symmetry closer to C_{2v} (mm) than to C_{6h} (6/mmm) (Colapietro et al., 1981; Sakai & Terauchi, 1981; Paixao et al., 2000). The distortion of the ring is not large but is significant and involves bond distances as well as angles. The endocyclic C—C—C angle ipso to the substituent is larger than 120° (especially in the optimized molecule; Fig. 1b), as expected from the σ-electron-withdrawing character of the $NH_3{}^+$ group (Domenicano & Murray-Rust, 1979). The aromatic C—C bonds involving the C atom ipso to the substituent, viz. C11—C12 and C11—C16, are shorter than the central C—C bonds of the ring, viz. C12—C13 and C15—C16. The differences in the C—C bonds within the ring in the crystal are greater than in the optimized bond lengths. The $C(aromatic)-Nsp^3$ distance is close to the lower band of the range reported for several anilinium salts (Allen et al., 1987).
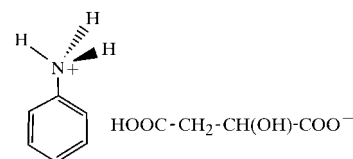
(I)

The anilinium residue in the crystal of (I) is involved in three hydrogen bonds as a donor. The H atoms of the $NH_3{}^+$ group form $N-H\cdots O$ hydrogen bonds with three neighbouring monodissociated DL-malate anions (see Table 2).

The conformation of the carbon skeleton of the malate anion in (I) is syn [$\psi = 179.7\,(2)°$], with the carboxylate group (COO⁻) almost coplanar with atoms C2 and O5 [$\varphi_2 = -8.8\,(2)°$]. The conformation of the carboxy group (COOH) around the terminal C—C bond is clinal [$\chi = 77.7\,(2)°$]. The ψ, φ_2 and χ torsion angles in (I) (ψ = C1—C2—C3—C4, φ_2 = O1—C1—C2—O5 and χ = C2—C3—C4—O4) describe the conformation of the malate ion as well as the conformation of the malic acid (Sluis & Kroon, 1985, 1989). In the optimized malate ion; the values of ψ, φ_2 and χ are -177.8, -3.9 and $61.7°$, respectively, and thus the conformation of the carbon skeleton of the optimized malate ion is anti. The optimized value of φ_2 is smaller than φ_2 in (I), and the O1—C1—C2—O5—H5O fragment deviates less from the plane than it does in (I) because of the formation of an intramolecular $O5-H5O\cdots O1$ hydrogen bond [$O5-H5O = 0.95$ Å, $H5O\cdots O1 = 1.87$ Å and $O5-H5O\cdots O1 = 126°$; for comparison with the X-ray geometry of this hydrogen bond, see

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organic compounds

Table 2]. The rotation of the terminal COOH group is greater in the crystal than in the optimized ion [χ = 61.7 and 77.7 (2)° in the optimized ion and in the crystal, respectively] because of the interaction of this group with the hydroxy group of a neighbouring malate ion and the formation of the O5—H5O$\cdots$O4($x - 1, y, z$) hydrogen bond. The optimized angle in the carboxy group (O1—C1—O2) is greater, and the angle in the non-dissociated carboxy group (O3—C4—O4) is smaller, than the corresponding angles in (I) (Table 1). These differences are explained by the steric effect of the lone-pair electron predicted by the valence-shell electron-pair repulsion model (Gillespie, 1963, 1992). Atom O5 is involved in two hydrogen bonds, one as a donor to a neighbouring malate anion and one as an acceptor to the NH$_3^+$ group of the anilinium residue.

The C1—C2, C2—C3 and C3—C4 bond lengths obtained from the X-ray analysis of (I) are shorter than the equivalent

Figure 2
The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

optimized bond lengths. A search of the Cambridge Structural Database (Allen, 2002) for structures containing the malate anion or malic acid shows that in the crystal of DL-malic acid (Sluis & Kroon, 1985), as well as in the crystal of L-malic acid (Sluis & Kroon, 1989), these C—C bonds range from 1.499 (4) to 1.529 (4) Å. The C—O bond lengths in the dissociated carboxy group are intermediate between single- and double-bond lengths, indicating delocalization of the π electron over both C—O bonds. The O1—C1—O2 angle of the carboxylate group (COO$^-$) is greater than the O3—C4—O4 angle of the carboxy group (COOH) in both the crystal and the optimized malate anion because of the steric effect of the lone-pair electrons on atoms O1 and O2 in relation to the non-dissociated COOH group.
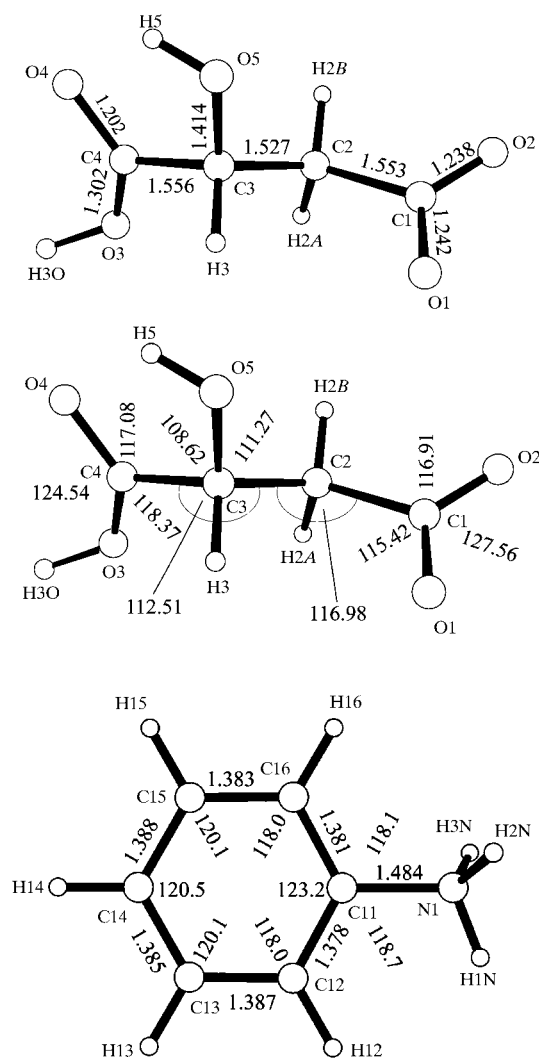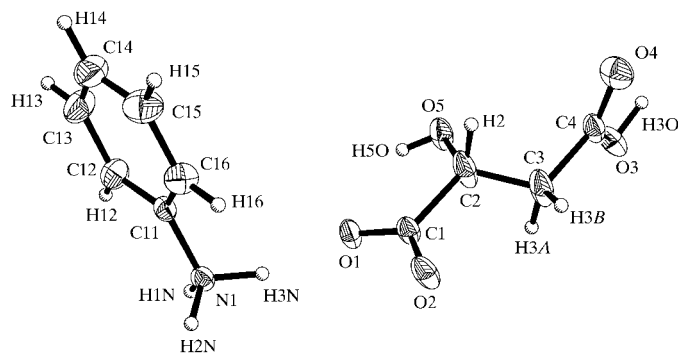
Figure 1
Results of the optimized *ab initio* calculations for the monodissociated malate anion and for the anilinium cation. Geometric parameters are reported in Å and °.
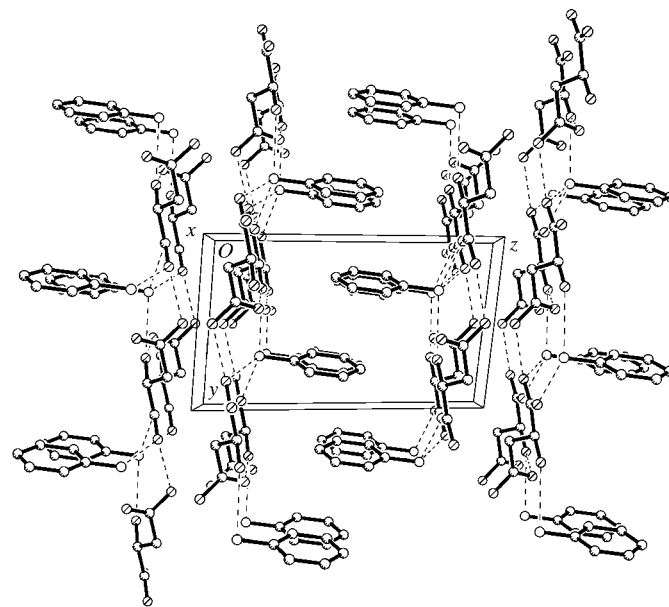
Figure 3
The crystal packing of (I), showing the alternating arrangement of back-to-back and face-to-face layers of the hydrogen-bonded anilinium–malate residues. Dashed lines represent hydrogen bonds and H atoms have been omitted for clarity.

Each monodissociated malate anion is connected by O—H$\cdots$O hydrogen bonds to four neighbouring malate ions, thus forming a sheet parallel to the (001) plane in the crystal. The anilinium cations are linked by N—H$\cdots$O hydrogen bonds to three malate ions in the sheet, thus forming two-dimensional layers. The benzene rings of the anilinium residues are almost perpendicular to the sheet of hydrogen-bonded malate ions. Two anilinium–malate layers, connected *via* hydrogen bonds, are oriented in an alternating face-to-face and back-to-back pattern (Fig. 3). The rings of the anilinium moieties are partially overlapping and interact slightly *via* the π–π clouds (separated by about 3.66 Å along the stack) formed by two face-to-face-oriented layers of interconnected anilinium and malate residues.

Experimental

Aniline was added to a solution of DL-malic acid in water (10%) and the resulting solution was evaporated slowly. After several days, colourless crystals of (I) appeared.

Crystal data

$C_6H_8N^+ \cdot C_4H_5O_5^-$	$D_m = 1.41$ Mg m^{-3}
$M_r = 227.21$	D_m measured by flotation in
Triclinic, $P\bar{1}$	1,2-dichloroethane/chloroform
$a = 6.180$ (1) Å	Mo $K\alpha$ radiation
$b = 7.545$ (2) Å	Cell parameters from 1339
$c = 12.425$ (2) Å	reflections
$\alpha = 91.23$ (3)°	$\theta = 3.2$–26.2°
$\beta = 102.27$ (3)°	$\mu = 0.11$ mm^{-1}
$\gamma = 108.80$ (3)°	$T = 293$ (2) K
$V = 533.38$ (22) Å^3	Parallelepiped, colourless
$Z = 2$	$0.28 \times 0.25 \times 0.21$ mm
$D_x = 1.415$ Mg m^{-3}	

Data collection

Kuma KM-4 diffractometer	1339 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.011$
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990*b*)	$\theta_{max} = 26.2°$
	$h = -6 \rightarrow 7$
	$k = -9 \rightarrow 8$
$T_{min} = 0.964$, $T_{max} = 0.978$	$l = -15 \rightarrow 15$
5133 measured reflections	
2123 independent reflections	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.230 (2)	C3—C4	1.513 (2)
O2—C1	1.256 (2)	C4—O4	1.199 (2)
C1—C2	1.516 (2)	C4—O3	1.288 (2)
C2—O5	1.358 (2)	N1—C11	1.448 (2)
C2—C3	1.507 (2)		
O1—C1—O2	126.53 (13)	C3—C2—C1	112.69 (14)
O1—C1—C2	115.36 (15)	C2—C3—C4	111.90 (14)
O2—C1—C2	117.91 (15)	O4—C4—O3	123.62 (14)
O5—C2—C3	113.78 (16)	O4—C4—C3	125.4 (2)
O5—C2—C1	114.18 (15)	O3—C4—C3	110.97 (18)

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
$wR(F^2) = 0.107$	$\Delta\rho_{min} = -0.25$ e Å^{-3}
$S = 1.09$	Extinction correction: *SHELXL*97
2113 reflections	Extinction coefficient: 0.078 (9)
164 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.058P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5O$\cdots$O1	0.82	2.13	2.608 (3)	117
O5—H5O$\cdots$O4^i	0.82	2.31	2.895 (3)	129
O3—H3O$\cdots$O2^{ii}	0.82	1.78	2.595 (3)	178
N1—H3N$\cdots$O1	0.89	1.89	2.757 (3)	165
N1—H2N$\cdots$O5^{iii}	0.89	1.97	2.821 (2)	159
N1—H1N$\cdots$O2^i	0.89	2.00	2.884 (3)	172

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y - 1, z$; (iii) $x, 1 + y, z$.

Data collection: *KM*-4 *CCD Software* (Kuma, 2000); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*97.

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