Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.251 (3)	C2—C3	1.511 (3)
O2—C1	1.252 (3)	N1—C4	1.483 (3)
O3—C3	1.204 (3)	C4—N1	1.483 (3)
O4—C3	1.312 (3)	C4—C5	1.517 (3)
C1—C2	1.535 (3)	C5—C5^{i}	1.520 (4)
O1—C1—O2	123.9 (2)	O3—C3—C2	122.5 (2)
O1—C1—C2	117.1 (2)	O4—C3—C2	113.5 (2)
O2—C1—C2	119.0 (2)	N1—C4—C5	110.3 (2)
C3—C2—C1	110.7 (2)	C4—C5—C5^{i}	111.6 (2)
O3—C3—O4	123.9 (2)		
N1—C4^{i}—C5^{i}—C5	177.9 (2)	C5^{i}—C5—C4—N1	177.9 (2)
C4^{i}—C5^{i}—C5—C4	180.0		

Symmetry code: (i) $2-x, 1-y, -z$.

The title structure was refined using *SHELXL93* (Sheldrick, 1993). After positional and anisotropic displacement parameter refinement of the non-H atoms, all H atoms, including that of the protonated carboxylate group, could be located in difference Fourier maps. The positional and isotropic displacement parameters of all H atoms were refined. Hydrogen bonds were deduced using *PARST* (Nardelli, 1983).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Molecular graphics: *NRCVAX PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL93*.

This work was supported by a CSIR grant to MRNM and partial financial assistance by Molecular Biophysics Unit, Indian Institute of Science (IISc), Bangalore, to AMB. Assistance from the data collection facility at the University of Oregon is gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Ramaswamy, S. & Murthy, M. R. N. (1990). *Curr. Sci.* **59**, 379–382.

Ramaswamy, S. & Murthy, M. R. N. (1991*a*). *Curr. Sci.* **60**, 173–176.

Ramaswamy, S. & Murthy, M. R. N. (1991*b*). *Curr. Sci.* **61**, 410–413.

Ramaswamy, S. & Murthy, M. R. N. (1991*c*). *Indian J. Biochem. Biophys.* **28**, 504–512.

Ramaswamy, S. & Murthy, M. R. N. (1992). *Acta Cryst.* B**48**, 488–492.

Ramaswamy, S. & Murthy, M. R. N. (1994). *J. Indian Inst. Sci.* **74**, 591–609.

Ramaswamy, S., Nethaji, M. & Murthy, M. R. N. (1989). *Curr. Sci.* **58**, 1160–1163.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 367–369

Imidazole-4-acetic Acid–Picric Acid (1/1) Complex

YASUKO IN,[a] HIROOMI NAGATA,[a] MITSUNOBU DOI,[a] TOSHIMASA ISHIDA[a] AND AKIO WAKAHARA[b]

[a]*Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-11, Japan, and* [b]*Fujisawa Pharmaceutical Co. Ltd, 2-1-6 Kashima, Yodogawa-ku, Osaka 532, Japan. E-mail: ishida@oysun01.oups.ac.jp*

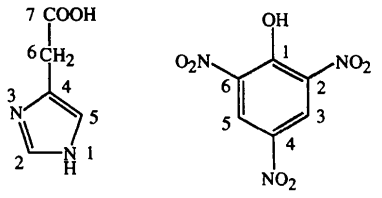
(*Received 18 July 1996; accepted 15 October 1996*)

Abstract

In the crystal structure of 4-(carboxymethyl)imidazol-3-ium picrate, $C_5H_7N_2O_2^+.C_6H_2N_3O_7^-$, the imidazole N3 atom is protonated and contacts the deprotonated phenol and nitro O atoms of the picrate anion through a bifurcated hydrogen bond. The carboxy group of the 4-(carboxymethyl)imidazolium cation is in a neutral state and participates in dimer formation between centrosymmetrically related molecules through O···H—O hydrogen bonds. No significant stacking interaction is observed between the aromatic rings of the two molecules, indicating the superiority of the hydrogen-bonding ability of imidazole-4-acetic acid over the π-donating ability of picric acid.

Comment

It is known that picric acid (PA) acts not only as an acceptor to form various π-stacking complexes with aromatic biomolecules, but also as an acidic ligand to form salts with polar non-aromatic molecules through specific electrostatic or hydrogen-bonding interactions. Picrates have therefore been used frequently in the identification or quantitative analysis of organic compounds through complex formation and their structural features have also been evaluated at the atomic level. As part of a series examining the interaction features of biomolecule–PA complexes, we have already analyzed the crystal structures of the picrates of tryptophan metabolites (Nagata, In, Doi, Ishida & Wakahara, 1995) and basic amino acids (Ishida, Nagata, In, Doi, Inoue, Extine & Wakahara, 1993; Nagata, In, Tomoo, Doi, Ishida & Wakahara, 1995) as typical aromatic and polar non-aromatic biomolecules, respectively. This paper presents the X-ray crystal structure of the 1:1 imidazole-4-acetic acid (ImAA)–PA complex. It is of interest to know whether π-stacking or hydrogen-bonding interaction is predominant in the complex formation, because the imidazole ring could be thought to exhibit both aromatic and polar non-aromatic behaviour depending on its environment.



ImAA PA

The hydrogen-bonding interaction between the ImAA and PA molecules is shown in Fig. 1. The bond lengths and angles indicate that ImAA adopts a cationic structure, with the N3*B* atom protonated and the carboxyl group neutralized, and forms a salt with PA, where the phenolic OH group is deprotonated. The crystal consists of the hydrogen-bonded 1:1 complex pair of ImAA and PA. The orientation of the carboxyl group with respect to the imidazole ring [N3*B*—C4*B*—C6*B*—C7*B* −74.9 (2)° and C4*B*—C6*B*—C7*B*—O7*B* −19.0 (2)°] belongs to one of the most frequently observed conformations for a carboxyl group attached to an aromatic ring (Ishida, Hamada, Inoue & Wakahara, 1990). Regarding the molecular conformation of PA, the nitro group at C6*A* is considerably twisted out of the benzene plane [C5*A*—C6*A*—N6*A*—O6′*A* −50.0 (2)°] and such a significant tilting appears to result from steric hindrance with the neighbouring carboxyl group of ImAA.

The crystal packing is schematically shown in Fig. 2, and hydrogen-bonding and electrostatic interaction parameters are listed in Table 2. The N3*B*—H group of ImAA is in contact with the phenolic and nitro O atoms of neighbouring PA molecules through a bifurcated hydrogen bond, thus making the two molecules almost coplanar [dihedral angle 6.2 (1)°]. The centrosymmetrically related ImAA molecules form a dimer structure through carboxyl O7′*B*—H7*B*···O7*A* hydrogen bonds. Since no notable overlapping was observed between the ImAA and PA molecules, the present result indicates that the imidazole ring behaves as a hydrogen-bonding donor rather than as a π-donor with respect to an acceptor molecule such as PA. A similar hydrogen-bonding interaction has also been observed in the imidazole–PA complex (Soriano-Garcia, Schatz-Levine, Toscano & Iribe, 1990).

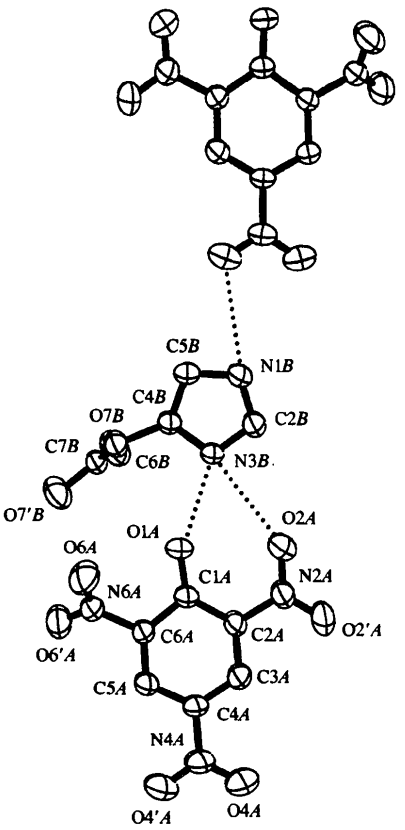


Fig. 1. The molecular conformations of ImAA and PA. Intermolecular hydrogen bonds are shown as dotted lines. Displacement ellipsoids are shown at the 50% probability level.

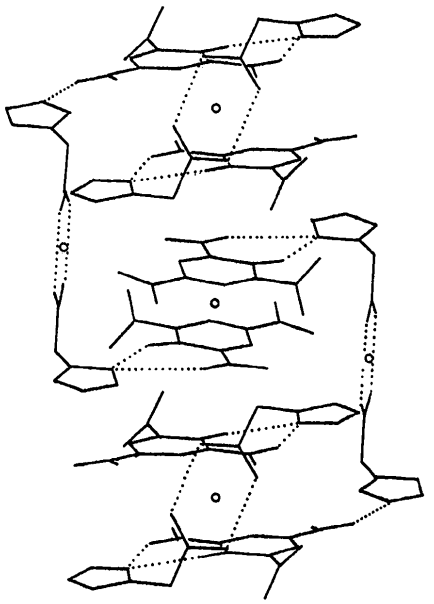


Fig. 2. Schematic crystal packing of the ImAA–PA complex. Dotted lines represent hydrogen bonds and open circles represent crystallographic centres of symmetry. The *c* axis is vertical and a diagonal line between the *a* and *b* axes is horizontal.

Experimental

The title complex was prepared by slow evaporation of an aqueous solution containing equimolar amounts of ImAA and PA.

Crystal data

$C_5H_7N_2O_2^+.C_6H_2N_3O_7^-$ Cu $K\alpha$ radiation
M_r = 355.23 λ = 1.5418 Å

Monoclinic
$C2/c$
a = 15.096 (3) Å
b = 15.381 (3) Å
c = 13.373 (3) Å
β = 116.431 (15)°
V = 2780.5 (10) Å^3
Z = 8
D_x = 1.697 Mg m^{-3}
D_m = 1.652 (2) Mg m^{-3}
D_m measured by flotation in a CCl_4–C_6H_6 mixture

Cell parameters from 25 reflections
θ = 20–23°
μ = 1.322 mm^{-1}
T = 293 (2) K
Plate
0.7 × 0.4 × 0.2 mm
Yellow

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan at $\chi \simeq 90°$ (Molecular Structure Corporation, 1992)
T_{min} = 0.460, T_{max} = 0.768
2371 measured reflections
2264 independent reflections

1933 reflections with $I > 2\sigma(I)$
R_{int} = 0.0375
θ_{max} = 63.04°
$h = -15 \rightarrow 17$
$k = 0 \rightarrow 17$
$l = -15 \rightarrow 0$
4 standard reflections every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R(F)$ = 0.0447
$wR(F^2)$ = 0.1761
S = 0.986
2244 reflections
227 parameters
H atoms fixed
$w = 1/[\sigma^2(F_o^2) + (0.0987P)^2 + 2.6211P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.043
$\Delta\rho_{max}$ = 0.284 e Å^{-3}
$\Delta\rho_{min}$ = −0.255 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0059 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1*A*—O1*A*	1.245 (3)	C6*A*—N6*A*	1.457 (3)
C1*A*—C6*A*	1.440 (3)	N6*A*—O6′*A*	1.211 (3)
C1*A*—C2*A*	1.445 (3)	N6*A*—O6*A*	1.217 (3)
C2*A*—C3*A*	1.376 (3)	N1*B*—C2*B*	1.321 (3)
C2*A*—N2*A*	1.451 (3)	N1*B*—C5*B*	1.367 (3)
N2*A*—O2*A*	1.215 (3)	C2*B*—N3*B*	1.323 (3)
N2*A*—O2′*A*	1.217 (3)	N3*B*—C4*B*	1.377 (3)
C3*A*—C4*A*	1.373 (3)	C4*B*—C5*B*	1.353 (3)
C4*A*—C5*A*	1.395 (3)	C4*B*—C6*B*	1.489 (3)
C4*A*—N4*A*	1.442 (3)	C6*B*—C7*B*	1.501 (3)
N4*A*—O4*A*	1.213 (3)	C7*B*—O7*B*	1.215 (3)
N4*A*—O4′*A*	1.221 (3)	C7*B*—O7′*B*	1.295 (3)
C5*A*—C6*A*	1.356 (3)		
O2*A*—N2*A*—O2′*A*	122.0 (2)	N1*B*—C2*B*—N3*B*	107.9 (2)
O2*A*—N2*A*—C2*A*	119.7 (2)	C2*B*—N3*B*—C4*B*	109.4 (2)
O2′*A*—N2*A*—C2*A*	118.2 (2)	C5*B*—C4*B*—N3*B*	106.2 (2)
O4*A*—N4*A*—O4′*A*	122.1 (2)	C5*B*—C4*B*—C6*B*	131.5 (2)
O4*A*—N4*A*—C4*A*	119.3 (2)	N3*B*—C4*B*—C6*B*	122.3 (2)
O4′*A*—N4*A*—C4*A*	118.6 (2)	C4*B*—C5*B*—N1*B*	107.0 (2)
O6′*A*—N6*A*—O6*A*	123.0 (2)	C4*B*—C6*B*—C7*B*	114.0 (2)
O6′*A*—N6*A*—C6*A*	118.9 (2)	O7*B*—C7*B*—O7′*B*	123.4 (2)
O6*A*—N6*A*—C6*A*	118.1 (2)	O7*B*—C7*B*—C6*B*	122.6 (2)
C2*B*—N1*B*—C5*B*	109.4 (2)	O7′*B*—C7*B*—C6*B*	113.9 (2)
C1*A*—C2*A*—N2*A*—O2*A*	1.0 (2)		
C1*A*—C2*A*—N2*A*—O2′*A*	−176.6 (3)		
C3*A*—C4*A*—N4*A*—O4*A*	11.4 (2)		
C3*A*—C4*A*—N4*A*—O4′*A*	−167.0 (3)		
C5*A*—C6*A*—N6*A*—O6*A*	128.0 (2)		
C5*A*—C6*A*—N6*A*—O6′*A*	−50.0 (2)		
N3*B*—C4*B*—C6*B*—C7*B*	−74.9 (2)		
C5*B*—C4*B*—C6*B*—C7*B*	106.2 (3)		
C4*B*—C6*B*—C7*B*—O7*B*	−19.0 (2)		
C4*B*—C6*B*—C7*B*—O7′*B*	161.9 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °) and electrostatic distances ($D\cdots A \leq 3.1$ Å)*

D—H···A	H···A	D···A	D—H···A
N3*B*—H3*B*···O1*A*^{i}	1.73	2.599 (3)	154.9
N3*B*—H3*B*···O2*A*^{i}	2.46	3.025 (3)	119.4
N1*B*—H1*B*···O4*A*^{ii}	2.60	3.082 (3)	113.5
O7′*B*—H7′*B*···O7*B*^{v}	1.84	2.659 (3)	170.4
O7*B*—H···O4*A*^{iii}	–	2.914 (3)	–
O4′*A*—H···O6′*A*^{iv}	–	2.862 (3)	–

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

TEXSAN (Molecular Structure Corporation, 1992) was used for data collection, cell refinement and data reduction. The structure was determined by direct methods using *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Full-matrix least-squares refinement on F^2 magnitudes with anisotropic displacement parameters for non-H atoms was performed with *SHELXL*93 (Sheldrick, 1993). The molecular graphics were drawn using *ORTEP*II (Johnson, 1976). The H-atom positions were observed on a difference Fourier map during the final refinement and were included only for the calculation of the structure factors. *MOLCON UNICS* (Fujii, 1979) was used to prepare material for publication.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Debaerdemaeker, T., Germain, G., Main, P., Tate, C. & Woolfson, M. M. (1987). *MULTAN*87. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.

Fujii, S. (1979). *MOLCON. The Universal Crystallographic Computing System–Osaka*, p. 66. The Computation Center, Osaka University, Japan.

Ishida, T., Hamada, M., Inoue, M. & Wakahara, A. (1990). *Acta Cryst.* C**46**, 2426–2428.

Ishida, T., Nagata, H., In, Y., Doi, M., Inoue, M., Extine, M. W. & Wakahara, A. (1993). *Chem. Pharm. Bull.* **41**, 433–438.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Nagata, H., In, Y., Doi, M., Ishida, T. & Wakahara, A. (1995). *Acta Cryst.* B**51**, 1051–1058.

Nagata, H., In, Y., Tomoo, K., Doi, M., Ishida, T. & Wakahara, A. (1995). *Chem. Pharm. Bull.* **43**, 1836–1843.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Soriano-Garcia, M., Schatz-Levine, M., Toscano, R. A. & Iribe, R. V. (1990). *Acta Cryst.* C**46**, 1556–1558.