saturated solution of silver *p*-tolylsulphonate, added dropwise with stirring at 363 K over 20 min. The title compound was separated, recrystallized twice and crystals were grown from methanol–water (10:1) by slow evaporation.

Crystal data

$C_{15}H_{16}NO_2^+.C_7H_7O_3S^-.H_2O$
M_r = 431.49
Monoclinic
$P2_1/c$
a = 10.9520 (10) Å
b = 19.853 (2) Å
c = 10.4960 (10) Å
β = 111.450 (10)°
V = 2124.1 (4) Å^3
Z = 4
D_x = 1.349 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 26 reflections
θ = 2–25°
μ = 0.191 mm^{-1}
T = 295 (2) K
Block
0.46 × 0.46 × 0.46 mm
Orange–red

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$
Absorption correction: none
3962 measured reflections
3743 independent reflections
2394 reflections with $I > 2\sigma(I)$
R_{int} = 0.0165

θ_{max} = 25°
$h = -13 \rightarrow 12$
$k = -23 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections
every 97 reflections
intensity decay: 2.23%

Refinement

Refinement on F^2
$R(F)$ = 0.0399
$wR(F^2)$ = 0.1048
S = 0.902
3743 reflections
372 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.007

$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0197 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

S—O1	1.428 (2)	N—C22	1.481 (3)
S—O3	1.437 (2)	C11—C15	1.465 (3)
S—O2	1.438 (2)	C15—C16	1.318 (3)
S—C5	1.767 (2)	C16—C17	1.456 (3)
O4—C8	1.356 (3)		

Table 2. *Intermolecular contacts (Å)*

O4···O6	2.671 (3)	C9···O6	3.270 (4)
O6···O3	2.835 (3)	C4···O2^{ii}	3.323 (3)
O6···O1^{i}	3.082 (3)	C19···O1^{iii}	3.225 (3)
O6···O2^{i}	3.098 (3)	C22···O4^{iv}	3.251 (4)

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

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1173). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Berkovitch-Yellin, Z. & Leiserowitz, L. (1984). *Acta Cryst.* B**40**, 159–165.
Krishnamohan Sharma, C. V. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 2345–2352.
Marder, S. R., Perry, J. W. & Tiemann, B. G. (1990). *Chem. Mater.* **2**, 685–690.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Okada, S., Masaki, A., Matsuda, H., Nakanishi, H., Kato, M. & Muramatsu, R. (1990). *Jpn J. Appl. Phys.* **29**, 1112–1115.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Acta Cryst. (1997). C**53**, 365–367

Extended Conformation of Putrescine Occurring on a Center of Symmetry in its 1:2 Complex with Malonic Acid

A. M. Babu,[a] Timothy J. R. Weakley[b] and M. R. N. Murthy[c]

[a]*Department of Physics, Government Science College (Affiliated to Bangalore University), Bangalore 560 001, India,* [b]*Department of Chemistry, University of Oregon, Eugene, OR 97403-1253, USA, and* [c]*Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560 012, India. E-mail: mrn@mbu.iisc.ernet.in*

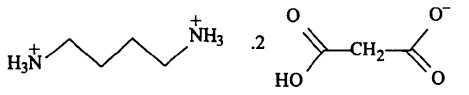
(*Received 6 June 1996; accepted 25 October 1996*)

Abstract

The 1,4-butane diammonium (putrescine) ion co-crystalizes with propanedioic acid (malonic acid) monoanions in space group *Pcab* (1,4-butane diammonium hydrogen propanedioate, $C_4H_{14}N_2^{2+}.2C_3H_3O_4^-$). One of the carboxylate moieties of malonic acid is protonated. The asymmetric unit of the crystal contains one molecule of malonic acid and half a molecule of putrescine. All three H atoms of the putrescine amino groups participate in hydrogen bonding.

Comment

Polyamines are very common biological cations. Single-crystal X-ray structures of polyamines complexed to different chemically distinct molecules provide information on the interactions responsible for their role as the most important biological cations. We have reported previously the structures of a number of polyamine salts and complexes (Ramaswamy, Nethaji & Murthy, 1989; Ramaswamy & Murthy, 1990, 1991*a*,*b*,*c*, 1992, 1994). In this context, we have crystalized the 1,4-butane diammonium (putrescine) ion with malonic acid monoanions and determined the structure of the title complex, (I).



(I)

The molecular structure of (I) is shown in Fig. 1. At neutral pH, malonic acid and putrescine carry two negative and two positive charges, respectively. In the crystal, however, one of the carboxylate groups of malonic acid is protonated, with a C—O bond length of 1.312 (3) Å, which is closer to that of an ideal single bond. The unit cell consists of eight malonic acid molecules, the negative charges of which are neutralized by the positive charges of four putrescine molecules which occur on inversion centres. Putrescine is in a completely extended conformation, with N1—C4—C5—C5^i and C4—C5—C5^i—C4^i torsion angles of 177.9 (2) and 180.0°, respectively [symmetry code: (i) $2-x, 1-y, -z$]. The positive charges of the putrescine molecules, which occur along the *b* axis, are neutralized by the carboxylate groups of two separate malonic acid molecules. Each amino group of the putrescine molecule is involved in three hydrogen bonds. In all the structures of polyamine complexes, a similar utilization of bonding potential is observed. A strong hydrogen bond exists between the deprotonated carboxyl group of malonic acid and the putrescine amino group. The deprotonated carboxylate group of malonic acid is involved in two hydrogen bonds. In contrast, the protonated carboxylate group is involved in only one hydrogen bond. The planes of the O3—C3—O4 (protonated) and O1—C2—O2 carboxylate groups make angles of 86.3 (2) and 57.0 (2)°, respectively, with the plane passing through atoms C1, C2 and C3 of malonic acid. The smaller value observed for the O1—C2—O2 group is probably due to the formation of two hydrogen bonds.

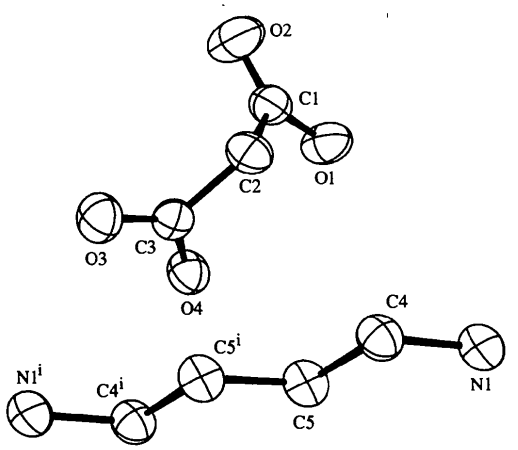


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

Putrescine dihydrochloride was passed through a Dowex1 column which retains chloride ions. The free amine eluted was neutralized to pH 7.0 by the addition of a saturated solution of malonic acid. This was layered with *n*-propanol and left undisturbed in a sealed test tube (liquid-diffusion technique). Transparent crystals were observed after a few days.

Crystal data

$C_4H_{14}N_2^{2+}.2C_3H_3O_4^-$
M_r = 296.3
Orthorhombic
Pcab
a = 7.921 (13) Å
b = 11.79 (3) Å
c = 14.714 (10) Å
V = 1374 (4) Å^3
Z = 4
D_x = 1.432 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14–15°
μ = 0.124 mm^{-1}
T = 293 (2) K
Transparent block
0.50 × 0.43 × 0.36 mm
Colorless

Data collection

Enraf–Nonius CAD-4 PC-driven diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2304 measured reflections
1996 independent reflections
1916 reflections with $I > 2\sigma(I)$
R_{int} not available
θ_{max} = 29.89°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 20$
3 standard reflections every 300 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0445
$wR(F^2)$ = 0.1199
S = 0.556
1996 reflections
134 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1067P)^2 + 0.3004P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.330
$\Delta\rho_{max}$ = 0.313 e Å^{-3}
$\Delta\rho_{min}$ = −0.137 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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.