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2-Amino-5-chloropyridinium 4-aminobenzoate

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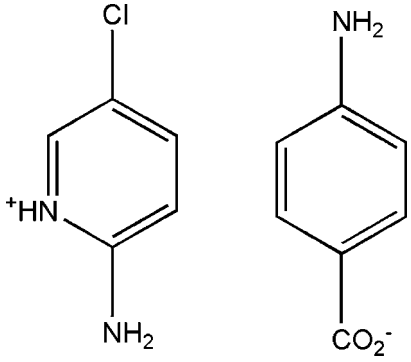
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.112; data-to-parameter ratio = 17.2.

In the title molecular salt, $C_5H_6ClN_2^+\cdot C_7H_6NO_2^-$, the cations and anions are connected by cation-to-anion and anion-to-anion N—H···O hydrogen bonds into a three-dimensional network. The dihedral angle between the ring and the CO_2 group in the anion is 7.14 (7)°.

Related literature

For general background to chloropyridinium derivatives, see: Brahadeeswaran *et al.* (2006); Tomaru *et al.* (1991). For N—H···O hydrogen bonds, see: Blessing (1986); Brown (1976).



Experimental

Crystal data

$C_5H_6ClN_2^+\cdot C_7H_6NO_2^-$
M_r = 265.70
Monoclinic, $P2_1/n$
a = 6.9879 (4) Å
b = 22.0074 (13) Å
c = 8.0554 (5) Å
β = 92.796 (1)°
V = 1237.33 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 293 K
0.20 × 0.19 × 0.18 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.941, T_{max} = 0.946
12108 measured reflections
3086 independent reflections
2642 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.112
S = 1.04
3086 reflections
179 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.86	1.76	2.6135 (15)	175
N2—H2A···O1^{i}	0.89 (2)	1.94 (2)	2.8216 (18)	172.1 (19)
N2—H2B···O1^{ii}	0.86 (2)	2.10 (2)	2.8776 (17)	150.3 (19)
N3—H3A···O1^{iii}	0.862 (19)	2.19 (2)	3.0357 (18)	167.4 (17)
N3—H3B···O2^{iv}	0.86 (2)	2.08 (2)	2.9291 (18)	171 (2)

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT6844).

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supplementary materials

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2-Amino-5-chloropyridinium 4-aminobenzoate

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Comment

Pyridine heterocycles and their derivatives are present in many large molecules having photo chemical, electro chemical and catalytic applications. Pyridine derivatives possess nonlinear optical (NLO) properties(Tomaru *et al.*, 1991). 4-*N*,*N*-dimethylamino-4′-*N*′-methyl stilbazolium tosylate (DAST) is used in generating and detecting terahertz (THz) frequencies (Brahadeeswaran *et al.*, 2006). An attempt is made to solve the pyridine based crystal structures to explore the NLO behaviour.

The *ORTEP* plot of the molecule is shown in Fig.1. The structure can be described as segregated $(C_5H_6ClN_2)^+$. $(C_7H_6NO_2)^-$ groups and connected *via* N—H···O hydrogen bonds (Blessing, 1986; Brown, 1976). The dihedral angle between the chloropyridinium ring and aminobenzoate group is 51.5 (7)°. The external bond angle [N1—C2—N2=] 118.1 (1)° at the attached amino group in pyridinium moiety is slightly widened due to the hydrogen bond formation between the ionic groups.

A dimer formation occurs through N—H···O hydrogen bonds between the symmetry related molecules(Fig.2). N—H···O type of hydrogen bonds stabilize the molecules in the unit cell.

Experimental

Methanol solutions of 2-amino-5-chloropyridine (64.28 mg, Aldrich) and 4-aminobenzoic acid (68.57 mg, Merck) were mixed together and stirred for about 1 h to get a homogeneous mixture. The resulting solution was allowed to evaporate at 303 K slowly in a water bath which has a temperature accuracy of ± 0.01°C at ambient atmosphere. Brown colour crystals with developed morphology of title compound were obtained after 12 days.

Refinement

H atoms bonded to aromatic C and N atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 Å) and allowed to ride on their parent atoms,with U_{iso}(H) = 1.2U_{eq}(C,N). The H atoms of the two NH_2 groups were freely refined.

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

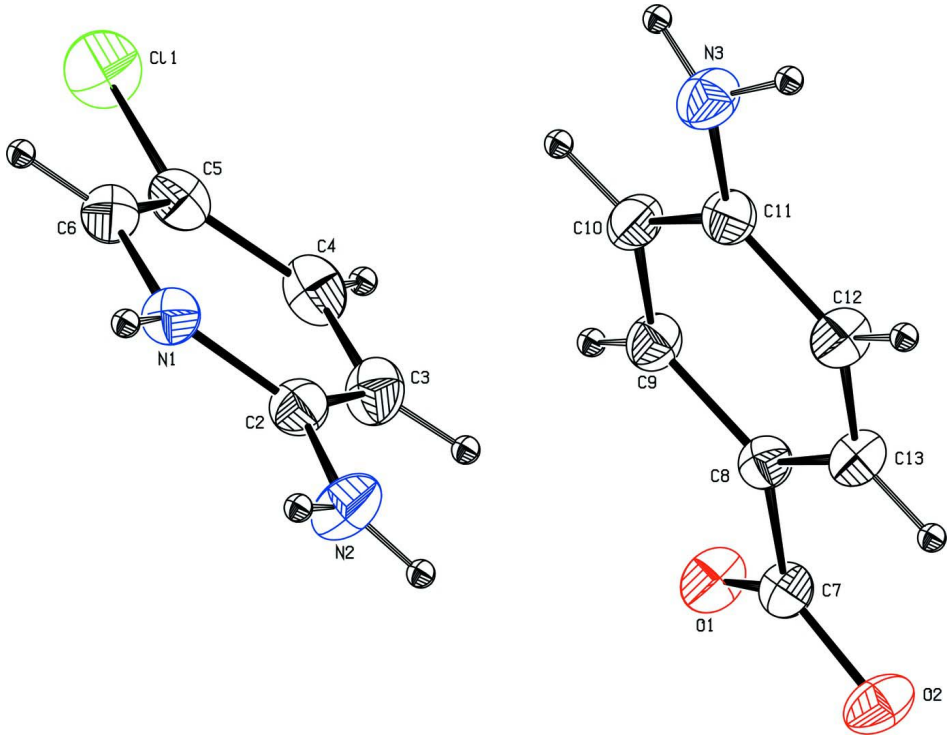

Figure 1

The molecular structure of the title compound, showing the atomic numbering and displacement ellipsoids drawn at 30% probability level.

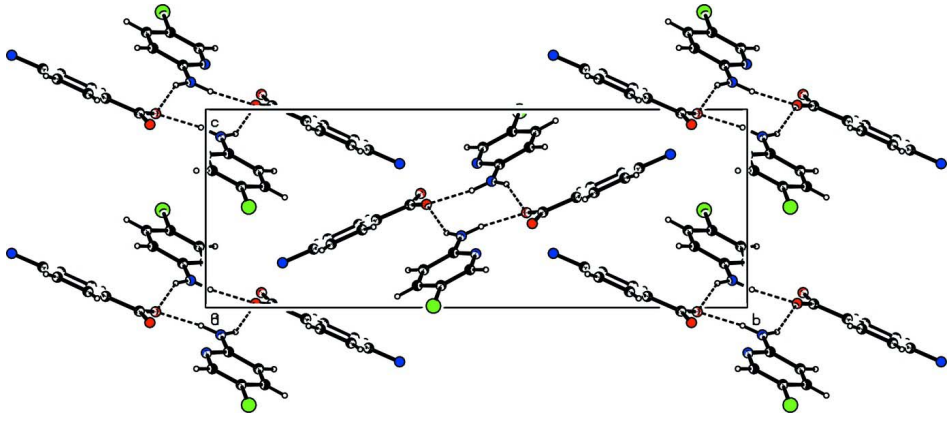

Figure 2

The crystal packing of the molecules viewed down *a* axis.

2-Amino-5-chloropyridinium 4-aminobenzoate

Crystal data

$C_5H_6ClN_2^+ \cdot C_7H_6NO_2^-$
M_r = 265.70
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 6.9879 (4) Å
b = 22.0074 (13) Å
c = 8.0554 (5) Å
β = 92.796 (1)°
V = 1237.33 (13) Å^3
Z = 4
$F(000)$ = 552
D_x = 1.426 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2642 reflections
θ = 1.9–28.4°
μ = 0.31 mm^{-1}
T = 293 K
Block, white crystalline
0.20 × 0.19 × 0.18 mm

Data collection

Bruker APEXII area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.941, T_{max} = 0.946
12108 measured reflections
3086 independent reflections
2642 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 28.4°, θ_{min} = 1.9°
h = −9→9
k = −29→29
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.112
S = 1.04
3086 reflections
179 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
$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.3359P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
C2	0.3159 (2)	0.04218 (6)	0.77668 (17)	0.0407 (3)
C3	0.3355 (2)	0.09763 (7)	0.6908 (2)	0.0479 (3)
H3	0.2372	0.1261	0.6889	0.057*
C4	0.4987 (2)	0.10919 (7)	0.61093 (19)	0.0486 (4)
H4	0.5133	0.1460	0.5563	0.058*
C5	0.6448 (2)	0.06560 (7)	0.61107 (17)	0.0431 (3)
C6	0.6216 (2)	0.01208 (6)	0.69117 (17)	0.0406 (3)
H6	0.7173	−0.0173	0.6911	0.049*
C7	0.71327 (19)	0.12257 (6)	1.01810 (16)	0.0359 (3)
C8	0.71041 (18)	0.18462 (6)	0.94334 (16)	0.0346 (3)
C9	0.87870 (19)	0.21125 (6)	0.89231 (17)	0.0389 (3)
H9	0.9937	0.1902	0.9066	0.047*

C10	0.87784 (19)	0.26832 (6)	0.82089 (17)	0.0407 (3)
H10	0.9923	0.2854	0.7895	0.049*
C11	0.70654 (19)	0.30071 (6)	0.79533 (16)	0.0371 (3)
C12	0.5373 (2)	0.27406 (6)	0.84646 (18)	0.0412 (3)
H12	0.4219	0.2948	0.8311	0.049*
C13	0.54024 (19)	0.21735 (6)	0.91937 (17)	0.0390 (3)
H13	0.4264	0.2006	0.9533	0.047*
N1	0.45860 (17)	0.00142 (5)	0.77144 (14)	0.0385 (3)
H1	0.4461	−0.0329	0.8210	0.046*
N2	0.1643 (2)	0.02799 (7)	0.86228 (19)	0.0545 (4)
N3	0.7058 (2)	0.35808 (6)	0.72634 (18)	0.0477 (3)
O1	0.86491 (14)	0.09238 (5)	1.02101 (14)	0.0471 (3)
O2	0.55877 (14)	0.10303 (4)	1.07566 (14)	0.0483 (3)
Cl1	0.85224 (7)	0.07952 (2)	0.50832 (6)	0.06516 (16)
H3A	0.598 (3)	0.3696 (9)	0.680 (2)	0.049 (5)*
H2A	0.155 (3)	−0.0086 (11)	0.909 (2)	0.067 (6)*
H2B	0.078 (3)	0.0551 (10)	0.877 (3)	0.069 (6)*
H3B	0.808 (3)	0.3657 (9)	0.676 (3)	0.062 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0455 (7)	0.0342 (6)	0.0423 (7)	0.0007 (5)	0.0014 (5)	−0.0021 (5)
C3	0.0525 (8)	0.0348 (7)	0.0557 (8)	0.0043 (6)	−0.0035 (7)	0.0047 (6)
C4	0.0605 (9)	0.0358 (7)	0.0488 (8)	−0.0081 (6)	−0.0060 (7)	0.0091 (6)
C5	0.0458 (7)	0.0437 (7)	0.0395 (7)	−0.0108 (6)	−0.0008 (5)	0.0013 (6)
C6	0.0414 (7)	0.0371 (7)	0.0432 (7)	−0.0019 (5)	0.0007 (5)	−0.0009 (5)
C7	0.0370 (6)	0.0310 (6)	0.0397 (6)	0.0004 (5)	0.0026 (5)	−0.0017 (5)
C8	0.0366 (6)	0.0310 (6)	0.0364 (6)	−0.0006 (5)	0.0032 (5)	−0.0013 (5)
C9	0.0330 (6)	0.0389 (7)	0.0447 (7)	0.0017 (5)	0.0026 (5)	0.0013 (5)
C10	0.0349 (6)	0.0418 (7)	0.0457 (7)	−0.0061 (5)	0.0048 (5)	0.0027 (6)
C11	0.0417 (7)	0.0319 (6)	0.0377 (6)	−0.0027 (5)	0.0014 (5)	−0.0015 (5)
C12	0.0366 (7)	0.0360 (6)	0.0512 (8)	0.0044 (5)	0.0050 (6)	0.0026 (6)
C13	0.0346 (6)	0.0359 (6)	0.0470 (7)	−0.0019 (5)	0.0071 (5)	0.0008 (5)
N1	0.0444 (6)	0.0297 (5)	0.0414 (6)	−0.0003 (4)	0.0041 (5)	0.0025 (4)
N2	0.0529 (8)	0.0424 (7)	0.0698 (9)	0.0093 (6)	0.0199 (7)	0.0069 (6)
N3	0.0450 (7)	0.0381 (6)	0.0600 (8)	−0.0030 (5)	0.0026 (6)	0.0104 (6)
O1	0.0389 (5)	0.0374 (5)	0.0654 (7)	0.0055 (4)	0.0072 (5)	0.0045 (4)
O2	0.0403 (5)	0.0372 (5)	0.0686 (7)	0.0042 (4)	0.0144 (5)	0.0137 (5)
Cl1	0.0575 (3)	0.0704 (3)	0.0685 (3)	−0.0175 (2)	0.0128 (2)	0.0112 (2)

Geometric parameters (Å, º)

C2—N2	1.329 (2)	C8—C13	1.3956 (18)
C2—N1	1.3433 (18)	C9—C10	1.3814 (19)
C2—C3	1.413 (2)	C9—H9	0.9300
C3—C4	1.360 (2)	C10—C11	1.3997 (19)
C3—H3	0.9300	C10—H10	0.9300
C4—C5	1.401 (2)	C11—N3	1.3794 (18)
C4—H4	0.9300	C11—C12	1.3997 (19)

C5—C6	1.357 (2)	C12—C13	1.3791 (19)
C5—Cl1	1.7312 (15)	C12—H12	0.9300
C6—N1	1.3573 (17)	C13—H13	0.9300
C6—H6	0.9300	N1—H1	0.8600
C7—O1	1.2500 (16)	N2—H2A	0.89 (2)
C7—O2	1.2706 (16)	N2—H2B	0.86 (2)
C7—C8	1.4921 (18)	N3—H3A	0.862 (19)
C8—C9	1.3937 (18)	N3—H3B	0.86 (2)
N2—C2—N1	118.11 (13)	C8—C9—H9	119.4
N2—C2—C3	123.76 (14)	C9—C10—C11	120.70 (12)
N1—C2—C3	118.14 (13)	C9—C10—H10	119.6
C4—C3—C2	119.78 (14)	C11—C10—H10	119.6
C4—C3—H3	120.1	N3—C11—C10	120.77 (13)
C2—C3—H3	120.1	N3—C11—C12	121.04 (13)
C3—C4—C5	119.95 (13)	C10—C11—C12	118.16 (12)
C3—C4—H4	120.0	C13—C12—C11	120.62 (12)
C5—C4—H4	120.0	C13—C12—H12	119.7
C6—C5—C4	119.40 (14)	C11—C12—H12	119.7
C6—C5—Cl1	120.23 (12)	C12—C13—C8	121.38 (12)
C4—C5—Cl1	120.37 (11)	C12—C13—H13	119.3
C5—C6—N1	119.95 (13)	C8—C13—H13	119.3
C5—C6—H6	120.0	C2—N1—C6	122.74 (12)
N1—C6—H6	120.0	C2—N1—H1	118.6
O1—C7—O2	123.22 (12)	C6—N1—H1	118.6
O1—C7—C8	119.25 (12)	C2—N2—H2A	120.4 (13)
O2—C7—C8	117.53 (11)	C2—N2—H2B	119.4 (14)
C9—C8—C13	117.89 (12)	H2A—N2—H2B	120.1 (19)
C9—C8—C7	120.59 (12)	C11—N3—H3A	115.5 (12)
C13—C8—C7	121.51 (12)	C11—N3—H3B	112.7 (14)
C10—C9—C8	121.23 (12)	H3A—N3—H3B	117.8 (18)
C10—C9—H9	119.4		
N2—C2—C3—C4	177.79 (15)	C7—C8—C9—C10	179.13 (12)
N1—C2—C3—C4	−2.3 (2)	C8—C9—C10—C11	−1.0 (2)
C2—C3—C4—C5	1.4 (2)	C9—C10—C11—N3	179.01 (13)
C3—C4—C5—C6	0.1 (2)	C9—C10—C11—C12	1.0 (2)
C3—C4—C5—Cl1	179.43 (12)	N3—C11—C12—C13	−178.26 (13)
C4—C5—C6—N1	−0.6 (2)	C10—C11—C12—C13	−0.2 (2)
Cl1—C5—C6—N1	−179.96 (10)	C11—C12—C13—C8	−0.5 (2)
O1—C7—C8—C9	−6.38 (19)	C9—C8—C13—C12	0.5 (2)
O2—C7—C8—C9	173.83 (12)	C7—C8—C13—C12	−178.37 (13)
O1—C7—C8—C13	172.44 (13)	N2—C2—N1—C6	−178.27 (13)
O2—C7—C8—C13	−7.35 (19)	C3—C2—N1—C6	1.8 (2)
C13—C8—C9—C10	0.3 (2)	C5—C6—N1—C2	−0.4 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.86	1.76	2.6135 (15)	175
N2—H2*A*···O1^{i}	0.89 (2)	1.94 (2)	2.8216 (18)	172.1 (19)
N2—H2*B*···O1^{ii}	0.86 (2)	2.10 (2)	2.8776 (17)	150.3 (19)
N3—H3*A*···O1^{iii}	0.862 (19)	2.19 (2)	3.0357 (18)	167.4 (17)
N3—H3*B*···O2^{iv}	0.86 (2)	2.08 (2)	2.9291 (18)	171 (2)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) *x*−1, *y*, *z*; (iii) *x*−1/2, −*y*+1/2, *z*−1/2; (iv) *x*+1/2, −*y*+1/2, *z*−1/2.