

2,6-Diaminopyridinium pyridinium-2,6-dicarboxylate:  
a redeterminationHossein Aghabozorg,\* Ali Akbari  
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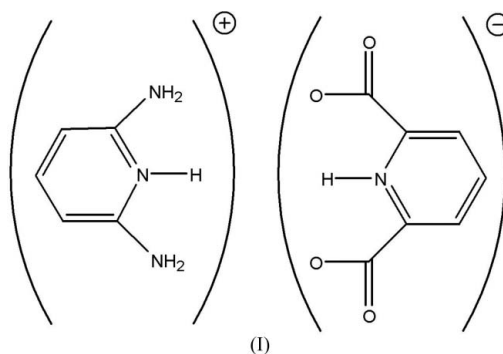
## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.052  
 $wR$  factor = 0.167  
Data-to-parameter ratio = 14.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The crystal structure of the title compound,  $\text{C}_5\text{H}_8\text{N}_3^+ \cdot \text{C}_7\text{H}_4\text{NO}_4^-$  or  $(\text{pydaH})^+(\text{pydcH})^-$  (pyda is 2,6-diaminopyridine and  $\text{pydcH}_2$  is pyridine-2,6-dicarboxylic acid), shows both intra- and intermolecular proton transfers from carboxyl groups to the ring N atoms of  $(\text{pydc})^{2-}$  and pyda. This determination corrects a previous report which formulated this compound as  $(\text{pydaH}_2)^{2+}(\text{pydc})^{2-}$  [Moghimi, Ranjbar, Aghabozorg, Jalali, Shamsipur, Yap & Rahbarnoohi (2002), *J. Mol. Struct.* **605**, 133–149]. Ion-pairing, hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions link the fragments to form a self-associated system.

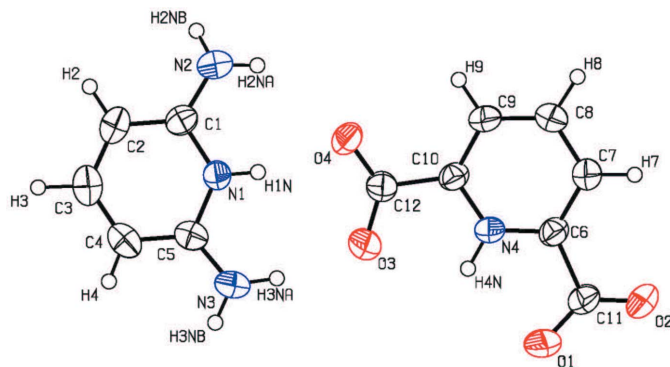
## Comment

Hydrogen-bonding interactions between carboxylic acids and 2-aminopyridine (pyda) units have been investigated in a recent publication (Bensemman *et al.*, 2003). We have previously reported some self-associated proton-transfer systems, using pyridine-2,6-dicarboxylic acid ( $\text{pydcH}_2$ ) and 4-hydroxypyridine-2,6-dicarboxylic acid ( $\text{hypydcH}_2$ ) as proton donors. The proton acceptors in these studies were creatinine (creat) and guanidine (G), which formed the proton-transfer compounds  $(\text{creatH})(\text{pydcH}) \cdot \text{H}_2\text{O}$ ,  $(\text{GH})_2(\text{pydc})$  and  $(\text{GH})(\text{hypydcH})$  (Moghimi, Sharif & Aghabozorg, 2004; Moghimi, Sheshmani *et al.*, 2004; Moghimi *et al.*, 2005). Hydrogen-bonding and ion-pairing interactions are observed in all of these compounds.



Here, we report the structure of a self-associated system,  $(\text{pydaH})^+(\text{pydcH})^-$ , (I). This determination corrects a previous report which formulated this compound as  $(\text{pydaH}_2)^{2+}(\text{pydc})^{2-}$ , (II) (Moghimi, Ranjbar, Aghabozorg, Jalali, Shamsipur, Yap & Rahbarnoohi, 2002). In (II), the protons were assigned to the amino groups of the cation, whereas in (I), they are assigned to the ring N atoms of both cation and anion. In (II), there was a short  $\text{N} \cdots \text{O}$  contact [2.770 (5)  $\text{\AA}$ ] between the ring N atom of the cation and a

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**Figure 1**

The structure of the title compound, showing the atom-numbering scheme and with displacement ellipsoids at the 50% probability level.

carboxyl O atom; this interaction corresponds to the hydrogen bond  $N1-H1N \cdots O4$  [ $D \cdots A = 2.788(3) \text{ \AA}$ ; Table 2] in (I).

Several metal complexes contain the  $(\text{pydaH})^+$  counterion, in which the proton is connected to the ring N atom (Aghabozorg *et al.*, 2005; Moghimi, Shokrollahi *et al.*, 2004; Ranjbar *et al.*, 2003*a,b*; Moghimi, Ranjbar, Aghabozorg, Jalali, Shamsipur & Chadha, 2002*a,b*; Ranjbar, Moghimi *et al.*, 2002; Ranjbar, Taghavipur *et al.*, 2002; Ranjbar *et al.*, 2001). Another ionic compound,  $(\text{pydaH})^+(\text{NO}_3)^-$ , also has the proton linked to the ring N atom (Aghabozorg *et al.*, 2005). Furthermore, the anionic fragment  $(\text{pydch})^-$  has been reported as the predominant form of dipicolinic acid at pH 3.5 (Peral & Gallego, 2000). These findings support our contention that the structure reported here is correct and that the structure of (II) is incorrect.

The structure of (I) shows both intra- and intermolecular proton transfers. Ion-pairing and hydrogen-bonding interactions link the components of the system. A number of  $N-H \cdots O$  hydrogen bonds with  $D \cdots A$  distances ranging from 2.598(3) to 3.128(3)  $\text{\AA}$  (Table 2) are observed in the crystal structure, producing a three-dimensional network (Fig. 2) There is evidence of  $\pi$ - $\pi$  stacking between parallel planes of  $(\text{pydaH})^+$  fragments, with an interplanar distance of about 3.3  $\text{\AA}$ .

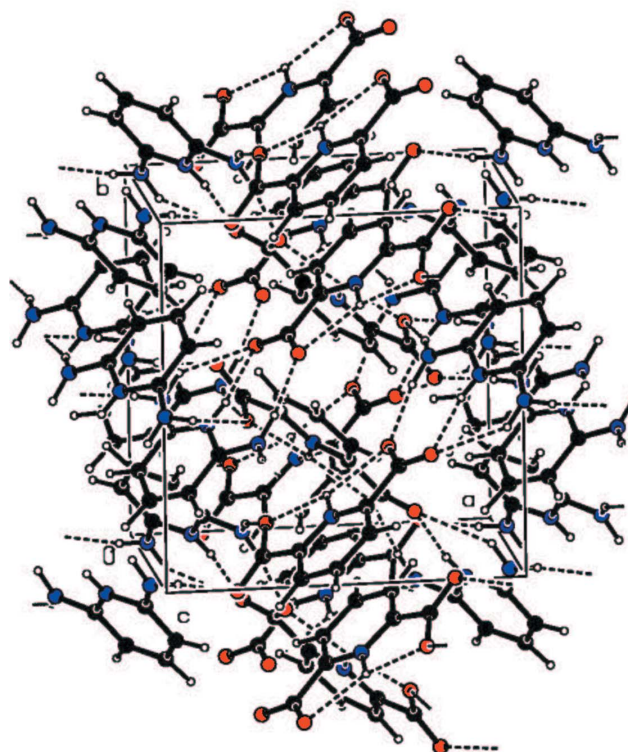
## Experimental

The title compound was prepared by the reaction of 2,6-diaminopyridine and pyridine-2,6-dicarboxylic acid in a 1:1 molar ratio in water. Light-yellow crystals of (I) were obtained by slow concentration of the solution at room temperature.

### Crystal data

$C_5H_8N_3^+ \cdot C_7H_4NO_4^-$   
 $M_r = 276.26$   
 Monoclinic,  $P2_1/c$   
 $a = 10.282(2) \text{ \AA}$   
 $b = 10.417(2) \text{ \AA}$   
 $c = 11.765(2) \text{ \AA}$   
 $\beta = 97.42(3)^\circ$   
 $V = 1249.6(4) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.468 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 24 reflections  
 $\theta = 11-12^\circ$   
 $\mu = 0.11 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Prism, yellow  
 $0.4 \times 0.3 \times 0.2 \text{ mm}$



**Figure 2**

The crystal packing of the title compound; hydrogen bonds are indicated by dashed lines.

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\theta/5/3\theta$  scans  
 Absorption correction: none  
 2919 measured reflections  
 2692 independent reflections  
 1596 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.059$

$\theta_{\text{max}} = 27.0^\circ$   
 $h = 0 \rightarrow 13$   
 $k = -1 \rightarrow 13$   
 $l = -15 \rightarrow 14$   
 2 standard reflections every 100 reflections  
 intensity decay: 3%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.167$   
 $S = 1.05$   
 2692 reflections  
 181 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 0.2P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.004$   
 $\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N1—C1	1.354 (3)	O3—C12	1.250 (3)
N1—C5	1.361 (3)	O4—C12	1.226 (3)
N2—C1	1.343 (3)	N4—C6	1.326 (3)
N3—C5	1.320 (3)	N4—C10	1.331 (3)
O1—C11	1.247 (3)	C6—C11	1.536 (3)
O2—C11	1.215 (3)	C10—C12	1.508 (3)
C1—N1—C5	124.2 (2)	O2—C11—O1	131.1 (2)
N2—C1—N1	116.3 (2)	O2—C11—C6	116.2 (2)
N3—C5—N1	117.0 (2)	O1—C11—C6	112.6 (2)
C6—N4—C10	125.27 (19)	O4—C12—O3	128.2 (2)
N4—C6—C11	115.35 (19)	O4—C12—C10	117.4 (2)
N4—C10—C12	115.60 (19)	O3—C12—C10	114.3 (2)

**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>
N1—H1N···O4	0.85	1.97	2.788 (3)	164
N3—H3NA···O3	0.94	1.97	2.888 (3)	167
N3—H3NB···O1 <sup>i</sup>	0.87	2.01	2.851 (3)	163
N4—H4N···O1	0.92	2.19	2.589 (3)	106
N4—H4N···O3	0.92	2.20	2.598 (3)	106
N2—H2NA···O4	0.89	2.41	3.128 (3)	138
N2—H2NB···O2 <sup>ii</sup>	0.86	1.99	2.838 (3)	170

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

H atoms attached to N atoms were located in a difference Fourier map and refined in the riding model with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ . All other H atoms were positioned geometrically and constrained to ride on their parent C atoms, with C—H distances of 0.93 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1984); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms, 1996); program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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