Title
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Acrinium 6-carboxypyridine-2-carboxylate monohydrate

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Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.001 Å; R factor = 0.035; wR factor = 0.105; data-to-parameter ratio = 14.1.

The title compound, C13H10N+C7H4NO4–·H2O or (acrH)+·(pydcH)−·H2O, is a monohydrate of acrinium cations and a mono-deprotonated pyridine-2,6-dicarboxylic acid. The structure contains a range of non-covalent interactions, such as O—N hydrogen bonds, as well as π−π stacking [range of centroid–centroid distances = 3.4783 (5)–3.8059 (5) Å]. The N—H···O hydrogen bond between the donor acrinium cation and the carboxylate acceptor is particularly strong. The average separation between the π-stacked acrinium planes is 3.42 (3) Å.

Related literature

For structures of acrinium salts, see: Aghabozorg et al. (2010); Attar Gharamaleki et al. (2010); Derikvand et al. (2009, 2010); Shaameri et al. (2001); Tabatabae et al. (2009).

Table 1

Hydrogen-bond geometry (Å, †).

<table>
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<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<td>1.958 (17)</td>
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<td>155.8 (16)</td>
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<td>1.555 (18)</td>
<td>2.5859 (9)</td>
<td>178.6 (16)</td>
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</table>

Symmetry code: (i) x + 1, y, z.

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELX97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

Additional supplementary material for this paper is available from the IUCr electronic archives (Reference: HG2777).

References


Electronic reprint
supplementary materials
Acridinium 6-carboxypyridine-2-carboxylate monohydrate

Z. Derikvand, M. M. Olmstead and J. Attar Gharamaleki

Comment

We have reported a number of crystal structures of protonated acridine and pyridine dicarboxylates (Derikvand et al., 2009, 2010; Aghabozorg et al., 2010; Attar Gharamaleki et al., 2010; Tabatabaei et al., 2009). Many other examples of acridinium salts are known, and they have \( \pi-\pi \) stacking of the acridinium ions and various types of hydrogen bonding in common. The molecular structure of the title compound, the 1:1 salt of acridinium and pyridine-2,6-dicarboxylate is illustrated in Fig. 1. The crystal structure shows one of the protons of the two carboxylic groups has been transferred to the nitrogen atom of the acridine molecule.

As expected, bond lengths of the –CO\(_2\) groups reflect the presence or lack of an acidic H atom. At distances of 1.2403 (11) Å and 1.2806 (11) Å, respectively, the O1—C19 and O2—C19 bond lengths are much closer to equality than O3—C20 and O4—C20, at 1.226 (11) Å and 1.3305 (11) Å. However, we can also point out that the O2—C19 bond is slightly longer than the O1—C19 bond, possibly due to there being two classical hydrogen bonds involving O2 and only one involving O1 (see Table 1). In fact, one of the hydrogen bonds for O2 can be classified as a very strong hydrogen bond, with an N···O distance of 2.5859 (9) Å. In a similar structure involving the acridinium salt of isophthalate (Shaameri et al., 2001), the analogous arrangement of cation and anion gives rise to a similar short hydrogen bond with N···O distance of 2.553 (2) Å. A depiction of the hydrogen bonded motif involving anion and cation fragments and water molecules is presented in Fig. 2. The hydrogen bonds between the water molecule and O2 serve to link the anions into a chain along the \( a \) axis direction. Symmetry code: \( i = x - 1, y, z \).

Additional noncovalent interactions cause the structure to form a self-assembled system. In the structure \( \pi-\pi \) stacking interactions between the acridinium ions average 3.42(3) Å (average deviation in square brackets). Sideways strong hydrogen bonds between O2 and the the proton of acridine gather the \( \pi \)-stack and the anionic chain together as shown in Fig. 3.

Experimental

A solution of pyridine-2,6-dicarboxylic acid (167 mg, 1 mmol) in water (10 ml) was added to a solution of acridine(179 mg, 1 mmol) in methanol (5 ml) and stirring for 30 minutes, a clear solution was obtained (Scheme 1). Yellow-gold block crystals suitable for X-ray crystallography were produced by slow evaporation of the solvent at room temperature after a week.

Refinement

All hydrogen atoms were freely refined.
supplementary materials

Figures

Fig. 1. Molecular structure of (acrH)$^+$(pydcH)$^-$. H$_2$O. Displacement ellipsoids are drawn at 50% probability level.

Fig. 2. Hydrogen bonding interactions. Symmetry code: $i = x - 1, y, z$.

Fig. 3. π-π Stacking interactions between cationic fragments and their link to anionic chains as viewed along [0 1 1].

Acridinium 6-carboxypyridine-2-carboxylate monohydrate

Crystal data

C$_{13}$H$_{10}$N$_2$·C$_2$H$_4$NO$_4$·H$_2$O

$Z = 2$

$M_r = 364.35$

$F(000) = 380$

Triclinic, $P\overline{1}$

$D_x = 1.472$ Mg m$^{-3}$

Hall symbol: -P 1

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

$a = 7.4842$ (3) Å

$\theta = 2.6–32.9^\circ$

$b = 8.6850$ (3) Å

$\mu = 0.11$ mm$^{-1}$

$c = 13.0305$ (4) Å

$T = 90$ K

$\alpha = 100.266$ (3)$^\circ$

$V = 0.32 \times 0.23 \times 0.17$ mm

$\beta = 93.851$ (2)$^\circ$

$\gamma = 97.766$ (2)$^\circ$

$V = 822.16$ (5) Å$^3$

$N_I = 822.16$ (4) Å$^3$

$N_{II} = 13.0305$ (4) Å


Data collection

Bruker SMART APEXII
diffractometer

4403 independent reflections

Radiation source: fine-focus sealed tube

graphite

4034 reflections with $I > 2\sigma(I)$

Detector resolution: 8.3 pixels mm$^{-1}$

$\omega$ scans

$h = -10 \rightarrow 10$

$\theta_{max} = 29.1^\circ$, $\theta_{min} = 2.6^\circ$

$R_{int} = 0.011$

$R$ factor refinement

$R$ factor

$wR$ factor

$S$ factor

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

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$\theta$

$\omega$

$\theta_{max}$

$\theta_{min}$

$R_{int}$

$R$ factor refinement

$wR$ factor refinement

$S$ factor refinement

$F(000)$

$D_x$

$Z$

$N_I$

$N_{II}$

$\theta$

$\omega$
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)
\(T_{\text{min}} = 0.966, T_{\text{max}} = 0.982\)
11632 measured reflections

Refinement

Primary atom site location: structure-invariant direct methods
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.035\)
\(wR(F^2) = 0.105\)
\(S = 1.07\)
4403 reflections
308 parameters
0 restraints

All H-atom parameters refined
\(w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 0.1884P]\)
where \(P = (F_o^2 + 2F_c^2)/3\)

\((\Delta\sigma)_{\text{max}} < 0.001\)
\(\Delta\rho_{\text{max}} = 0.48\ \text{e} \cdot \text{Å}^{-3}\)
\(\Delta\rho_{\text{min}} = -0.20\ \text{e} \cdot \text{Å}^{-3}\)

Special details

Geometry. All e.s.d.’s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.’s are taken into account individually in the estimation of e.s.d.’s in distances, angles and torsion angles; correlations between e.s.d.’s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.’s is used for estimating e.s.d.’s involving l.s. planes.

Refinement. Refinement of \(F^2\) against ALL reflections. The weighted \(R\)-factor \(wR\) and goodness of fit \(S\) are based on \(F^2\), conventional \(R\)-factors \(R\) are based on \(F\), with \(F\) set to zero for negative \(F^2\). The threshold expression of \(F^2 > \sigma(F^2)\) is used only for calculating \(R\)-factors(gt) etc. and is not relevant to the choice of reflections for refinement. \(R\)-factors based on \(F^2\) are statistically about twice as large as those based on \(F\), and \(R\) factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\(\text{Å}^2\))

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<th>(y)</th>
<th>(z)</th>
<th>(U_{\text{iso}}/U_{\text{eq}})</th>
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supplementary materials

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### Geometric parameters (Å, °)

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supplementary materials

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| C7—C6—C1 | 118.53 (8) | C16—C17—C18 | 117.69 (8) |
| C7—C6—C5 | 122.96 (8) | C16—C17—H17 | 122.0 (9) |
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| C7—C8—C13 | 118.48 (8) | O1—C19—O2 | 125.44 (8) |
| C7—C8—C9 | 123.10 (8) | O1—C19—C14 | 119.23 (8) |
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| C6—C7—C8—C9 | 178.91 (8) | N2—C14—C19—O1 | 5.15 (12) |
| C7—C8—C9—C10 | 178.03 (8) | C15—C14—C19—O1 | −176.72 (8) |
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*Hydrogen-bond geometry (Å, °)*

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sup-6
supplementary materials

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Symmetry codes: (i) x+1, y, z.
supplementary materials

Fig. 2
supplementary materials

Fig. 3

[Diagram of molecular structure]