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## L-Histidyl-L-tyrosinium Dichloride Dihydrate, $C_{15}H_{20}N_4O_4^{2+} \cdot 2Cl^- \cdot 2H_2O$

THOMAS STEINER

*Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14195 Berlin, Germany. E-mail: steiner@chemie.fu-berlin.de*

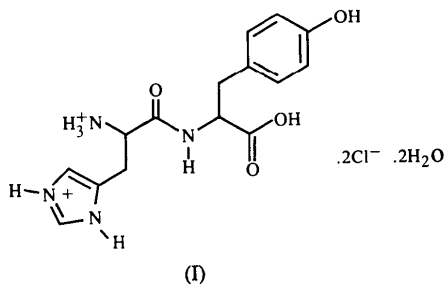
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### Abstract

The His–Tyr dipeptide is doubly protonated. The positively charged side chain of the histidine residue is tightly coordinated by O and  $Cl^-$  hydrogen-bond acceptors. Both C–H groups of the imidazole ring donate weak hydrogen bonds.

### Comment

The crystal structure analysis of the title compound, (I), was undertaken to establish the system of hydrogen bonds (see Jeffrey & Saenger, 1991), in particular those formed by the imidazole ring of the histidine residue. Since (I) was crystallized from a solution in dilute HCl, the dipeptide in the crystal structure is found as a dication (Fig. 1), with positive charges at the N-terminus atom (N1) and at the histidine side chain. The C-terminus is uncharged. The positive charge is balanced by two  $Cl^-$  ions, and in addition, two water molecules are co-crystallized.



The conformation of the dipeptide is conventional and need not be discussed here. The same is true for the  $O-H \cdots O$ ,  $O-H \cdots Cl^-$ ,  $N-H \cdots O$  and  $N-H \cdots Cl^-$  hydrogen bonds (Table 3). Of interest is the intermolecular environment of the histidine side chain (Fig. 2). This positively charged group is tightly coordinated by O and  $Cl^-$  hydrogen-bond acceptors in an almost coplanar arrangement. All imidazole N–H and C–H groups donate hydrogen bonds to these acceptors, those formed by C5–H and N4–H being three-centered (bifurcated). It is quite usual for not only the N–H, but also both C–H groups of protonated histidine side chains, to

be involved in hydrogen bonding (e.g. Steiner, 1995; for background reading on  $C-H \cdots O$  interactions, see Desiraju, 1991). Also some tyrosine C–H groups and  $Cl-H$  (i.e. the histidine  $C^\alpha-H$ ) are engaged in  $C-H \cdots O$  interactions (Table 3).

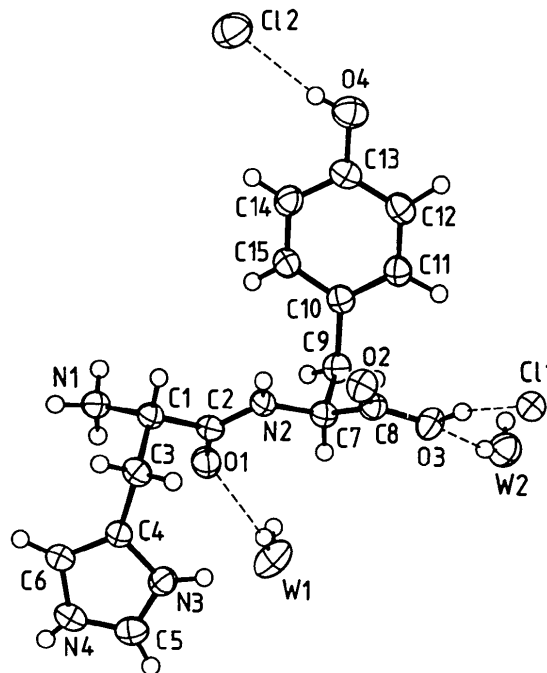


Fig. 1. Molecular structure and atom labeling of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

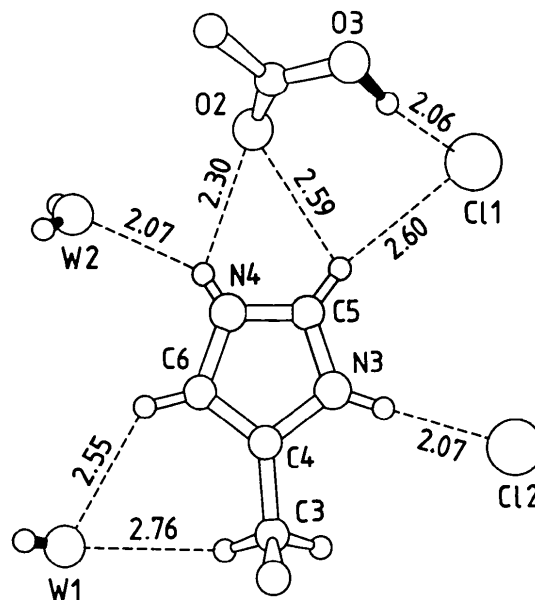


Fig. 2. The hydrogen-bonding pattern around the protonated histidine side chain. Numerical values of  $H \cdots X$  distances (Å) are given for normalized H-atom positions.

## Experimental

The title dipeptide is commercially available (Sigma) and was crystallized by slow evaporation of a solution in 6% HCl.

## Crystal data

C <sub>15</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub> <sup>2+</sup> ·2Cl <sup>-</sup> ·2H <sub>2</sub> O	Cu Kα radiation
<i>M<sub>r</sub></i> = 427.28	λ = 1.54176 Å
Monoclinic	Cell parameters from 25 reflections
<i>P</i> 2 <sub>1</sub>	θ = 9.6–25.2°
<i>a</i> = 6.6813 (4) Å	μ = 3.249 mm <sup>-1</sup>
<i>b</i> = 14.7787 (9) Å	<i>T</i> = 293 (2) K
<i>c</i> = 10.2608 (9) Å	Plate
β = 96.29 (2)°	0.50 × 0.30 × 0.05 mm
<i>V</i> = 1007.06 (12) Å <sup>3</sup>	Colorless
<i>Z</i> = 2	
<i>D<sub>x</sub></i> = 1.409 Mg m <sup>-3</sup>	
<i>D<sub>m</sub></i> not measured	

## Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer	<i>R</i> <sub>int</sub> = 0.0233
ω/2θ scans	θ <sub>max</sub> = 59.94°
Absorption correction: see text	<i>h</i> = -7 → 7
1648 measured reflections	<i>k</i> = -16 → 0
1555 independent reflections	<i>l</i> = 0 → 11
1522 observed reflections	3 standard reflections
[ <i>I</i> > 2σ( <i>I</i> )]	frequency: 60 min
	intensity decay: 1.3%

## Refinement

Refinement on <i>F</i> <sup>2</sup>	Δρ <sub>max</sub> = 0.262 e Å <sup>-3</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.0257	Δρ <sub>min</sub> = -0.194 e Å <sup>-3</sup>
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.0825	Extinction correction: none
<i>S</i> = 1.101	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
1543 reflections	Absolute configuration: Flack (1983)
340 parameters	Flack parameter = -0.002 (13)
All H-atom parameters refined	
<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0503 <i>P</i> ) <sup>2</sup> + 0.1026 <i>P</i> ]	
where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3	
(Δ/σ) <sub>max</sub> = -0.001	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cl1	0.39459 (10)	0.49999 (5)	0.30959 (6)	0.0422 (2)
Cl2	-0.37090 (14)	1.09801 (6)	0.12361 (10)	0.0665 (3)
OW1	-0.1667 (4)	0.5847 (2)	0.9610 (3)	0.0648 (7)
OW2	-0.2244 (4)	0.4142 (2)	0.4933 (3)	0.0504 (6)
N1	-0.0358 (4)	0.9442 (2)	0.9006 (2)	0.0360 (5)
C1	0.1108 (4)	0.8912 (2)	0.8329 (2)	0.0337 (6)
C2	0.0142 (4)	0.8000 (2)	0.7926 (2)	0.0327 (6)
O1	-0.0866 (3)	0.76088 (15)	0.8686 (2)	0.0448 (5)
C3	0.3071 (4)	0.8783 (2)	0.9225 (3)	0.0364 (6)
C4	0.2841 (4)	0.8386 (2)	1.0541 (3)	0.0311 (6)
C5	0.2888 (4)	0.7330 (2)	1.2065 (3)	0.0415 (7)
C6	0.2602 (4)	0.8781 (2)	1.1703 (3)	0.0363 (6)
N3	0.3001 (3)	0.7467 (2)	1.0802 (2)	0.0386 (5)
N4	0.2625 (3)	0.8108 (2)	1.2619 (3)	0.0393 (6)
N2	0.0541 (4)	0.7679 (2)	0.6784 (2)	0.0343 (5)

C7	-0.0100 (4)	0.6795 (2)	0.6296 (3)	0.0349 (6)
C8	0.1381 (4)	0.6483 (2)	0.5368 (3)	0.0357 (6)
O2	0.2651 (3)	0.69610 (15)	0.4991 (2)	0.0450 (5)
O3	0.1062 (3)	0.56279 (13)	0.4988 (2)	0.0440 (5)
C9	-0.2267 (4)	0.6808 (2)	0.5596 (3)	0.0377 (6)
C10	-0.2434 (4)	0.7385 (2)	0.4379 (3)	0.0344 (6)
C11	-0.2188 (4)	0.7024 (2)	0.3149 (3)	0.0381 (6)
C12	-0.2234 (4)	0.7565 (2)	0.2045 (3)	0.0412 (7)
C13	-0.2504 (4)	0.8488 (2)	0.2168 (3)	0.0379 (7)
C14	-0.2775 (4)	0.8855 (2)	0.3369 (3)	0.0417 (7)
C15	-0.2730 (5)	0.8311 (2)	0.4460 (3)	0.0399 (7)
O4	-0.2550 (3)	0.9008 (2)	0.1049 (2)	0.0517 (6)

Table 2. Selected geometric parameters (Å, °)

N1—C1	1.485 (4)	C7—C8	1.518 (4)
C1—C2	1.529 (4)	C7—C9	1.544 (4)
C1—C3	1.530 (4)	C8—O2	1.200 (4)
C2—O1	1.230 (3)	C8—O3	1.333 (4)
C2—N2	1.318 (4)	C9—C10	1.507 (4)
C3—C4	1.495 (4)	C10—C15	1.386 (4)
C4—C6	1.354 (4)	C10—C11	1.396 (4)
C4—N3	1.385 (4)	C11—C12	1.384 (4)
C5—N4	1.302 (4)	C12—C13	1.383 (5)
C5—N3	1.323 (4)	C13—C14	1.376 (4)
C6—N4	1.368 (4)	C13—O4	1.380 (4)
N2—C7	1.448 (4)	C14—C15	1.376 (5)
N1—C1—C3	110.5 (2)	C3—C1—C2	111.2 (2)
N1—C1—C2	108.1 (2)		

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

Data for normalized H-atom positions are based on bond lengths of O—H = 0.98, N—H = 1.04 and C—H = 1.09 Å.

	D—H	H...A	D...A	D—H...A	H <sub>norm</sub> ...A
OW1—H1W1...Cl2 <sup>i</sup>	1.09 (5)	2.05 (5)	3.122 (3)	170 (4)	2.15
OW1—H2W1...O1	0.67 (6)	2.20 (6)	2.841 (3)	161 (6)	1.91
OW2—H1W2...Cl1 <sup>ii</sup>	0.77 (5)	2.50 (5)	3.254 (3)	166 (5)	2.30
OW2—H2W2...O3	0.76 (7)	2.36 (7)	3.111 (4)	169 (6)	2.15
N1—H1N1...Cl1 <sup>iii</sup>	0.90 (3)	2.26 (3)	3.154 (3)	170 (3)	2.13
N1—H2N1...OW1 <sup>iv</sup>	0.97 (5)	1.83 (5)	2.783 (4)	170 (4)	1.75
N1—H3N1...O4 <sup>v</sup>	0.95 (4)	1.92 (4)	2.761 (3)	147 (3)	1.84
N1—H3N1...O1	0.95 (4)	2.35 (4)	2.745 (3)	105 (3)	2.33
C1—HC1...OW2 <sup>vi</sup>	0.98 (3)	2.64 (3)	3.528 (3)	151 (2)	2.55
C3—HC3...OW1 <sup>vii</sup>	0.98 (4)	2.82 (4)	3.444 (4)	122 (3)	2.76
N3—HN3...Cl2 <sup>viii</sup>	0.88 (4)	2.23 (4)	3.105 (3)	178 (4)	2.07
N4—HN4...OW2 <sup>ix</sup>	0.73 (4)	2.33 (4)	2.975 (4)	148 (4)	2.07
N4—HN4...O2 <sup>x</sup>	0.73 (4)	2.47 (4)	2.965 (3)	127 (3)	2.30
C6—HC6...OW1 <sup>xi</sup>	0.93 (4)	2.66 (4)	3.368 (4)	134 (3)	2.55
C5—HC5...Cl1 <sup>xii</sup>	0.87 (4)	2.81 (4)	3.649 (3)	163 (3)	2.60
C5—HC5...O2 <sup>xiii</sup>	0.87 (4)	2.66 (4)	3.073 (4)	110 (3)	2.59
N2—HN2...OW2 <sup>xiv</sup>	0.73 (4)	2.37 (4)	3.084 (4)	164 (4)	2.08
N2—HN2...O2	0.73 (4)	2.33 (4)	2.658 (3)	109 (4)	2.25
O4—HO4...Cl2	0.81 (4)	2.23 (4)	3.027 (3)	167 (4)	2.07
C15—HC15...Cl1 <sup>xv</sup>	0.86 (4)	2.92 (4)	3.691 (4)	150 (3)	2.72
C12—HC12...OW1 <sup>xvi</sup>	1.02 (4)	2.73 (4)	3.611 (4)	145 (3)	2.67
C12—HC12...O1	1.02 (4)	2.76 (4)	3.661 (3)	148 (3)	2.70
C14—HC14...O3 <sup>xvii</sup>	0.94 (4)	2.56 (4)	3.255 (4)	131 (3)	2.46
O3—HO3...Cl1	1.05 (5)	1.99 (5)	3.027 (2)	169 (4)	2.06

Symmetry codes: (i) -1 - *x*, *y* - ½, 1 - *z*; (ii) *x* - 1, *y*, *z*; (iii) -*x*, *y* + ½, 1 - *z*; (iv) -*x*, *y* + ½, 2 - *z*; (v) *x*, *y*, *z* + 1; (vi) -*x*, *y* - ½, 1 - *z*; (vii) *x*, *y*, *z* - 1.

For technical reasons, the absorption correction mandatory in the case of μ = 3.249 mm<sup>-1</sup> could not be applied because the crystal was damaged before its dimensions could be measured; this did not lead to a suspiciously low *R* value. All H-atom positions were located from difference Fourier maps and refined isotropically.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure:

*SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1180). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 3-[(2-Phenylsulfonyl)ethenyl]-4H-1-benzopyran-4-one

YU-SHENG CHEN,<sup>a</sup> MASSOOD KHAN,<sup>b</sup> S. NARASINGA RAO,<sup>a\*</sup> M. KRISHNAIAH<sup>c</sup> AND K. V. NARAYANA RAJU<sup>c</sup>

<sup>a</sup>Department of Physics, University of Central Oklahoma, Edmond, Oklahoma 73034, USA, <sup>b</sup>Department of Chemistry, University of Oklahoma, Norman, Oklahoma, USA, and <sup>c</sup>Department of Physics, Sri Venkateswara University, Tirupati, India

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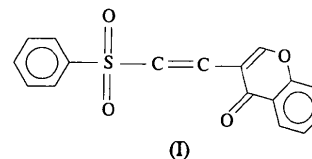
## Abstract

In the title compound, C<sub>17</sub>H<sub>12</sub>O<sub>4</sub>S, the bond distances reflect electron delocalization in the O4—C10=C9—C8=C7 chain. The molecule contains three nearly planar segments, namely, the benzopyranone group, the

phenyl ring and the ethylene group. The sulfonyl plane is inclined at an angle of 84.6(2)° to the plane of the ethylene group, including its immediate substituents, and at an angle of 14.4(1)° to the benzopyranone group. In the structure of the related compound 3-[2-(4-chlorophenylsulfonyl)ethenyl]-4H-1-benzopyran-4-one [Krishnaiah, Narayana Raju, Lu, Chen & Narasinga Rao (1995). *Acta Cryst.* **C51**, 2429–2430], the corresponding angles are 60.3(2) and 51.5(2)°, respectively.

## Comment

Sulfones are compounds in which the S atom is bonded to two C atoms and two terminal O atoms in a tetrahedral arrangement (Truce, Klingler & Brand, 1984). Sulfones have shown activity as antibacterial and antifungal agents. Dapsone has proven effective against leprosy, while diasone is highly effective against streptococcal and pneumococcal infections (Kharasch, Stampa & Nudenberg, 1953). The antifungal activity of some unsaturated sulfones has been found to be dependent upon substituent and stereochemical effects. The title compound, 3-[2-(phenylsulfonyl)ethenyl]-4H-1-benzopyran-4-one, (I), has been observed to display antifungal activity against *Curvularia lunata* and *Furarium oxysporum* (Mukundam, 1990).



The crystal and molecular structure of (I) (Fig. 1) has been determined in order to study its stereochemistry and is part of a series of compounds derived from these antifungal agents having different substituents at the 6 position of the 4H-1-benzopyran-4-one ring. Our aim is to observe the influences of these changes on the conformation of the ethenylsulfone moiety.

The title molecule contains three nearly planar segments, namely, the benzopyranone group, the phenyl

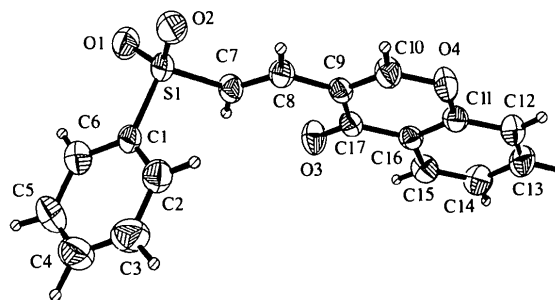


Fig. 1. An *ORTEP* plot (Johnson, 1965) of (I) with ellipsoids at the 50% probability level.