# organic papers

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# Pyridinium (2R,3R)-tartrate

In the title compound, $C_5H_6N^+ \cdot C_4H_5O_6{}^-$, the pyridine molecule exists as a cation and the tartaric acid molecule as a semi-tartrate anion. The semi-tartrate anions are linked by O—H$\cdots$O hydrogen bonds to form hollow columns running parallel to the *a* axis. The pyridinium cations, trapped in the columns, are linked to the semi-tartrate anions *via* strong N—H$\cdots$O hydrogen bonds.

## Comment

Carboxylic acids are believed to have existed in the prebiotic Earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971) and they exhibit characteristic intermolecular interactions and aggregation patterns. Also, the use of carboxyl groups as primary building blocks in the design of crystal structures (Desiraju, 1989; MacDonald & Whitesides, 1994) is regarded as an important step towards the prediction of crystal structures. Pyridine, owing to its structural compactness and conformational rigidity, might serve as a perfect candidate for use as a structural unit in recognizing and characterizing fundamental interaction patterns in crystal structures. The structure determination of pyridinium tartrate, (I), is part of an ongoing programme aimed at characterizing intermolecular interaction patterns in the crystal structures of proton-transfer complexes of carboxylic acids. Some of the earlier work on the crystal structures of proton-transfer complexes of pyridinium are: pyridinium trifluoroacetate (Palmore & McBride-Wieser, 1997), pyridinium picrate (Botoshansky *et al.*, 1994), bis-(pyridinium) pamoate (Blackburn *et al.*, 1996), pyridinium trihydrogen dimalonate (Djinovic & Golic, 1992), pyridinium nitrate at 120 and 290 K (Batsanov, 2004*a,b*), pyridinium oxalate oxalic acid dihydrate (Rajagopal *et al.*, 2003) and pyridinium methylsulfonate (Bolte *et al.*, 2001).



(I)
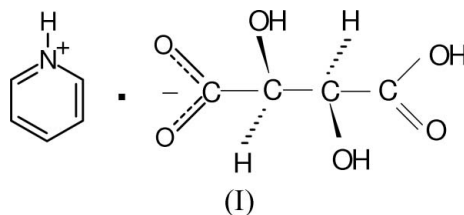
The pyridine molecule of (I) exists in the cationic form, with a protonated ring N atom. The C9—N1—C5 angle of 121.4 (4)° is significantly different from that observed in the neutral pyridine molecule [116.6 (2)°; Mootz & Wusson, 1981]. The tartaric acid molecule exists as a semi-tartrate anion, with an uncharged carboxyl group and a charged carboxylate ion. The angle between the planes of the two halves of the semi-tartrate ion, O1/O2/C1/C2/O3 and O6/O5/C4/C3/O4, is
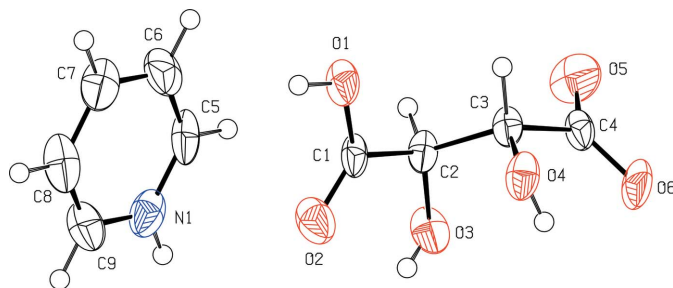
**Figure 1**
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.
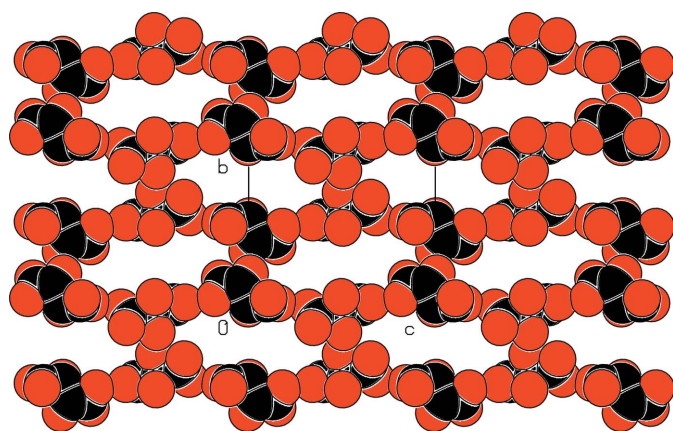


**Figure 2**
The aggregation of the semi-tartrate anions of (I), leading to hollow columns along the short *a* axis.
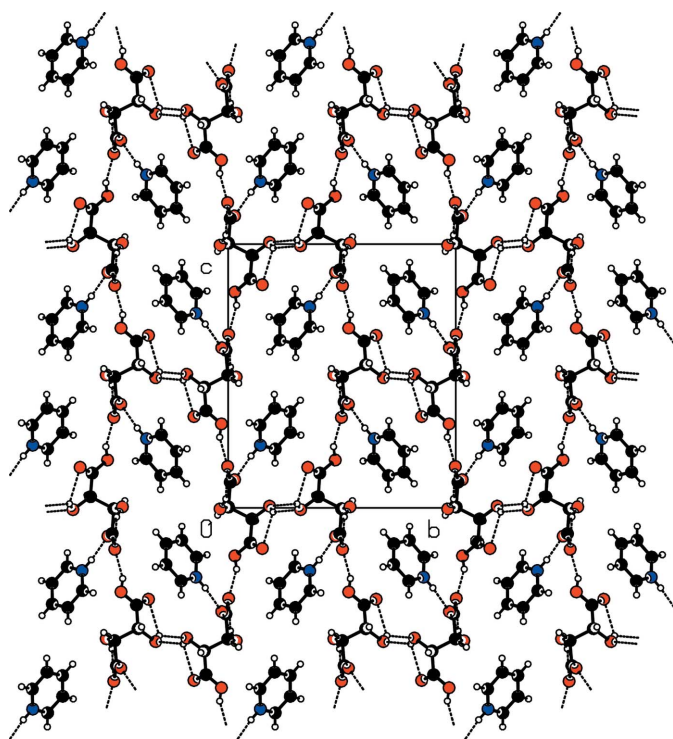


**Figure 3**
The packing of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

58.6 (3)°, which is close to the value of 54.6 (4)° observed for tartaric acid with the same diastereomeric form as the anionin (I) (Okaya *et al.*, 1966).

The packing of the ions is stabilized by a three-dimensional hydrogen-bonded network (Table 1). The semi-tartrate anions are linked *via* O—H···O intermolecular hydrogen bonds to form hollow columns running along the short *a* axis (Fig. 2). The pyridinium cations are trapped in the columns (Fig. 3). The pyridine N atom is involved in a rather strong hydrogen bond with the O atom of the carboxylate anion, leading to an ion pair of the type N—H$^+$···$^-$OOC, with N···O = 2.664 (4) Å (Table 1). The crystal structure may be described as an inclusion complex, with the semi-tartrate anion as the host and the pyridinium cation as the guest.

## Experimental

Colourless prismatic single crystals of (I) were grown from a saturated aqueous solution containing pyridine and tartaric acid in a 1:1 stoichiometric ratio.

*Crystal data*

$C_5H_6N^+ \cdot C_4H_5O_6^-$
$M_r = 229.19$
Orthorhombic, $P2_12_12_1$
$a = 5.0390\ (13)$ Å
$b = 13.220\ (2)$ Å
$c = 15.318\ (2)$ Å
$V = 1020.5\ (3)$ Å$^3$
$Z = 4$
$D_x = 1.492$ Mg m$^{-3}$

$D_m = 1.50$ Mg m$^{-3}$
$D_m$ measured by flotation in a liquid mixture of xylene and bromoform
Mo $K\alpha$ radiation
$\mu = 0.13$ mm$^{-1}$
$T = 300\ (2)$ K
Prism, colourless
$0.25 \times 0.20 \times 0.12$ mm

*Data collection*

Nonius MACH3 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.97$, $T_{max} = 0.99$
1149 measured reflections

1068 independent reflections
852 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 25.0°$
2 standard reflections frequency: 60 min intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.142$
$S = 1.07$
1068 reflections
149 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1053P)^2 + 0.1376P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.27$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.105 (15)

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···O6$^i$ | 0.82 | 1.78 | 2.554 (3) | 157 |
| O3—H3···O3$^{ii}$ | 0.82 | 2.41 | 3.105 (3) | 142 |
| O4—H4···O5$^{iii}$ | 0.82 | 1.97 | 2.768 (4) | 163 |
| N1—H1A···O5$^{ii}$ | 0.86 | 1.79 | 2.644 (4) | 172 |
| C5—H5···O3$^{iv}$ | 0.93 | 2.58 | 3.481 (5) | 162 |
| C6—H6···O2$^v$ | 0.93 | 2.45 | 3.169 (5) | 134 |
| C7—H7···O4$^i$ | 0.93 | 2.48 | 3.331 (5) | 152 |

Symmetry codes: (i) $-x+\frac{1}{2}, -y+2, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iii) $x-1, y, z$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (v) $x+1, y, z$.

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H atoms were placed in calculated positions and allowed to ride on their respective carrier atoms, with N—H = 0.86, O—H = 0.82 and C—H = 0.93–0.98 Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$ for the OH group and $1.2U_{eq}(C,N)$ for the NH, CH and CH$_2$ groups. In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

## References

Batsanov, A. S. (2004a). *Acta Cryst.* E**60**, o2426–o2428.
Batsanov, A. S. (2004b). *Acta Cryst.* E**60**, o2424–o2425.
Blackburn, A. C., Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 1269–1272.
Bolte, M., Griesinger, C. & Sakhaii, P. (2001). *Acta Cryst.* E**57**, o458–o460.
Botoshansky, M., Herbstein, F. H. & Kapon, M. (1994). *Acta Cryst.* B**50**, 191–200.
Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*. Amsterdam: Elsevier.
Djinović, K. & Golič, L. (1992). *Acta Cryst.* **48**, 1046–1048.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1996). *XCAD4*. University of Marburg, Germany.
Kvenvolden, K. A., Lawless, J. G. & Ponnamperuma, C. (1971). *Proc. Natl Acad. Sci. USA*, **68**, 486–490.
MacDonald, J. C. & Whitesides, G. M. (1994). *Chem. Rev.* **94**, 2383–2420.
Miller, S. L. & Orgel, L. E. (1974). *The Origins of Life on Earth*. New Jersey: Prentice–Hall.
Mootz, D. & Wusson, H. G. (1981). *J. Chem. Phys.* **75**, 1517–1522.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Okaya, Y., Stemple, N. R. & Kay, M. I. (1966). *Acta Cryst.* **21**, 237–243.
Palmore, G. T. R. & McBride-Wieser, M. T. (1997). *Acta Cryst.* C**53**, 1904–1907.
Rajagopal, K., Tamilselvi, V., Krishnakumar, R. V. & Natarajan, S. (2003). *Acta Cryst.* E**59**, o742–o744.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Gottingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.