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Comparison of the methyl ester of L-tyrosine hydrochloride and its methanol monosolvate

Iwona Bryndal, Mariusz Jaremko,* Łukasz Jaremko and Tadeusz Lis

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie Street, 50-383 Wrocław, Poland
Correspondence e-mail: jaremko@gmail.com

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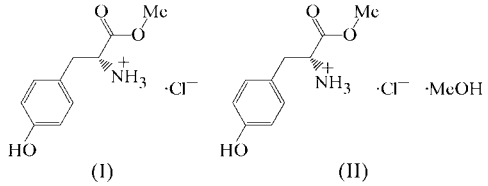
Solvent-free (2*S*)-methyl 2-ammonio-3-(4-hydroxyphenyl)-propionate chloride, $C_{10}H_{14}NO_3^+\cdot Cl^-$, (I), and its methanol solvate, $C_{10}H_{14}NO_3^+\cdot Cl^-\cdot CH_3OH$, (II), are obtained from different solvents: crystallization from ethanol or propan-2-ol gives the same solvent-free crystals of (I) in both cases, while crystals of (II) were obtained by crystallization from methanol. The structure of (I) is characterized by the presence of two-dimensional layers linked together by N—H···Cl and O—H···Cl hydrogen bonds and also by C—H···O contacts. Incorporation of the methanol solvent molecule in (II) introduces additional O—H···O hydrogen bonds linking the two-dimensional layers, resulting in the formation of a three-dimensional network.

Comment

Although L-tyrosine is one of the 20 natural amino acids which are the basic building blocks of proteins, there are surprisingly few references in the literature to the structures of short peptides containing L-tyrosine methyl ester. The simplest of the peptides described, *N*-acetyl-L-leucyl-L-tyrosine methyl ester, containing the two amino acids L-leucine and L-tyrosine, was reported by Karle & Flippen-Anderson (1989). Another paper (Claeys-Bruno *et al.*, 2001) describes the structure



of a cobalt(III) chiroporphyrin complex containing the methyl ester of D-tyrosine hydrochloride. The present paper describes the first solid-state study of L-tyrosine methyl ester hydrochloride, both solvent-free [compound (I)] and as a methanol monosolvate [compound (II)].

Crystals of (I) were obtained from ethanol or propan-2-ol, while crystals of (II) were isolated from methanol, crystallizing in space groups $P2_12_12_1$ and $P2_1$, respectively (Figs. 1 and 2). We have compared the crystal structures of (I) and (II), principally by analysis of selected torsion angles and hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995). The superposition of the L-tyrosine methyl ester cations is shown

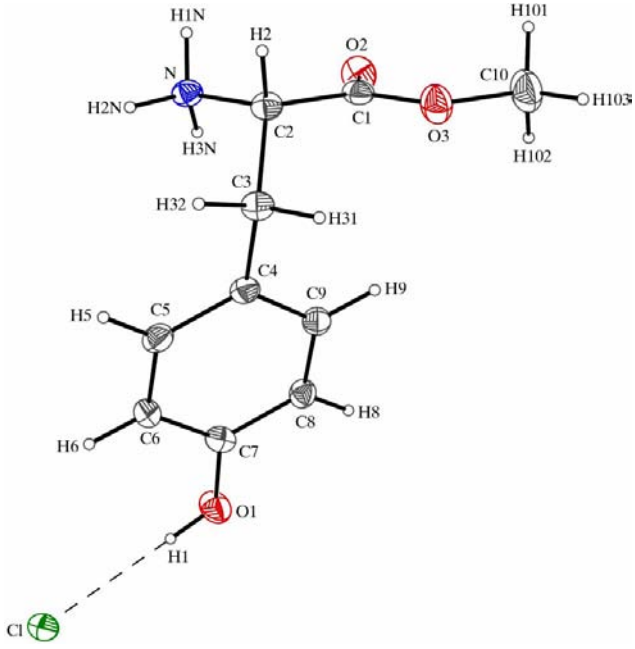


Figure 1
A view of (I), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond.

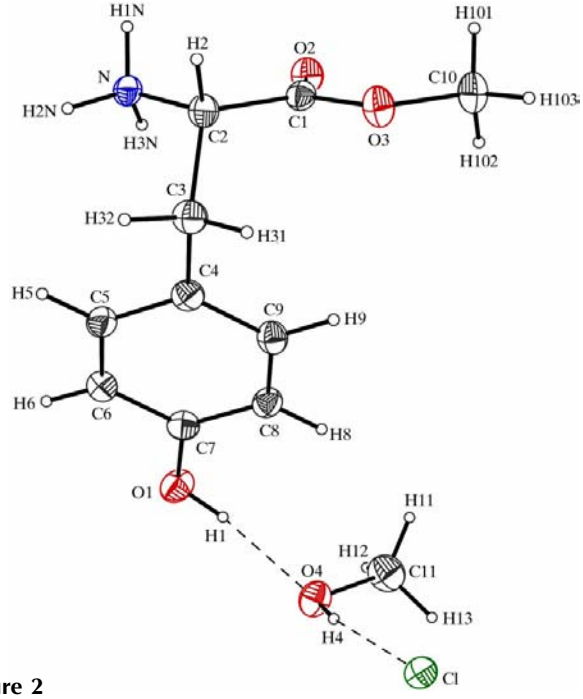


Figure 2
A view of (II), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. The dashed lines indicate the intramolecular hydrogen bonds.

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in Fig. 3. The values of the C2—C3—C4—C9 (χ^{22}) and C2—C3—C4—C5 (χ^{21}) torsion angles [88.3 (2) and −90.8 (2)°, respectively, in (II), and 71.2 (2) and −111.3 (2)° in (I)] show only small differences in the orientation of the aromatic rings towards the plane defined by atoms C1/C2/N. The angle between the plane defined by atoms C1/C2/N and that of ring C4–C9 is 68.2 (1)° in (I) and 64.6 (2)° in (II). Previously reported values for the torsion angles of L-tyrosine sulfate (Sridhar *et al.*, 2002) are noticeably different because of the possible rotation around the C2—C3 and C3—C4 bonds, showing their dependence on crystal-packing forces. The backbone conformation angles N—C2—C1—O2 (ψ^1) are 0.9 (2) and −2.2 (3)° in (I) and (II), respectively. Previous reports of the structures of L-tyrosine (Mostad *et al.*, 1972) and L-tyrosinamide hydrochloride monohydrate (Kolev *et al.*, 2005) noted that the backbone torsion angles can adopt very different values for similar compounds, depending on the molecules present and their arrangement in the solid state. Significant differences can also exist within one crystal structure, as reported for bis(L-tyrosinium) sulfate monohydrate, where two independent cations are present in the asymmetric unit (Sridhar *et al.*, 2002).

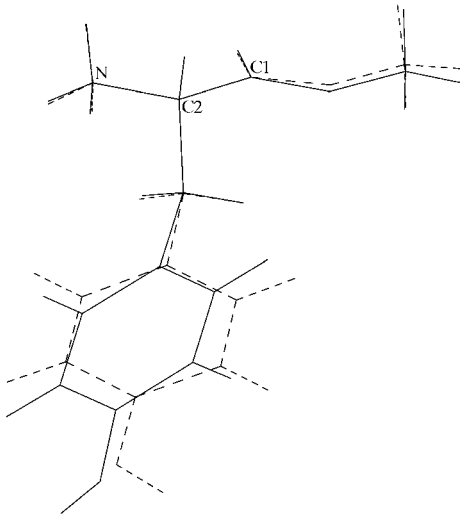

Figure 3
Superposition of the cations in (I) (dashed lines) and (II) (solid lines), using atoms C1, C2 and N as the common reference points.

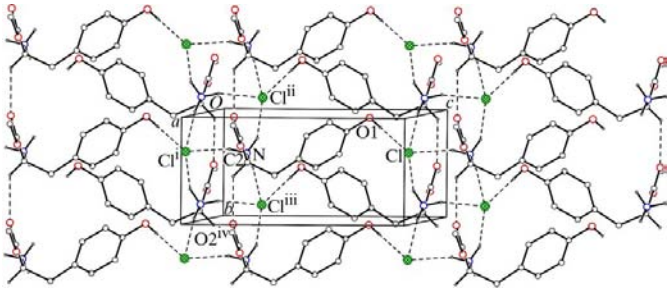

Figure 4
A view of the two-dimensional arrangement of (I), viewed along the *a* axis. For clarity, H atoms not involved in the hydrogen bonds have been omitted. [Symmetry codes: (i) $x, y, z-1$; (ii) $-x, y-\frac{1}{2}, -z+1$; (iii) $-x, y+\frac{1}{2}, -z+1$; (iv) $x, y+1, z$.]

The crystal structures of compounds (I) and (II) are characterized by the presence of Cl^- anions which engage in numerous interactions. The N···Cl distances are in the ranges 3.117 (2)–3.212 (2) and 3.166 (2)–3.207 (2) Å for (I) and (II), respectively, and are comparable with the average value of 3.207 (4) Å for this type of interaction (Steiner, 1998). In addition to strong N—H···Cl and O—H···Cl hydrogen bonds, both crystal structures also feature weak C—H···O interactions (Figs. 4 and 5).

In compound (I), the ester cations are indirectly linked *via* Cl^- anions through intermolecular N—H···Cl and O—H···Cl hydrogen bonds. Each Cl^- anion acts as an acceptor for three hydrogen bonds from protonated amino groups. Therefore, the N—H1···N···Cl hydrogen bond is common to two adjacent ring motifs, forming a 'puckered ladder' of hydrogen bonds, which can be described as $R_4^2(8)$. The fourth hydrogen bond, O1—H1···Cl, exists between the Cl^- anion and the hydroxyl group of another ester cation. The participation of the hydroxyl group in the hydrogen-bonding network causes the formation of two-dimensional antiparallel molecular layers containing ester cations and Cl^- anions. Within these layers, the ester cations are linked directly by C2—H2···O2^{iv} interactions [symmetry code: (iv) $x, y+1, z$; Table 2] between the methyl and methoxycarbonyl groups of adjacent ester cations. Propagation of the hydrogen-bonding $C(4)$ motif generates a chain running along the *b* axis (Fig. 4).

In compound (II), each Cl^- anion accepts four hydrogen bonds which can be divided into two groups. The first group is part of a group of hydrogen bonds linking each Cl^- anion with three different cations *via* their protonated amino groups and its arrangement is analogous to that seen in (I). The second type of hydrogen bond, in which the Cl^- anion is the acceptor, is a linkage between the methanol solvent molecule and the Cl^- anion, consisting of a single O4—H4···Cl hydrogen bond. The ester cations are linked *via* the ring of four hydrogen bonds between two different Cl^- anions and two amino groups of the ester cations, which can be described as $R_4^2(8)$. Thus, a 'puckered ladder' motif of hydrogen bonds analogous to that observed in (I) can be also be recognized. However, the

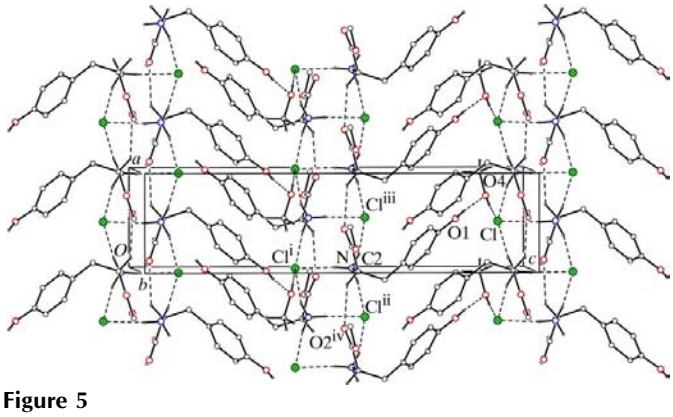

Figure 5
A view of the three-dimensional network of (II), viewed along the *b* axis. For clarity, H atoms (except those of the methanol molecules) not involved in the hydrogen bonds shown have been omitted. [Symmetry codes: (i) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x-1, y, z$.]

presence of the methanol solvent molecule results in a different arrangement for (II), namely a three-dimensional network. Additionally, the ester cations of (II) are linked directly by C2—H2···O2^{iv} interactions [symmetry code: (iv) $x-1, y, z$], resulting in a $C(4)$ hydrogen-bonding motif similar to that in (I), with the chains running along the a axis (Fig. 5).

Experimental

The methyl ester of L-tyrosine hydrochloride was prepared according to the standard procedure of Wróbel *et al.* (1983). L-Tyrosine (30 g, 0.166 mol) was suspended in absolute methanol (450 ml) and saturated with gaseous hydrogen chloride until it dissolved completely. The resulting solution was cooled in an ice bath for 3 h and left in a refrigerator overnight. After the solvent had been removed *in vacuo*, the product was isolated (yield 33.37 g, 0.144 mol, 87%). Single crystals of (I) suitable for X-ray diffraction studies were obtained by slow evaporation from solutions of L-tyrosine methyl ester hydrochloride in either ethanol or propan-2-ol. Single crystals of (II) were obtained by slow evaporation from a methanol solution of L-tyrosine methyl ester hydrochloride.

Compound (I)

Crystal data

$C_{10}H_{14}NO_3^+\cdot Cl^-$
$M_r = 231.67$
Monoclinic, $P2_1$
$a = 9.943$ (3) Å
$b = 5.351$ (2) Å
$c = 11.154$ (3) Å
$\beta = 105.38$ (3)°
$V = 572.2$ (3) Å^3
$Z = 2$
$D_x = 1.345$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8187 reflections
$\theta = 4.8$–35°
$\mu = 0.32$ mm^{-1}
$T = 100$ (2) K
Plate, colourless
0.40 × 0.35 × 0.10 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
13013 measured reflections
3754 independent reflections
2890 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 35.0°$
$h = -15 \rightarrow 16$
$k = -8 \rightarrow 6$
$l = -18 \rightarrow 18$

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C7	1.368 (2)	N—C2	1.492 (2)
O2—C1	1.206 (2)	C1—C2	1.514 (2)
O3—C1	1.323 (2)	C2—C3	1.534 (2)
O3—C10	1.453 (2)	C3—C4	1.513 (2)
C10—O3—C1—O2	1.1 (3)	N—C2—C3—C4	52.0 (2)
N—C2—C1—O2	0.9 (2)	C2—C3—C4—C5	−111.3 (2)
O2—C1—C2—C3	125.26 (18)	C2—C3—C4—C9	71.2 (2)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Cl	0.84	2.31	3.1524 (15)	180
N—H1N···Cl^{i}	0.91	2.24	3.1166 (15)	163
N—H3N···Cl^{ii}	0.91	2.44	3.2118 (19)	142
N—H2N···Cl^{iii}	0.91	2.27	3.1686 (19)	168
C2—H2···O2^{iv}	1.00	2.38	3.166 (2)	135

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.091$
$S = 1.00$
3754 reflections
139 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Absolute structure: Flack (1983), with 1013 Friedel pairs
Flack parameter: 0.06 (5)

Compound (II)

Crystal data

$C_{10}H_{14}NO_3^+\cdot Cl^-\cdot CH_4O$
$M_r = 263.71$
Orthorhombic, $P2_12_12_1$
$a = 5.424$ (2) Å; $b = 11.080$ (3) Å
$c = 21.647$ (5) Å
$V = 1300.9$ (7) Å^3
$Z = 4$
$D_x = 1.346$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 11981 reflections
$\theta = 4.1$–75.9°
$\mu = 2.65$ mm^{-1}
$T = 100$ (2) K
Plate, colourless
0.52 × 0.15 × 0.06 mm

Data collection

Kuma KM-4 CCD diffractometer
ω and φ scans
Absorption correction: analytical (*CrysAlis RED*)
$T_{min} = 0.462$, $T_{max} = 0.857$
12812 measured reflections
2563 independent reflections
2462 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 75.9°$
$h = -6 \rightarrow 4$
$k = -13 \rightarrow 13$
$l = -23 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.108$
$S = 1.06$
2563 reflections
160 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2 + 0.4385P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0101 (11)
Absolute structure: Flack (1983), with 964 Friedel pairs
Flack parameter: −0.02 (2)

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C7	1.372 (3)	N—C2	1.487 (2)
O2—C1	1.206 (3)	C1—C2	1.517 (3)
O3—C1	1.335 (3)	C2—C3	1.536 (3)
O3—C10	1.454 (3)	C3—C4	1.513 (3)
C10—O3—C1—O2	−1.2 (3)	N—C2—C3—C4	55.8 (2)
N—C2—C1—O2	−2.2 (3)	C2—C3—C4—C5	−90.8 (2)
O2—C1—C2—C3	121.4 (2)	C2—C3—C4—C9	88.3 (2)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4	0.84	1.88	2.715 (2)	173
O4—H4···Cl	0.84	2.27	3.0938 (18)	167
N—H1N···Cl^{i}	0.91	2.32	3.1659 (18)	155
N—H2N···Cl^{ii}	0.91	2.29	3.192 (2)	170
N—H3N···Cl^{iii}	0.91	2.33	3.207 (2)	162
C2—H2···O2^{iv}	1.00	2.46	3.219 (3)	132
C9—H9···O1^{v}	0.95	2.54	3.434 (3)	157
C10—H103···O4^{v}	0.98	2.52	3.328 (3)	140

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

The known absolute configuration of L-tyrosine was assumed and confirmed by refinement of the Flack (1983) parameter. All H atoms were located in difference Fourier maps, and in the final refinement cycles they were treated as riding on their parent atoms, with C—H = 0.95–1.00 Å, N—H = 0.91 Å and O—H = 0.84 Å, and U_{iso}(H) = 1.2U_{eq}(parent atom), except for methyl H atoms, where U_{iso}(H) = 1.5U_{eq}(C).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1620). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (1997). *XP*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Claeys-Bruno, M., Toronto, D., Pecaut, J., Bardet, M. & Marchon, J. C. (2001). *J. Am. Chem. Soc.* **123**, 11067–11068.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Karle, I. L. & Flippen-Anderson, J. L. (1989). *Acta Cryst.* C**45**, 791–795.
Kolev, T., Spiteller, M., Sheldrick, W. S., Mayer-Figge, H. & Van Almsick, T. (2005). *Acta Cryst.* E**61**, o3819–o3821.
Mostad, A., Nissen, H. M. & Rømming, C. (1972). *Acta Chem. Scand.* **26**, 3819–3833.
Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Poland, Wrocław, Poland.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sridhar, B., Srinivasan, N. & Rajaram, R. K. (2002). *Acta Cryst.* E**58**, o211–o214.
Steiner, T. (1998). *Acta Cryst.* B**54**, 456–463.
Wróbel, J. T. (1983). *Preparatyka i elementy syntezy organicznej*. Warszawa: PWN. (In Polish.)