

molecular F...F and F...O distances are 3.02 and 3.03 Å, respectively. The O—H...O hydrogen bond, 2.648 (3) Å, (Fig. 2) is not significantly different from the bond in the trichloroacetic acid dimer, 2.666 (5) Å (Jönsson & Hamilton, 1972). It is also comparable to the O—H...O bond in the non-substituted acetic acid chain structure, 2.625 (5) Å (Nahringbauer, 1970), 2.631 (8) Å (Jönsson, 1971). The dimer is nearly planar. The deviations of the atoms from the plane through one of the carboxyl groups and from the least-squares plane through O(1), O(2), C(1) and C(2) are given in Table 2 and are very similar to those found in the trichloroacetic acid dimer. The CF₃COOH molecule has a perfectly staggered conformation. The torsion angle F(1)—C(2)—C(1)—O(1) is 29.1 (3)°, compared to 11.5 (4)° and 6.3 (1.6)° in CCl₃COOH and CH₃COOH, respectively. C(1)—C(2), 1.526 (5) Å, is significantly longer, and the O(1)—C(1)—O(2) angle, 128.1 (3)°, larger than the corresponding bond and angle in acetic acid, 1.478 (6) Å and 121.3 (5)°. Similar observations were made for the chloro-substituted acetic acid. The opening of the O—C—O

angle is most probably associated with the different hydrogen bonding: dimer and chain, respectively. The CF₃ group is similar to CF₃ groups found in other structures (*e.g.* Lundgren, 1978) with an average C—F bond of 1.332 Å, and average C—C—F and F—C—F angles of 110.7 and 108.3°, respectively.

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Table 2. *Least-squares planes*

Atoms defining the plane and its equation

I: O(1), O(2), C(1)

$$-3.0703x - 2.7228y - 5.7464z + 2.8184 = 0$$

II: O(1), O(2), C(1), C(2)

$$-2.7403x - 2.6854y - 6.1167z + 2.9345 = 0$$

Displacements from plane (Å)

	Plane I	Plane II
O(1)	0.000	-0.004 (2)
O(2)	0.000	-0.004 (2)
C(1)	0.000	0.023 (3)
C(2)	-0.103 (3)	-0.006 (3)
O(1')	-0.110 (2)	-0.243 (2)
O(2')	-0.110 (2)	-0.244 (2)
C(1')	-0.110 (2)	-0.270 (2)

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1-Methylimidazolium Oxalurate

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Abstract. (C₄H₇N₂)⁺.(C₃H₃N₂O₄)⁻, m.p. 423 K, *P* $\bar{1}$, *a* = 7.718 (4), *b* = 8.062 (4), *c* = 9.603 (4) Å, α = 69.34 (4), β = 62.52 (4), γ = 67.22 (4)°, *Z* = 2, *D*_m = 1.490 Mg m⁻³. The crystal structure determination was based on the X-ray intensities (Mo *K* α) of 1779

reflections collected by diffractometer. Parameter refinement by the full-matrix least-squares method gave *R* = 0.058. The longer carboxylate C—O bond (1.259 vs 1.230 Å) involves the O atom which forms the salt bridge (NH...O, 2.78 Å) and another hydrogen bond.

Introduction. Crystals of the oxalurate salt were obtained from a solution of 1-methylimidazole and parabanic acid in absolute ethanol. Parabanic acid (imidazoletrione) was hydrolyzed (Andrews & Sell, 1955) presumably with water absorbed from the atmosphere. This reaction also occurred when efforts to form a crystal complex of parabanic acid with 9-ethyladenine led to a remarkable crystal structure containing parabanic acid, oxalurate anion, 9-ethyladeninium cation and water (Shieh & Voet, 1975), hereafter known as the adenine complex.

Crystal data* were measured with a computer-controlled four-circle diffractometer and graphite-monochromated Mo $K\alpha$ radiation. Integrated intensities were obtained for 2152 reflections, including all with $\sin \theta/\lambda < 0.59 \text{ \AA}^{-1}$, using a crystal $0.35 \times 0.25 \times 0.20 \text{ mm}$, and $\theta/2\theta$ scans. The variance in an intensity was assumed to be $\sigma^2(I) = \sigma^2 + (0.02I)^2$ where σ^2 is the variance from counting statistics. There were no corrections for X-ray absorption or extinction. The phase problem was solved by symbolic addition and

* The unit cell given in the *Abstract* was used in the structure determination. The Niggli reduced cell ($a = 7.718$, $b = 8.062$, $c = 9.132 \text{ \AA}$, $\alpha = 92.51$, $\beta = 111.10$, $\gamma = 112.78^\circ$) is obtained by the transformation $(-1, 0, 0/0, 1, 0/1, 0, -1)$.

Table 1. *Atomic parameters with e.s.d.'s*

The atomic parameters are fractional coordinates ($\times 10^4$ for non-hydrogen, $\times 10^3$ for H atoms) with respect to the crystal axes. E.s.d.'s in parentheses refer to the least significant digit in the parameter value.

	<i>x</i>	<i>y</i>	<i>z</i>
(a) 1-Methylimidazolium cation			
N(1)	1678 (2)	173 (2)	5821 (2)
C(1)	492 (4)	-608 (4)	7466 (3)
C(2)	1436 (3)	1943 (3)	5144 (2)
N(3)	2794 (3)	2105 (3)	3677 (2)
C(4)	3944 (4)	407 (3)	3387 (3)
C(5)	3254 (3)	-799 (3)	4722 (2)
H(11)	130 (5)	-135 (4)	805 (4)
H(12)	-17 (5)	-137 (4)	741 (3)
H(13)	-30 (5)	23 (5)	803 (4)
H(2)	43 (3)	292 (3)	569 (2)
H(3)	288 (4)	315 (4)	302 (3)
H(4)	484 (4)	27 (3)	246 (3)
H(5)	354 (3)	-204 (3)	498 (2)
(b) Oxalurate anion			
N(1)	1010 (3)	3711 (3)	8360 (2)
C(2)	2545 (2)	4303 (2)	7169 (2)
O(2)	2624 (2)	4998 (2)	5791 (1)
N(3)	4184 (2)	4096 (2)	7546 (2)
C(4)	4378 (3)	3380 (2)	9000 (2)
O(4)	3122 (2)	2756 (2)	10214 (1)
C(5)	6364 (3)	3419 (2)	9003 (2)
O(5)	6621 (2)	2723 (2)	10281 (2)
O(6)	7521 (2)	4163 (2)	7694 (1)
H(11)	-10 (4)	389 (3)	820 (2)
H(12)	106 (4)	327 (3)	930 (3)
H(3)	521 (3)	443 (3)	679 (2)

extended to 252 reflections by the tangent formula (Karle & Karle, 1966). Atomic parameters* (Table 1) were refined by a full-matrix least-squares procedure minimizing the function $\sum w\Delta^2$ where $\Delta = |F_o| - |F_c|$ and $w = \sigma^{-2}(F_o)$ and the summation was with respect to 1779 reflections with $I > 2\sigma(I)$. X-ray scattering factors were those of Cromer & Waber (1965) for C, N and O atoms, and Stewart, Davidson & Simpson (1965) for H. Refinement converged with $R = \sum |\Delta|/\sum |F_o| = 0.058$.

Discussion. The structure of the 1-methylimidazolium cation is similar to that of 1-methylimidazole in its crystal complex with barbital (Wang & Craven, 1979). Both rings are nearly planar (Table 2). There are small

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34040 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Best least-squares planes*

(a) Equations referred to the crystal axes in the form $Ax + By + Cz = D$ where (x, y, z) are fractional coordinates and A, B, C, D are in \AA

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
1-Methylimidazolium cation	7.2509	3.7158	7.0689	5.4028
Oxalurate anion	-0.1042	7.1735	3.7022	5.7172
Urea group	0.0621	7.2673	3.6818	5.7813
Peptide group	-0.0867	7.1985	3.6344	5.6697
Carboxylate group	-0.1488	7.0989	3.9003	5.8443

(b) Distances of atoms from the planes (\AA)

(i) 1-Methylimidazolium cation		(ii) Oxalurate anion	
N(1)	-0.007	N(1)	0.029
C(1)	0.006	C(2)	-0.003
C(2)	-0.003	O(2)	-0.015
N(3)	0.004	N(3)	-0.029
C(4)	0.002	C(4)	-0.006
C(5)	-0.002	O(4)	0.009
H(11)*	0.729	C(5)	0.002
H(12)*	-0.798	O(5)	-0.026
H(13)*	0.142	O(6)	0.040
H(2)*	-0.004	H(11)*	0.110
H(4)*	-0.053	H(12)*	0.062
H(5)*	-0.068	H(3)*	-0.078

(iii) Subunits of oxalurate anion

Urea		Peptide		Carboxylate	
N(1)	0.000	C(2)	0.011	C(4)	0.000
C(2)	0.001	N(3)	-0.015	C(5)	-0.001
O(2)	0.000	C(4)	-0.004	O(5)	0.000
N(3)	0.000	O(4)	-0.001	O(6)	0.000
H(11)*	0.064	C(5)	0.008	O(4)*	0.049
H(12)*	0.028	H(3)*	-0.057	N(3)*	-0.056
H(3)*	-0.028	N(1)*	0.031		
C(4)*	0.016	O(5)*	-0.030		

* Atoms not included in the calculation of the plane.

but significant differences in bond lengths and angles (Fig. 1) which follow the same pattern as was observed in comparing the imidazolium cation with imidazole (Craven, McMullan, Bell & Freeman, 1977). Notable in Fig. 1 is the opening of the ring angle at N(3) by 4.5° as a result of protonation.

The structure of the oxalurate anion is similar to that observed in the adenine complex (Shieh & Voet, 1975), including the intramolecular $\text{NH}\cdots\text{O}$ hydrogen bond (Fig. 2). When the anion is subdivided the atoms within each of the urea, peptide and carboxylate fragments are almost coplanar (Table 2) as in the adenine complex. The torsion angles in the bonds linking these fragments (Table 3) show that the anion is slightly puckered from

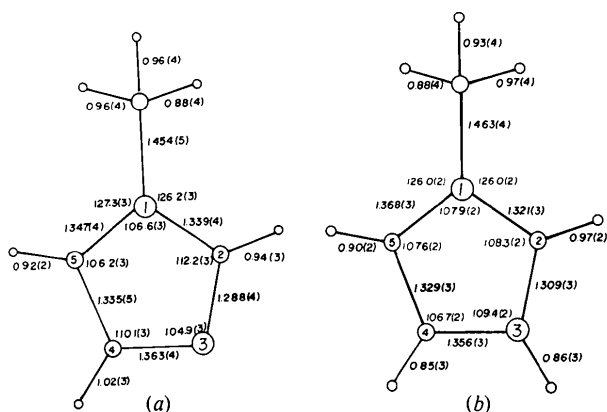


Fig. 1. Bond lengths (\AA) and angles ($^\circ$) in (a) 1-methylimidazole (Wang & Craven, 1979), (b) 1-methylimidazolium cation (present work). Largest circles represent nitrogen atoms, N(1) and N(3).

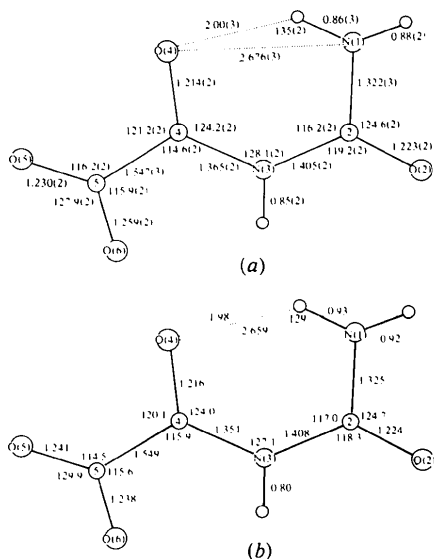


Fig. 2. Bond lengths (\AA) and angles ($^\circ$) in oxalurate anion in (a) 1-methylimidazolium salt (present work), (b) adenine complex (Shieh & Voet, 1975).

Table 3. Torsion angles ($^\circ$)

The e.s.d.'s in torsion angles are 2° for angles involving H otherwise 0.3° .

(a) 1-Methylimidazolium cation

C(2)-N(1)-C(1)-H(11)	-122
C(2)-N(1)-C(1)-H(12)	119
C(2)-N(1)-C(1)-H(13)	-9

(b) Oxalurate anion

	Present work	Adenine complex
N(1)-C(2)-N(3)-C(4)	-1.0	9.0
C(2)-N(3)-C(4)-C(5)	-178.0	-179.0
N(3)-C(4)-C(5)-O(5)	-177.5	-167.3

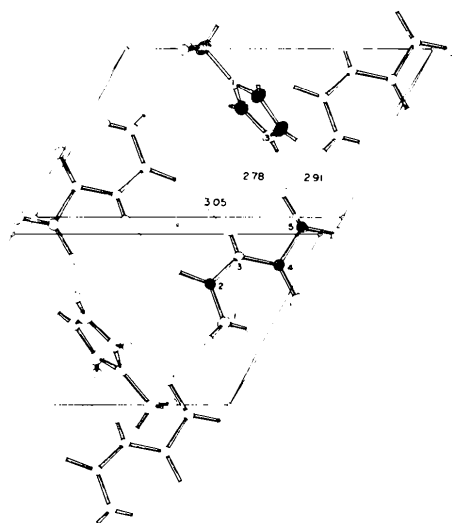


Fig. 3. The crystal structure of 1-methylimidazolium oxalurate. Atoms are represented by 25% probability thermal ellipsoids.

planarity, but there is less puckering than in the adenine complex. Most oxalurate bond lengths and angles agree with those in the adenine complex, although the difference (0.015 \AA) in the N(3)-C(4) length may be significant. There is an interesting difference in the carboxylate C-O bonds in the two structures, which appears to be related to the hydrogen bonding. In the adenine complex, both O atoms form two hydrogen bonds and the C-O bond lengths ($1.238, 1.241 \text{ \AA}$) are the same within the experimental error ($\sigma = 0.002 \text{ \AA}$). In the 1-methylimidazolium salt the C-O bond with O(6), which forms both the salt bridge and a second hydrogen bond (Fig. 3), is longer (1.259 vs 1.230 \AA) than the C-O bond with O(5) which is not hydrogen bonded.

There are three intermolecular hydrogen bonds in the crystal structure (Fig. 3). The shortest is the salt bridge between the cation N(3)H group and the anion O(6).

The N...O distance is 2.78 Å and the N-H...O angle is 158°. The dihedral angle between the planes of the bridged molecules is 80°. There is also a hydrogen bond N(1)H(1)...O(6) which links oxalurate anions head to tail to form ribbons parallel to the *a* axis. This has an N...O distance of 2.91 Å and the NH...O angle is 175°. The oxalurate ribbons are crosslinked through pairs of N(3)H(3)...O(2) hydrogen bonds which are relatively weak. The N...O distances are 3.05 Å and NH...O angles are 155°.

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cyclo(-L-Prolyl-D-tert-leucyl-)

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Abstract. C₁₁H₁₈N₂O₂, orthorhombic, *P*2₁2₁2, *Z* = 4, FW 210.3, *a* = 10.942 (2), *b* = 16.438 (4), *c* = 6.452 (1) Å, *D_x* = 1.20, *D_m* = 1.14 Mg m⁻³, λ(Cu Kα) = 1.5418 Å (graphite monochromator); the final *R* = 0.046 on 794 observed reflexions [*F*_o² > 3σ(*F*_o²)] in the range 0 < 2θ ≤ 68°. The molecules are linked by hydrogen bonds to form chains [N(2)–H(1)...O(1): N(2)...O(2) = 2.894 (4), H(1)...O(1) = 2.053 (4) Å, ∠N(2)–H(1)...O(1) = 153 (3)°].

Introduction. Colourless transparent prismatic crystals of the title compound were prepared by Pospíšek & Bláha (1976) at the Institute of Organic Chemistry and Biochemistry, Praha. Our main interest was in the molecular conformation of the 2,5-piperazinedione ring with the bulky side chain of the *tert*-butyl group.

Measurement of integrated intensities of 2364 reflexions with *h* ≥ 0, *k* ≥ 0, *l* ≧ 0 was made on a Syntex *P*2₁ four-circle diffractometer. The scan range (2θ_{α₁} – 1°, 2θ_{α₂} + 1°) and a variable scan rate from 1.2 to 29.3° min⁻¹ were used. Three standard reflexions showed no unusual fluctuations. The data were corrected for background, Lorentz and polarization effects and for coincidence of pulses. The quality of the measurement was tested by

$$r = 2 \frac{\sum_{\substack{hkl \\ l > 0}} |I_{hkl} - I_{hk\bar{l}}|}{\sum_{\substack{hkl \\ l > 0}} I_{hkl} + I_{hk\bar{l}}} = 0.048$$

for both dependent sets of reflexions.

The structure was solved by direct methods with the tangent formula. For the set with the best figures of merit an *E* map was calculated and all non-hydrogen atoms were identified. They were refined anisotropically by full-matrix least squares to *R* = 0.102. An attempt to locate H atoms from a difference synthesis failed. We calculated positions for the H atoms with an isotropic temperature factor *B* = 3.4 Å². Positional and thermal parameters (anisotropic for non-hydrogen and isotropic for H atoms) were refined in three blocks (the last cycle in one block) to a final *R* = 0.046. Weights 1/σ(*F*_o²) were used. The final difference synthesis displayed no features > 0.2 e Å⁻³.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34026 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.