

Abolghasem Moghimi,^a
Hossein Aghabozorg,^{b*}
Janet Soleimannejad^c and
Farshid Ramezani^b

^aDepartment of Chemistry, University of Imam Hossein, Tehran, Iran, ^bDepartment of Chemistry, Teacher Training University, 49 Mofateh Avenue 15614, Tehran, Iran, and ^cDepartment of Chemistry, Faculty of Science, Ilam University, Ilam, Iran

Correspondence e-mail:
aghabozorg@saba.tmu.ac.ir

Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(C-C)$ = 0.003 Å
R factor = 0.056
wR factor = 0.133
Data-to-parameter ratio = 14.8

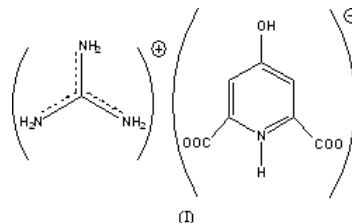
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Guanidinium 4-hydroxypyridinium-2,6-dicarboxylate

The crystal structure of the title compound, $CH_6N_3^+ \cdot C_7H_4NO_5^-$, shows that both intra- and intermolecular proton transfers have occurred. Hydrogen-bonding interactions, in addition to ion-pairing forces, are observed between the cation and anion.

Comment

Recently there has been considerable interest in proton transfer systems and their structures (Smith *et al.*, 1999; Zafar *et al.*, 2000). Several proton transfer systems using pyridine-2,6-dicarboxylic acid as proton donor have been synthesized and their crystal structures have been reported (Moghimi *et al.*, 2002; Moghimi, Sheshmani *et al.*, 2004; Moghimi, Sharif & Aghabozorg, 2004). The proton acceptor fragments in these studies were 2,6-pyridinediamine, guanidine and creatinine. We report here on a proton transfer system containing guanidine and 4-hydroxypyridine-2,6-dicarboxylic acid.



The molecular structure of the title compound, (I), is shown in Fig. 1 and selected geometric parameters are given in Table 1. The crystal structure of (I) shows that a single proton from one of the carboxyl groups was transferred to the double-bonded N atom of the guanidine molecule. On the

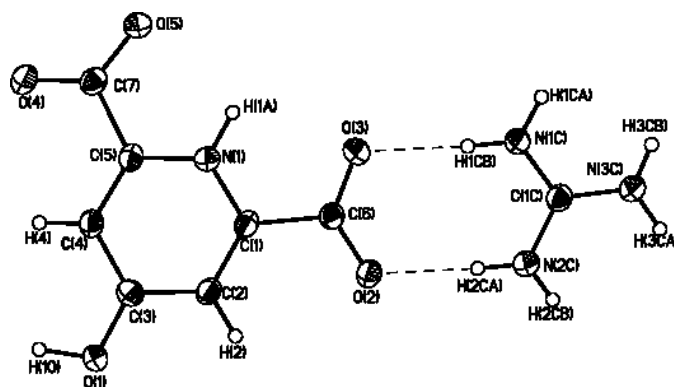


Figure 1
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. Dashed lines indicate hydrogen bonds.

Received 20 December 2004
Accepted 12 January 2005
Online 29 January 2005

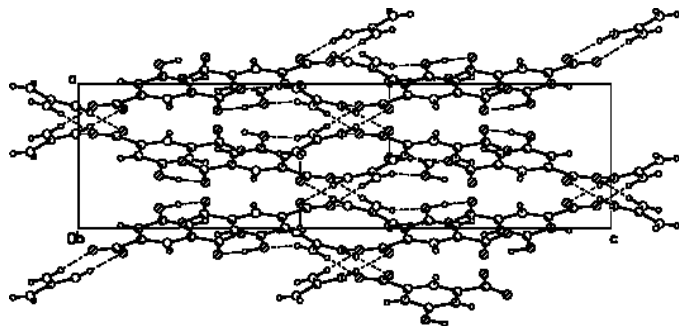


Figure 2

The crystal packing of (I), viewed down the *b* axis; hydrogen bonds are indicated by dashed lines.

other hand, an interesting feature exhibited by the crystal structure is that an intramolecular proton transfer has occurred from the other carboxyl group to the N atom of the aromatic ring. This intramolecular proton transfer was not observed in previous work, in which pyridine-2,6-dicarboxylic acid was used as the proton donor and guanidine as the proton acceptor (Moghimi, Sharif & Aghabozorg, 2004). It seems that the existence of a hydroxy group in the starting material has an important role in the present work, causing the proton transfer process to be different from that in the system mentioned above.

In the crystal structure of (I), non-covalent interactions cause the structure to form a self-assembled system (Fig. 2). These interactions, as expected, consist of ion-pairing and hydrogen-bonding forces. The O1—H1O···O5ⁱ hydrogen bond (Table 2) is extremely strong and, as expected, the O—H distance is significantly increased. This phenomenon has been noted previously by Steiner (2002).

Experimental

An aqueous solution of sodium hydroxide was added to guanidine hydrochloride in a 1:1 molar ratio. The resulting suspension was stirred for 1 h and filtered. 4-Hydroxypyridine-2,6-dicarboxylic acid was added to the filtered solution in a 1:1 molar ratio, and the reaction mixture was heated to boiling point for 10 min. Yellow crystals of (I) were obtained from the solution after two days at room temperature in 88% yield.

Crystal data

CH₆N₃⁺·C₇H₄NO₅⁻
M_r = 242.20
 Orthorhombic, *Pbca*
a = 6.824 (3) Å
b = 11.887 (6) Å
c = 25.224 (10) Å
V = 2046.1 (16) Å³
Z = 8
D_x = 1.572 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 2575 reflections
 θ = 3.2–17.3°
 μ = 0.13 mm⁻¹
T = 120 (2) K
 Prism, yellow
 0.50 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
T_{min} = 0.874, *T_{max}* = 0.954
 8560 measured reflections

2395 independent reflections
 1568 reflections with *I* > 2σ(*I*)
R_{int} = 0.037
 θ_{\max} = 28.0°
h = -4 → 9
k = -14 → 15
l = -33 → 22

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.056
wR (*F*²) = 0.133
S = 1.03
 2395 reflections
 162 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 2.2P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1—C3	1.315 (3)	N1—C1	1.356 (3)
O2—C6	1.253 (3)	N1—C5	1.356 (3)
O3—C6	1.260 (3)	N1C—C1C	1.335 (3)
O4—C7	1.243 (3)	N2C—C1C	1.336 (3)
O5—C7	1.274 (3)	N3C—C1C	1.331 (3)
C1—N1—C5	122.44 (18)	O3—C6—C1	115.57 (18)
N1—C1—C2	119.30 (19)	O2—C6—C1	116.81 (18)
N1—C1—C6	115.98 (18)	O4—C7—C5	117.60 (19)
O1—C3—C4	122.6 (2)	O5—C7—C5	115.13 (19)
O1—C3—C2	119.5 (2)	O4—C7—O5	127.3 (2)
N1—C5—C7	117.45 (18)	N2C—C1C—N3C	120.7 (2)
N1—C5—C4	119.79 (19)	N1C—C1C—N2C	118.7 (2)
O2—C6—O3	127.6 (2)	N1C—C1C—N3C	120.65 (19)

Table 2

Hydrogen-bond 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>
O1—H1O···O5 ⁱ	1.01	1.48	2.492 (2)	173
N1C—H1CB···O3	0.90	2.02	2.915 (3)	175
N1C—H1CA···O2 ⁱⁱ	0.97	1.93	2.874 (3)	163
N2C—H2CA···O2	0.89	2.00	2.883 (3)	175
N2C—H2CB···O1 ⁱⁱⁱ	0.85	2.21	3.010 (3)	156
N3C—H3CA···O4 ^{iv}	0.90	1.96	2.853 (3)	170
N3C—H3CB···O3 ^v	0.86	2.19	3.021 (3)	161

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

H atoms were located in difference Fourier maps and refined using a riding model. For N- and O-bound H atoms (N—H = 0.85–0.97 Å, O—H = 1.01 Å) the *U*_{iso}(H) values were refined, while for C-bound H atoms (C—H = 0.93 Å), the *U*_{iso}(H) values were set at 1.2*U*_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Ilam University is acknowledged for support of this work.

References

- Bruker. (1998). *SMART* (Version 5.059) and *SAINT-Plus* (Version 6.01). Bruker AXS Inc., Madison, Wisconsin, USA.
- Moghimi, A., Ranjbar, M., Aghabozorg, H., Jalali, F., Shamsipur, M., Yap, G. P. A. & Rahbarnoochi, H. (2002). *J. Mol. Struct.* **605**, 133–149.
- Moghimi, A., Sharif, M. A. & Aghabozorg, H. (2004). *Acta. Cryst.* **E60**, o1790–o1792.
- Moghimi, A., Shashmani, S., Shokrollahi, A., Aghabozorg, H., Shamsipur, M., Kickelbick, G., Carla Aragoni, M. & Lippolis, V. (2004). *Z. Anorg. Allg. Chem.* **630**, 617–624.

Sheldrick, G. M. (1998). *SADABS* (Version 2.01) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Smith, G., Pascoe, C. E., Kennard, C. H. L. & Byriel, K. A. (1999). *Aust. J. Chem.* **52**, 71–74.

Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
Zafar, A., Geib, S. J., Hamuro, Y., Carr, A. J. & Hamilton, A. D. (2000). *Tetrahedron*, **56**, 8419–8427.