

Data collection

Stoe AED-4 four-circle diffractometer	$R_{\text{int}} = 0.0123$
ω - θ scans	$\theta_{\text{max}} = 30.03^\circ$
Absorption correction: none	$h = -23 \rightarrow 23$
3174 measured reflections	$k = -12 \rightarrow 12$
1747 independent reflections	$l = 0 \rightarrow 11$
1292 observed reflections	4 standard reflections
$[I > 2\sigma(I)]$	frequency: 120 min
	intensity decay: <1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R(F) = 0.0377$	$\Delta\rho_{\text{max}} = 0.425 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.1185$	$\Delta\rho_{\text{min}} = -0.186 \text{ e } \text{\AA}^{-3}$
$S = 1.040$	Extinction correction: none
1747 reflections	Atomic scattering factors
89 parameters	from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.2061P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$			
	x	y	z	U_{eq}
O1	0.43274 (5)	0.22979 (9)	0.10006 (13)	0.0319 (2)
O2	0.55785 (6)	0.10204 (10)	-0.0518 (2)	0.0475 (3)
O3	0.64056 (5)	0.24775 (8)	-0.19972 (11)	0.0302 (2)
C1	0.53848 (6)	0.36706 (10)	-0.04674 (13)	0.0221 (2)
C2	0.46767 (6)	0.35979 (10)	0.04885 (14)	0.0232 (2)
C3	0.43051 (6)	0.49337 (11)	0.09363 (14)	0.0236 (2)
C7	0.57882 (6)	0.22629 (12)	-0.0982 (2)	0.0266 (2)
C8	0.68173 (7)	0.11251 (13)	-0.2561 (2)	0.0351 (3)
C9	0.74834 (8)	0.1629 (2)	-0.3680 (2)	0.0433 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O1—C2	1.3580 (12)	C1—C2	1.4114 (14)
O2—C7	1.2169 (14)	C1—C7	1.4795 (14)
O3—C7	1.3290 (14)	C2—C3	1.3867 (14)
O3—C8	1.4566 (13)	C3—C1'	1.3958 (14)
C1—C3'	1.3958 (14)	C8—C9	1.499 (2)
C7—O3—C8	116.03 (9)	C3—C2—C1	118.47 (9)
C3'—C1—C2	119.89 (9)	C2—C3—C1'	121.64 (9)
C3'—C1—C7	120.46 (9)	O2—C7—O3	122.80 (10)
C2—C1—C7	119.64 (9)	O2—C7—C1	123.40 (11)
O1—C2—C3	117.22 (9)	O3—C7—C1	113.79 (9)
O1—C2—C1	124.31 (9)	O3—C8—C9	106.87 (10)
C8—O3—C7—O2	1.1 (2)	C3'—C1—C7—O3	-5.0 (2)
C8—O3—C7—C1	-179.14 (10)	C2—C1—C7—O3	174.30 (9)
C3'—C1—C7—O2	174.79 (12)	C7—O3—C8—C9	179.93 (11)
C2—C1—C7—O2	-5.9 (2)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

The C and O atoms were refined with anisotropic displacement parameters. The H atoms were located from a difference map and refined with free isotropic displacement parameters (groupwise for methyl and methylene) using a riding model, with aromatic C—H distances of 0.95, methylene C—H distances of 0.99 and methyl C—H distances of 0.98 \AA . The atom HO1 was refined with free coordinates and free isotropic displacement parameters.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a).

Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *CIFTAB* in *SHELXTL/PC*.

This project has been supported by the A. Messer Foundation, the Deutsche Forschungsgemeinschaft, the State of Hesse and the Fonds der Chemischen Industrie.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: SK1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2633–2636

Maltol Hydrochloride

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(Received 23 February 1996; accepted 30 April 1996)

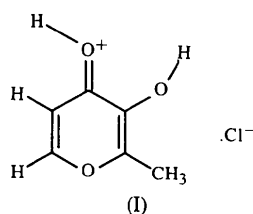
Abstract

The unit cell of the title compound, 3-hydroxy-2-methyl-4H-pyran-4-onium chloride, $\text{C}_6\text{H}_7\text{O}_3^+\text{Cl}^-$, contains Cl^- anions and carbonyl-protonated maltolium cations connected into perfectly planar ribbons *via* hydrogen bonding. The C=O bond length is increased by *ca* 0.06 \AA upon protonation whereas greater delocalization in the

ring π -system makes the double bonds 0.02 Å longer and the single bonds 0.02–0.03 Å shorter than in the neutral molecule.

Comment

The crystal of 3-hydroxy-2-methyl-4*H*-pyran-4-onium chloride, (I), contains Cl⁻ anions and cationic maltol units protonated at the O4 carbonyl group, as found earlier for 3-hydroxy-2,6-dimethyl-4-pyrone hydrobromide (Hope, 1965). The ring and its substituents are perfectly coplanar, with all the atoms (except for two methyl H atoms) lying on a crystallographic mirror plane.



Comparison of bond lengths (Table 2) with those of 2-ethyl-3-hydroxy-4-pyrone (Brown *et al.*, 1995) shows that π -electron delocalization is enhanced by protonation (Fig. 1). The double-bond character of the C4=O4 bond is decreased considerably, its distance being 1.307 (3) Å compared with 1.241 (3) Å in the neutral system. The two ring double bonds are lengthened by *ca* 0.023 Å, whereas the four single bonds are shortened by 0.015–0.031 Å. This is accompanied by relatively large variations of the intra-ring angles: +3.6 (C4), -2.2 (C3, C5), -0.7 (C6) and +1.3° (O1). Large variations are also noted for C3—C4—O4 (-3.4°) and C4—C3—O3 (+3.4°). Both electron distribution and hydrogen bonding most likely contribute to these angular changes.

Maltol forms chelates with various metals *via* the O3 and O4 atoms (Orvig, Rettig & Trotter, 1987; Luo, Rettig & Orvig, 1993; Ahmet, Frampton & Silver, 1988; Annan, Peppe & Tuck, 1990; Archer *et al.*, 1991; Denekamp *et al.*, 1992; Bhattacharya *et al.*, 1994). The bond lengths are usually not accurate enough to reveal a pattern as above, although the C4=O4 bond is definitely lengthened (mean 1.266, range 1.238–1.296 Å). Large variations of the angles in the O3—C3—C4—O4 region can be ascribed to steric strain imposed by chelate-ring closure.

A view of the unit cell is shown in Fig. 2. Maltolium cations related by the 2₁ axis along *a* define an infinite ribbon which closely resembles that of polymorph (1) of 2-ethyl-3-hydroxy-4-pyrone (Brown *et al.*, 1995). In the latter compound, neutral units are connected along the ribbon by intermolecular O3—H...O4 hydrogen bonds. In the present case, the similarly oriented maltolium cations are joined by a Cl⁻ anion making an O3—H...Cl bond to one cation and an O4—H...Cl bond to the next (Table 3). Besides these two interactions,

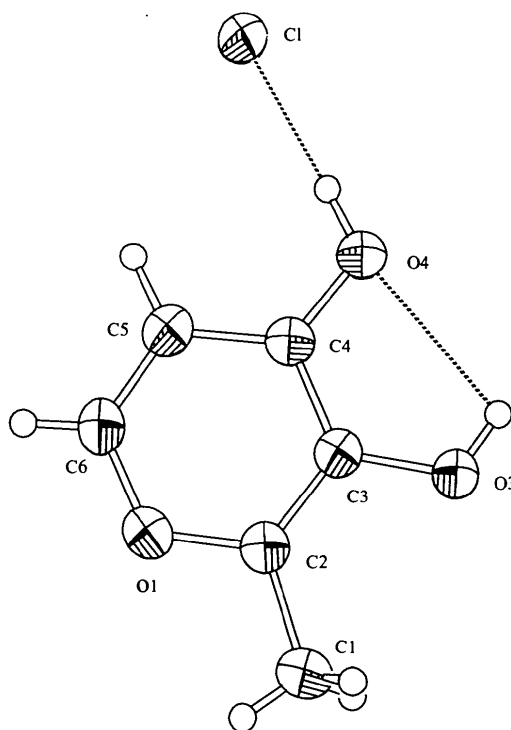


Fig. 1. ORTEPII (Johnson, 1976) drawing of the title molecule. Ellipsoids correspond to 40% probability.

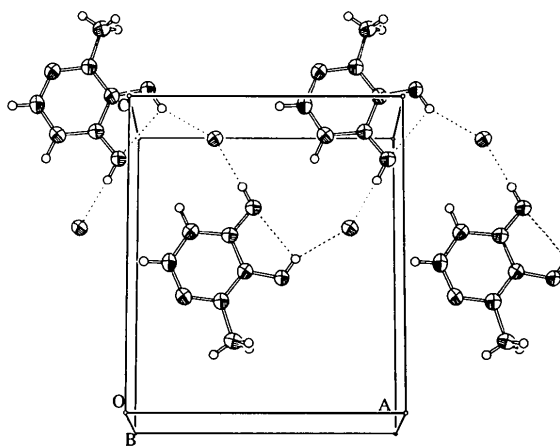


Fig. 2. ORTEPII (Johnson, 1976) drawing of a ribbon of hydrogen-bonded maltolium and chloride ions running along the *a* axis in the crystallographic mirror plane perpendicular to *b*. Ellipsoids correspond to 40% probability.

the environment of the Cl⁻ anion includes two intra-ribbon C—H...Cl⁻ contacts [with H5 at 2.85 (3) Å and H6($\frac{1}{2} + x$, y , $\frac{3}{2} - z$) at 2.63 (3) Å], as well as two interactions [3.294 (1) Å] with endocyclic O1 atoms in adjacent layers. These parallel ribbons running along the *a* axis define perfectly planar layers perpendicular to *b* in the crystallographic mirror planes, separated by

b/2. Contacts between the ribbons within the layer and between adjacent layers involve normal van der Waals interactions.

Experimental

The title compound was first obtained as a byproduct during the reaction of maltol with NbCl₅ in dry benzene. It was eventually prepared by bubbling HCl gas into a maltol solution in the same solvent. Moisture-sensitive colorless crystals were obtained by recrystallization from CH₂Cl₂.

Crystal data

C₆H₇O₃·Cl⁻

M_r = 162.57

Orthorhombic

Pnma

a = 9.676 (2) Å

b = 6.579 (2) Å

c = 11.215 (2) Å

V = 713.9 (3) Å³

Z = 4

D_x = 1.512 Mg m⁻³

D_m not measured

Cu Kα radiation

λ = 1.5418 Å

Cell parameters from 25 reflections

θ = 20.0–25.0°

μ = 4.312 mm⁻¹

T = 213 (2) K

Plate

0.38 × 0.26 × 0.09 mm

White

Data collection

Enraf–Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction:

by integration from crystal shape

T_{min} = 0.33, *T_{max}* = 0.68

4715 measured reflections

732 independent reflections

590 observed reflections
[*I* > 2σ(*I*)]

R_{int} = 0.052

θ_{max} = 70°

h = 0 → 11

k = 0 → 8

l = 0 → 13

5 standard reflections

frequency: 30 min

intensity decay: 1.6%

Refinement

Refinement on *F*²

R(*F*) = 0.0267

wR(*F*²) = 0.0713

S = 0.973

732 reflections

81 parameters

All H-atom parameters

refined

w = 1/[σ²(*F_o*) + (0.0366*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = -0.001

Δρ_{max} = 0.18 e Å⁻³

Δρ_{min} = -0.20 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0056 (7)

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 (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cl	0.30918 (6)	1/4	0.89711 (5)	0.0468 (2)
O1	0.1979 (2)	1/4	0.38281 (14)	0.0443 (4)
O3	0.5588 (2)	1/4	0.44224 (15)	0.0510 (5)
O4	0.4517 (2)	1/4	0.66952 (15)	0.0488 (5)
C1	0.3808 (3)	1/4	0.2420 (2)	0.0490 (7)
C2	0.3350 (2)	1/4	0.3679 (2)	0.0388 (5)

C3	0.4220 (2)	1/4	0.4640 (2)	0.0383 (5)
C4	0.3656 (2)	1/4	0.5797 (2)	0.0380 (5)
C5	0.2211 (2)	1/4	0.5911 (2)	0.0424 (6)
C6	0.1435 (3)	1/4	0.4916 (2)	0.0484 (7)

Table 2. Selected geometric parameters (Å, °)

O1—C6	1.329 (3)	C2—C3	1.368 (3)
O1—C2	1.338 (3)	C3—C4	1.408 (3)
O3—C3	1.346 (3)	C4—C5	1.404 (3)
O4—C4	1.307 (3)	C5—C6	1.345 (3)
C1—C2	1.480 (3)		
C6—O1—C2	120.5 (2)	C2—C3—C4	119.2 (2)
O1—C2—C3	120.8 (2)	O4—C4—C5	124.4 (2)
O1—C2—C1	114.6 (2)	O4—C4—C3	117.6 (2)
C3—C2—C1	124.6 (2)	C5—C4—C3	118.0 (2)
O3—C3—C2	117.5 (2)	C6—C5—C4	118.7 (2)
O3—C3—C4	123.3 (2)	O1—C6—C5	122.7 (2)

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O4	0.85 (4)	2.41 (4)	2.752 (3)	105 (3)
O3—H3...Cl ⁱ	0.85 (4)	2.23 (4)	3.019 (2)	156 (3)
O4—H4...Cl ⁱ	0.87 (4)	2.03 (4)	2.901 (2)	178 (3)

Symmetry code: (i) ½ + *x*, *y*, ¾ - *z*.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

The financial support of the Natural Sciences and Engineering Research Council of Canada and the Fonds FCAR du Ministère de l'Éducation du Québec is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1175). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2636–2638

1,1'-Diketone and 1,1'-Dinitrile Derivatives of 2,2'-Biimidazole

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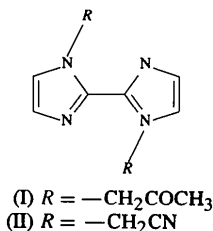
(Received 7 February 1996; accepted 7 May 1996)

Abstract

The crystal structures of 2,2'-biimidazole-1,1'-diacetone, C₁₂H₁₄N₄O₂, and 2,2'-biimidazole-1,1'-diacetonitrile, C₁₀H₈N₆, have been determined. Both molecules crystallize with coplanar rings having substituents in a *trans* disposition with a center of inversion located midway between the bridging C atoms.

Comment

Derivatives containing the 2,2'-biimidazole moiety have been incorporated in the synthesis of various organic polymers (Liu, Kokorudz & Collier, 1988; Elmer & Collier, 1993) and macrocyclic complexes (Kandil & Collier, 1988; Lehn & Regnouf de Vains, 1989). The crystal structure determinations of 1,1'-di(2-propanone)-2,2'-biimidazole, (I), and 1,1'-di(cyaomethyl)-2,2'-biimidazole, (II), were undertaken to elucidate better the stereochemical reactivity of the molecules and to model the conformation of such macrocyclic and polymeric systems.



In both structures, which lie about inversion centers, the biimidazole ring atoms (C1, C2, C3, N1, N2 and their inversion-related partners) exhibit an essentially

coplanar conformation, as expected in an aromatic system. The two ten-atom least-squares planes have standard deviations and maximum values of 0.0018 and 0.0048, and 0.00042 and 0.0014 Å for (I) and (II), respectively. The C5 atoms are out of this plane by 1.312(4) and 1.235(3) Å and the values of the C1—N1—C4—C5 torsion angles are -70.5(3) and -75.2(2)° for (I) and (II), respectively. Although both (I) and (II) adopt a *trans* orientation in the solid state, ongoing investigations have demonstrated that both molecules assume a *cis* configuration when chelating a metal center through the N atoms. Bond lengths and angles lie within 1σ of observed ranges for 2,2'-biimidazole (Cromer, Ryan & Storm, 1987) and its related dinitro derivatives (Bryan *et al.*, 1995; Cromer & Storm, 1990).

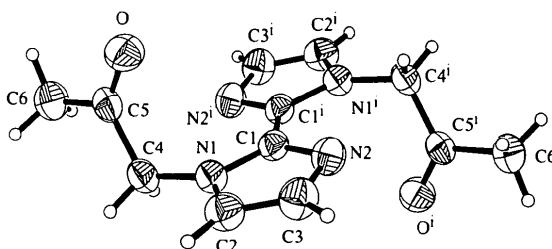


Fig. 1. View of (I) showing the labeling of the non-H atoms [symmetry code: (i) $-x, 1-y, 1-z$]. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small spheres of arbitrary radii.

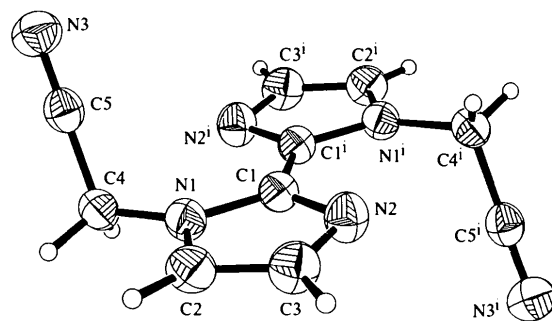


Fig. 2. View of (II) showing the labeling of the non-H atoms [symmetry code: (i) $1-x, -y, 1-z$]. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small spheres of arbitrary radii.

Experimental

The preparation of (I) and (II) has been described by Barnett, Secondo & Collier (1996). Crystals were grown by slow evaporation from acetone and warm methanol for compounds (I) and (II), respectively.

Compound (I)

Crystal data

C₁₂H₁₄N₄O₂
M_r = 246.3

Mo Kα radiation
 λ = 0.71073 Å