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2-Amino-5-chloropyrimidin-1-ium hydrogen maleate

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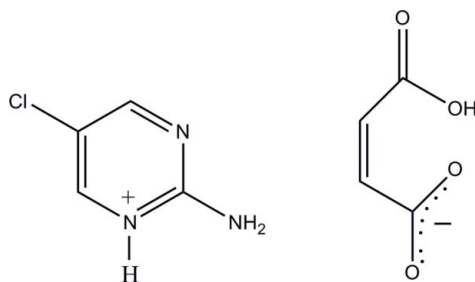
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.038; wR factor = 0.109; data-to-parameter ratio = 21.4.

In the title salt, $\text{C}_4\text{H}_5\text{ClN}_3^+\cdot\text{C}_4\text{H}_3\text{O}_4^-$, the 2-amino-5-chloropyrimidinium cation is protonated at one of its pyrimidine N atoms. In the roughly planar (r.m.s. deviation = 0.026 Å) hydrogen malate anion, an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond generates an $S(7)$ ring. In the crystal, the protonated N atom and the 2-amino group of the cation are hydrogen bonded to the carboxylate O atoms of the anion via a pair of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, forming an $R_2^2(8)$ ring motif. The ion pairs are connected via further $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and a short $\text{C}-\text{H}\cdots\text{O}$ interaction, forming layers lying parallel to the bc plane.

Related literature

For background to pyrimidine compounds, see: Glidewell *et al.* (2003); Panneerselvam *et al.* (2004). For details of maleic acid, see: James & Williams (1974); Bertolasi *et al.* (1980). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_4\text{H}_5\text{ClN}_3^+\cdot\text{C}_4\text{H}_3\text{O}_4^-$

$M_r = 245.62$

Monoclinic, $P2_1/c$
 $a = 9.3974$ (6) Å
 $b = 5.5167$ (4) Å
 $c = 20.0654$ (13) Å
 $\beta = 95.264$ (1)°
 $V = 1035.86$ (12) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.37$ mm⁻¹
 $T = 296$ K
 $0.42 \times 0.36 \times 0.13$ mm

Data collection

Bruker APEXII DUO CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.860$, $T_{\max} = 0.954$

12808 measured reflections
 3443 independent reflections
 2745 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.109$
 $S = 1.04$
 3443 reflections
 161 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.35$ e Å⁻³
 $\Delta\rho_{\min} = -0.36$ e Å⁻³

Table 1
 Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N}2-\text{H}1\text{N}2\cdots\text{O}4^{\text{i}}$	0.881 (19)	1.810 (18)	2.6897 (14)	177.6 (19)
$\text{N}3-\text{H}1\text{N}3\cdots\text{O}1^{\text{ii}}$	0.860 (17)	2.592 (18)	3.0814 (16)	117.2 (14)
$\text{N}3-\text{H}1\text{N}3\cdots\text{O}2^{\text{ii}}$	0.860 (17)	2.128 (17)	2.9795 (16)	170.2 (16)
$\text{N}3-\text{H}2\text{N}3\cdots\text{O}3^{\text{i}}$	0.893 (18)	1.975 (18)	2.8629 (17)	172.8 (16)
$\text{O}1-\text{H}1\text{O}3\cdots\text{O}3$	0.86 (3)	1.60 (3)	2.4514 (15)	179 (3)
$\text{C}2-\text{H}2\text{A}\cdots\text{O}2^{\text{iii}}$	0.93	2.39	3.3117 (17)	173

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

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

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6543).

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supporting information

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2-Amino-5-chloropyrimidin-1-ium hydrogen maleate

Hoong-Kun Fun, Madhukar Hemamalini and Venkatachalam Rajakannan

S1. Comment

Pyrimidine compounds have attracted much attention for their biological activities and molecular structures. The crystal structures of some 2-amino-substituted pyrimidine compounds, such as 2-amino-4-methoxy 6-methylpyrimidine (Glidewell *et al.*, 2003) and 2-amino-4,6-dimethyl pyrimidinium bromide (Panneerselvam *et al.*, 2004) have previously been elucidated. A study of the structural chemistry of maleic acid and related substances arises from the fact that these systems possess short but highly strained hydrogen bonds (James & Williams, 1974). The crystal structures of maleic acid (James & Williams, 1974) and carbinoxamine maleate (Bertolasi *et al.*, 1980) have been reported in the literature. We report here the molecular structure of a title compound (I), formed from the reaction of 2-amino-5-chloropyrimidine with maleic acid. It was prepared in order to extend our study on D—H···A hydrogen bonding in organic systems.

The asymmetric unit of the title compound is shown in Fig. 1. The 2-amino-5-chloropyrimidinium (N1,N2/C1–C4) cation is essentially planar, with a maximum deviation of 0.004 (1) Å for atom N1. In the 2-amino-5-chloropyrimidine molecule, a wide angle [C1—N2—C4 = 121.33 (10)°] is subtended at the protonated N2 atom. In the hydrogen malate anion, an intramolecular O—H···O hydrogen bond generates an *S*(7) (Bernstein *et al.*, 1995) ring and results in a folded conformation.

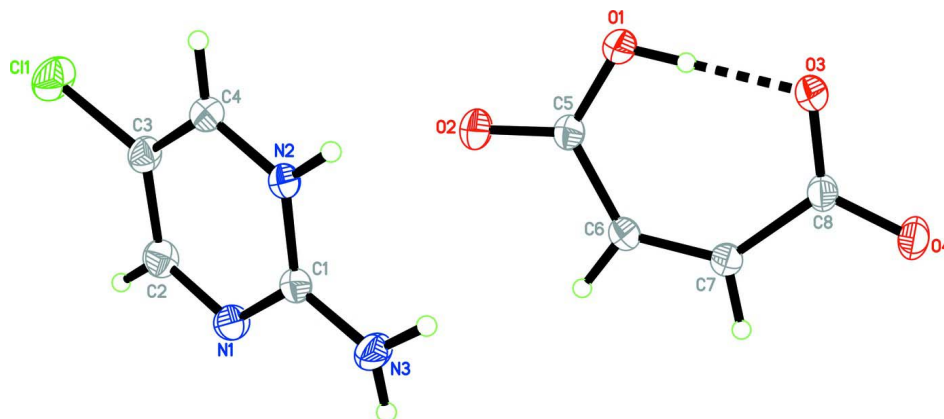
In the crystal structure, (Fig. 2), the protonated N atom and the 2-amino group of the cation are hydrogen bonded to the carboxylate O atoms of the anion *via* a pair of N—H···O hydrogen bonds, forming an *R*²₂(8) ring motif. The ion pairs are further connected *via* N—H···O and C—H···O hydrogen bonds (Table 1), forming a layer parallel to the *bc* plane.

S2. Experimental

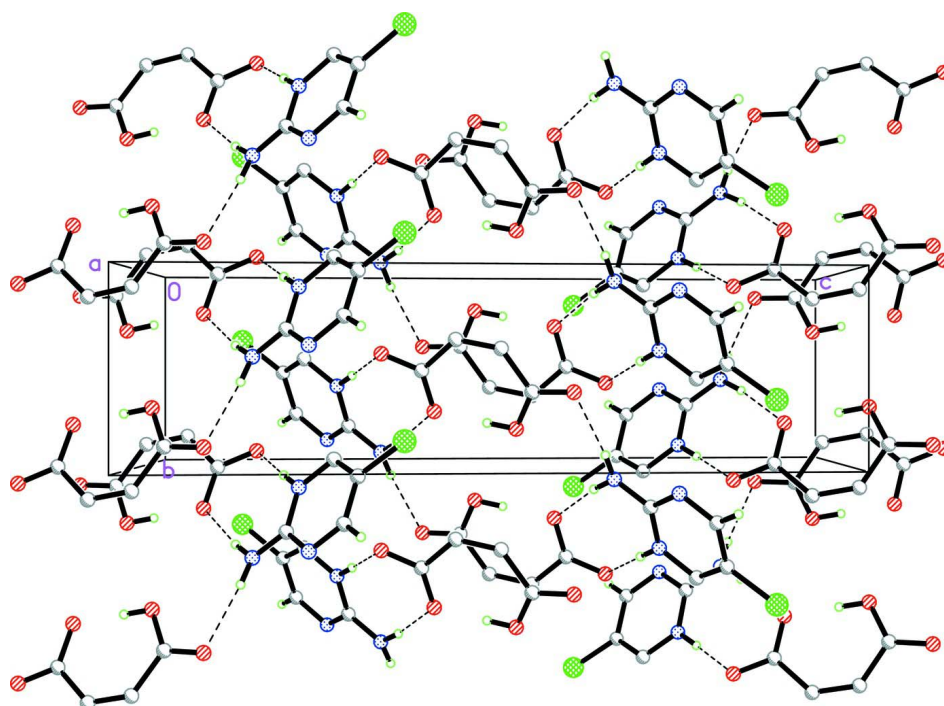
A hot methanol solution (20 ml) of 2-amino-5-chloropyrimidine (32 mg, Aldrich) and maleic acid (29 mg, Merck) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and colourless blocks of the title compound appeared after a few days.

S3. Refinement

Atoms H1N2, H1N3, H2N3 and H1O3 were located from a difference Fourier maps and refined freely [N—H = 0.858 (19)–0.89 (2) Å and O—H = 0.86 (3) Å]. The remaining H atoms were positioned geometrically [C—H = 0.93 Å] and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

**Figure 1**

The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids. Intramolecular hydrogen bonds shown by dashed lines.

**Figure 2**

The crystal packing of title compound (I).

2-Amino-5-chloropyrimidin-1-ium hydrogen maleate

Crystal data

$C_4H_5ClN_3^+ \cdot C_4H_3O_4^-$

$M_r = 245.62$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 9.3974$ (6) Å

$b = 5.5167$ (4) Å

$c = 20.0654$ (13) Å

$\beta = 95.264$ (1)°

$V = 1035.86$ (12) Å³

$Z = 4$

$F(000) = 504$

$D_x = 1.575$ Mg m⁻³

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

Cell parameters from 4623 reflections

$\theta = 2.8\text{--}31.4^\circ$
 $\mu = 0.37\text{ mm}^{-1}$
 $T = 296\text{ K}$

Block, colourless
 $0.42 \times 0.36 \times 0.13\text{ mm}$

Data collection

Bruker APEXII DUO CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2009)
 $T_{\min} = 0.860$, $T_{\max} = 0.954$

12808 measured reflections
 3443 independent reflections
 2745 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 31.7^\circ$, $\theta_{\text{min}} = 2.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -7 \rightarrow 8$
 $l = -29 \rightarrow 29$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.109$
 $S = 1.04$
 3443 reflections
 161 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.2504P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.35\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36\text{ e \AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.07132 (4)	0.34821 (8)	0.119864 (19)	0.05434 (13)
O1	0.34314 (14)	0.1959 (2)	0.47054 (5)	0.0547 (3)
O2	0.20761 (12)	0.3832 (2)	0.39206 (5)	0.0483 (3)
O3	0.44057 (12)	0.28155 (19)	0.58566 (5)	0.0477 (3)
O4	0.43276 (11)	0.5756 (2)	0.65981 (4)	0.0456 (2)
N1	0.14846 (11)	0.8848 (2)	0.24914 (5)	0.0364 (2)
N2	0.32969 (11)	0.59171 (19)	0.27016 (5)	0.0305 (2)
N3	0.32863 (14)	0.9408 (2)	0.33347 (6)	0.0424 (3)
C1	0.26868 (12)	0.8052 (2)	0.28452 (5)	0.0307 (2)
C2	0.09165 (13)	0.7456 (3)	0.20036 (6)	0.0372 (3)
H2A	0.0086	0.7977	0.1757	0.045*
C3	0.15083 (13)	0.5224 (2)	0.18395 (6)	0.0343 (2)

C4	0.27274 (13)	0.4492 (2)	0.22009 (6)	0.0335 (2)
H4A	0.3160	0.3033	0.2104	0.040*
C5	0.26812 (14)	0.3825 (2)	0.44879 (6)	0.0351 (3)
C6	0.25815 (15)	0.6000 (2)	0.49162 (6)	0.0391 (3)
H6A	0.2049	0.7265	0.4714	0.047*
C7	0.31273 (15)	0.6453 (2)	0.55439 (6)	0.0387 (3)
H7A	0.2921	0.7985	0.5703	0.046*
C8	0.40123 (13)	0.4898 (2)	0.60285 (5)	0.0328 (2)
H1N2	0.4062 (19)	0.537 (4)	0.2941 (9)	0.048 (5)*
H1N3	0.2848 (19)	1.066 (3)	0.3469 (9)	0.047 (5)*
H2N3	0.402 (2)	0.884 (3)	0.3604 (9)	0.051 (5)*
H1O3	0.376 (3)	0.225 (5)	0.5110 (14)	0.093 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0550 (2)	0.0562 (2)	0.0486 (2)	-0.00891 (17)	-0.01285 (15)	-0.01739 (16)
O1	0.0821 (8)	0.0392 (6)	0.0379 (5)	0.0180 (5)	-0.0202 (5)	-0.0097 (4)
O2	0.0577 (6)	0.0494 (6)	0.0343 (5)	0.0033 (5)	-0.0154 (4)	-0.0049 (4)
O3	0.0627 (6)	0.0412 (5)	0.0358 (4)	0.0183 (5)	-0.0148 (4)	-0.0045 (4)
O4	0.0498 (5)	0.0551 (6)	0.0298 (4)	0.0150 (5)	-0.0085 (4)	-0.0093 (4)
N1	0.0357 (5)	0.0351 (5)	0.0367 (5)	0.0036 (4)	-0.0055 (4)	-0.0018 (4)
N2	0.0331 (5)	0.0313 (5)	0.0261 (4)	0.0025 (4)	-0.0023 (3)	0.0008 (4)
N3	0.0491 (7)	0.0373 (6)	0.0376 (5)	0.0081 (5)	-0.0136 (5)	-0.0095 (5)
C1	0.0338 (5)	0.0305 (5)	0.0272 (5)	0.0001 (4)	-0.0009 (4)	0.0010 (4)
C2	0.0319 (5)	0.0412 (7)	0.0369 (6)	-0.0007 (5)	-0.0065 (4)	0.0009 (5)
C3	0.0354 (6)	0.0361 (6)	0.0306 (5)	-0.0068 (5)	-0.0023 (4)	-0.0029 (5)
C4	0.0387 (6)	0.0310 (6)	0.0306 (5)	-0.0009 (5)	0.0018 (4)	-0.0018 (4)
C5	0.0399 (6)	0.0342 (6)	0.0298 (5)	-0.0010 (5)	-0.0045 (4)	-0.0006 (4)
C6	0.0492 (7)	0.0335 (6)	0.0326 (5)	0.0106 (5)	-0.0070 (5)	0.0002 (5)
C7	0.0495 (7)	0.0335 (6)	0.0316 (5)	0.0110 (5)	-0.0039 (5)	-0.0031 (5)
C8	0.0330 (5)	0.0381 (6)	0.0265 (5)	0.0040 (5)	-0.0012 (4)	-0.0004 (4)

Geometric parameters (Å, °)

C11—C3	1.7201 (12)	N3—H1N3	0.858 (19)
O1—C5	1.3005 (16)	N3—H2N3	0.89 (2)
O1—H1O3	0.86 (3)	C2—C3	1.4027 (19)
O2—C5	1.2248 (15)	C2—H2A	0.9300
O3—C8	1.2645 (16)	C3—C4	1.3599 (17)
O4—C8	1.2475 (14)	C4—H4A	0.9300
N1—C2	1.3178 (17)	C5—C6	1.4837 (18)
N1—C1	1.3512 (15)	C6—C7	1.3393 (17)
N2—C4	1.3473 (15)	C6—H6A	0.9300
N2—C1	1.3527 (15)	C7—C8	1.4916 (17)
N2—H1N2	0.880 (18)	C7—H7A	0.9300
N3—C1	1.3192 (16)		

C5—O1—H1O3	108.0 (18)	C2—C3—C11	120.76 (9)
C2—N1—C1	117.60 (11)	N2—C4—C3	118.81 (11)
C4—N2—C1	121.33 (10)	N2—C4—H4A	120.6
C4—N2—H1N2	117.2 (12)	C3—C4—H4A	120.6
C1—N2—H1N2	121.4 (12)	O2—C5—O1	120.36 (12)
C1—N3—H1N3	120.2 (12)	O2—C5—C6	119.16 (12)
C1—N3—H2N3	120.3 (12)	O1—C5—C6	120.46 (11)
H1N3—N3—H2N3	117.3 (16)	C7—C6—C5	131.05 (12)
N3—C1—N1	119.11 (11)	C7—C6—H6A	114.5
N3—C1—N2	119.47 (11)	C5—C6—H6A	114.5
N1—C1—N2	121.41 (10)	C6—C7—C8	130.40 (12)
N1—C2—C3	122.92 (11)	C6—C7—H7A	114.8
N1—C2—H2A	118.5	C8—C7—H7A	114.8
C3—C2—H2A	118.5	O4—C8—O3	122.95 (11)
C4—C3—C2	117.92 (11)	O4—C8—C7	116.77 (11)
C4—C3—C11	121.32 (10)	O3—C8—C7	120.28 (10)
C2—N1—C1—N3	179.67 (12)	C2—C3—C4—N2	0.81 (18)
C2—N1—C1—N2	0.63 (18)	C11—C3—C4—N2	-179.38 (9)
C4—N2—C1—N3	-179.27 (12)	O2—C5—C6—C7	179.72 (16)
C4—N2—C1—N1	-0.23 (18)	O1—C5—C6—C7	-2.0 (2)
C1—N1—C2—C3	-0.3 (2)	C5—C6—C7—C8	-0.8 (3)
N1—C2—C3—C4	-0.4 (2)	C6—C7—C8—O4	-177.01 (16)
N1—C2—C3—C11	179.77 (10)	C6—C7—C8—O3	2.8 (2)
C1—N2—C4—C3	-0.52 (17)		

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>
N2—H1N2...O4 ⁱ	0.881 (19)	1.810 (18)	2.6897 (14)	177.6 (19)
N3—H1N3...O1 ⁱⁱ	0.860 (17)	2.592 (18)	3.0814 (16)	117.2 (14)
N3—H1N3...O2 ⁱⁱ	0.860 (17)	2.128 (17)	2.9795 (16)	170.2 (16)
N3—H2N3...O3 ⁱ	0.893 (18)	1.975 (18)	2.8629 (17)	172.8 (16)
O1—H1O3...O3	0.86 (3)	1.60 (3)	2.4514 (15)	179 (3)
C2—H2A...O2 ⁱⁱⁱ	0.93	2.39	3.3117 (17)	173

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y+1, z$; (iii) $-x, y+1/2, -z+1/2$.