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Pyridinium 5-nitrothiophene-2-carboxylate

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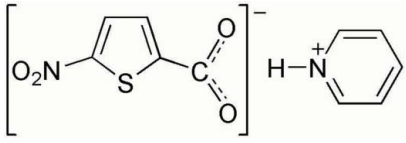
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.039; wR factor = 0.080; data-to-parameter ratio = 12.8.

The anion of the title compound, $C_5H_6N^+\cdot C_5H_2NO_4S^-$, is approximately planar, with the carboxylate and nitro group planes forming dihedral angles of 7.5 (3) and 3.5 (3)°, respectively, with the thiophene ring. In the crystal structure, the cations and anions are linked into a two-dimensional network parallel to (011) by N—H···O and C—H···O hydrogen bonds.

Related literature

For the uses of 5-nitrothiophene-2-carboxylic acid, see: Cao *et al.* (2003). For the synthesis, see: Marques *et al.* (2002). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_5H_6N^+\cdot C_5H_2NO_4S^-$
M_r = 252.24
Triclinic, $P\overline{1}$
a = 6.0940 (12) Å
b = 7.3390 (15) Å
c = 13.296 (3) Å
α = 77.30 (3)°
β = 81.52 (3)°
γ = 71.00 (3)°
V = 546.6 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 298 K
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.915, T_{max} = 0.971
2194 measured reflections
1990 independent reflections
1657 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.080
S = 1.00
1990 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H6···O2	0.86	1.74	2.594 (3)	176
C3—H3···O1	0.93	2.49	3.156 (3)	129
C1—H1···O3^{i}	0.93	2.55	3.254 (3)	133
C4—H4···O1^{ii}	0.93	2.44	3.210 (3)	141

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank the Center of Testing and Analysis, Nanjing University, for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5088).

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supporting information

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S1. Comment

5-Nitrothiophene-2-carboxylic acid is an important intermediate used to synthesize raltitrexed (trade name Tomudex), an antimetabolite drug used in cancer chemotherapy (Cao *et al.*, 2003). We report here the crystal structure of the title compound (Fig. 1).

Bond lengths and angles in both cation and anion are within normal ranges (Allen *et al.*, 1987). The anion is approximately planar; the C6/O1/O2 and N2/O3/O4 planes form dihedral angles of 7.5 (3)° and 3.5 (3)°, respectively, with the thiophene ring. In the crystal structure, the cations and anions are linked into a two-dimensional network (Fig. 2) by N—H···O and C—H···O hydrogen bonds.

S2. Experimental

5-Nitrothiophene-2-carboxylic acid was prepared by the method reported in literature (Marques *et al.*, 2002). Single crystals were obtained by dissolving 5-nitrothiophene-2-carboxylic acid (0.5 g, 2.89 mmol) in pyridine (50 ml) and evaporating the solvent slowly at room temperature for about 20 d.

S3. Refinement

After checking their presence in the difference map, all the H atoms were positioned geometrically [N—H = 0.86 and C—H = 0.93 Å] and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

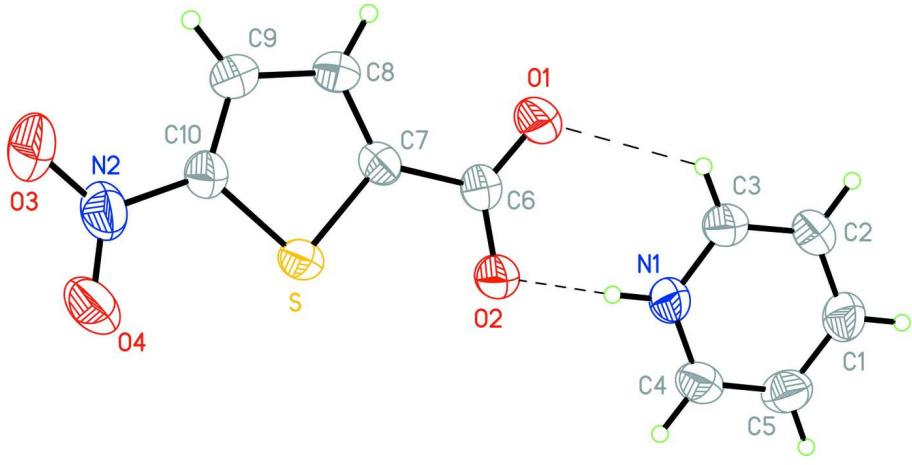

Figure 1

The asymmetric unit of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

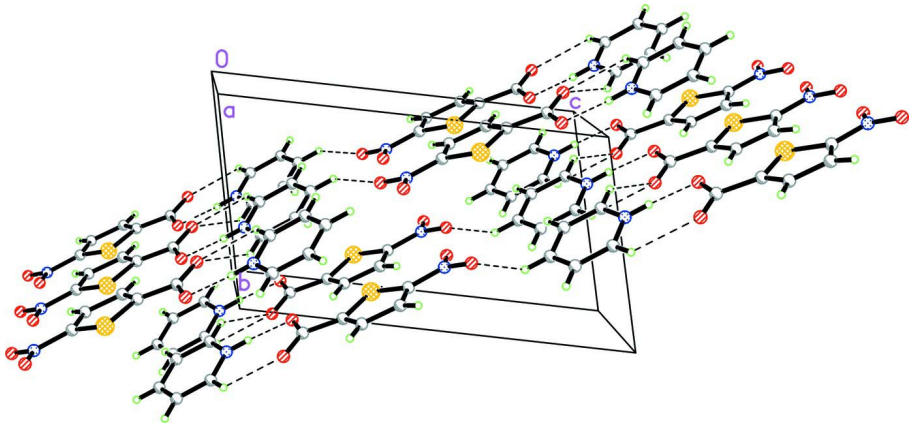

Figure 2

Crystal packing of the title compound. hydrogen bonds are shown as dashed lines.

Pyridinium 5-nitrothiophene-2-carboxylate

Crystal data

$C_5H_6N^+·C_5H_2NO_4S^-$
M_r = 252.24
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 6.0940 (12) Å
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c = 13.296 (3) Å
α = 77.30 (3)°
β = 81.52 (3)°
γ = 71.00 (3)°
V = 546.6 (2) Å^3
Z = 2
F(000) = 260
D_x = 1.533 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–13°
μ = 0.30 mm^{-1}
T = 298 K
Block, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.915, T_{max} = 0.971
2194 measured reflections
1990 independent reflections
1657 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 25.3°, θ_{min} = 1.6°
h = 0→7
k = −8→8
l = −15→15
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.080
S = 1.00
1990 reflections
155 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 0.48P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0313 (18)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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}
S	0.14233 (10)	0.12191 (9)	0.65371 (4)	0.04471 (19)
O1	−0.0782 (3)	−0.1820 (3)	0.90222 (13)	0.0592 (5)
O2	0.2305 (3)	−0.0690 (3)	0.86414 (12)	0.0534 (5)
O3	−0.1575 (4)	0.3584 (3)	0.40288 (14)	0.0753 (6)
O4	0.1837 (3)	0.3262 (3)	0.44510 (14)	0.0691 (6)
N2	−0.0093 (4)	0.3011 (3)	0.46450 (15)	0.0538 (5)
C6	0.0413 (4)	−0.0881 (3)	0.84465 (17)	0.0419 (5)
C7	−0.0384 (4)	0.0149 (3)	0.74043 (16)	0.0375 (5)
C8	−0.2423 (4)	0.0392 (3)	0.70084 (17)	0.0438 (6)
H8	−0.3598	−0.0095	0.7374	0.053*
C9	−0.2565 (4)	0.1453 (4)	0.59945 (18)	0.0469 (6)
H9	−0.3833	0.1760	0.5608	0.056*
C10	−0.0599 (4)	0.1972 (3)	0.56517 (17)	0.0427 (5)
N1	0.3544 (3)	−0.2797 (3)	1.04230 (14)	0.0437 (5)
H6	0.3164	−0.2065	0.9836	0.052*
C1	0.4731 (4)	−0.5108 (4)	1.22741 (19)	0.0518 (6)
H1	0.5143	−0.5902	1.2908	0.062*
C2	0.2816 (4)	−0.5107 (4)	1.18469 (19)	0.0521 (6)
H2	0.1911	−0.5896	1.2189	0.063*
C3	0.2254 (4)	−0.3937 (4)	1.09159 (18)	0.0481 (6)
H3	0.0960	−0.3932	1.0620	0.058*
C4	0.5408 (4)	−0.2773 (4)	1.08249 (18)	0.0496 (6)
H4	0.6285	−0.1969	1.0470	0.060*
C5	0.6035 (4)	−0.3923 (4)	1.17561 (19)	0.0529 (6)
H5	0.7335	−0.3906	1.2038	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0397 (3)	0.0594 (4)	0.0383 (3)	−0.0262 (3)	−0.0043 (2)	0.0019 (3)
O1	0.0587 (11)	0.0758 (13)	0.0452 (10)	−0.0380 (10)	−0.0053 (8)	0.0121 (9)
O2	0.0500 (10)	0.0674 (12)	0.0460 (10)	−0.0303 (9)	−0.0133 (8)	0.0084 (8)
O3	0.0928 (15)	0.0900 (16)	0.0461 (11)	−0.0385 (12)	−0.0276 (11)	0.0126 (10)

O4	0.0766 (13)	0.0872 (15)	0.0508 (11)	−0.0496 (12)	0.0058 (10)	0.0027 (10)
N2	0.0697 (15)	0.0555 (14)	0.0393 (11)	−0.0277 (12)	−0.0060 (11)	−0.0010 (10)
C6	0.0437 (13)	0.0418 (13)	0.0382 (12)	−0.0141 (11)	−0.0038 (10)	−0.0016 (10)
C7	0.0373 (12)	0.0384 (12)	0.0370 (12)	−0.0159 (10)	0.0013 (9)	−0.0035 (9)
C8	0.0355 (12)	0.0505 (14)	0.0459 (13)	−0.0190 (11)	−0.0012 (10)	−0.0024 (11)
C9	0.0389 (13)	0.0553 (15)	0.0485 (14)	−0.0182 (11)	−0.0105 (10)	−0.0030 (11)
C10	0.0470 (13)	0.0473 (14)	0.0340 (12)	−0.0180 (11)	−0.0057 (10)	−0.0009 (10)
N1	0.0438 (11)	0.0481 (12)	0.0353 (10)	−0.0144 (9)	−0.0036 (8)	0.0016 (9)
C1	0.0519 (15)	0.0557 (16)	0.0409 (13)	−0.0138 (12)	−0.0077 (11)	0.0037 (11)
C2	0.0538 (15)	0.0504 (15)	0.0527 (15)	−0.0254 (12)	−0.0040 (12)	0.0041 (12)
C3	0.0437 (13)	0.0541 (15)	0.0491 (14)	−0.0214 (12)	−0.0086 (11)	−0.0014 (12)
C4	0.0424 (13)	0.0602 (16)	0.0479 (14)	−0.0237 (12)	0.0007 (11)	−0.0040 (12)
C5	0.0417 (14)	0.0702 (18)	0.0484 (14)	−0.0199 (13)	−0.0078 (11)	−0.0074 (13)

Geometric parameters (Å, º)

S—C10	1.705 (2)	N1—C4	1.331 (3)
S—C7	1.717 (2)	N1—C3	1.335 (3)
O1—C6	1.233 (3)	N1—H6	0.86
O2—C6	1.275 (3)	C1—C2	1.371 (3)
O3—N2	1.218 (3)	C1—C5	1.374 (3)
O4—N2	1.230 (3)	C1—H1	0.93
N2—C10	1.432 (3)	C2—C3	1.361 (3)
C6—C7	1.492 (3)	C2—H2	0.93
C7—C8	1.364 (3)	C3—H3	0.93
C8—C9	1.400 (3)	C4—C5	1.364 (3)
C8—H8	0.93	C4—H4	0.93
C9—C10	1.360 (3)	C5—H5	0.93
C9—H9	0.93		
C10—S—C7	89.85 (11)	C4—N1—C3	121.1 (2)
O3—N2—O4	123.7 (2)	C4—N1—H6	119.4
O3—N2—C10	118.7 (2)	C3—N1—H6	119.4
O4—N2—C10	117.6 (2)	C2—C1—C5	119.3 (2)
O1—C6—O2	126.8 (2)	C2—C1—H1	120.3
O1—C6—C7	118.1 (2)	C5—C1—H1	120.3
O2—C6—C7	115.03 (19)	C3—C2—C1	119.2 (2)
C8—C7—C6	129.1 (2)	C3—C2—H2	120.4
C8—C7—S	112.21 (16)	C1—C2—H2	120.4
C6—C7—S	118.70 (16)	N1—C3—C2	120.6 (2)
C7—C8—C9	113.0 (2)	N1—C3—H3	119.7
C7—C8—H8	123.5	C2—C3—H3	119.7
C9—C8—H8	123.5	N1—C4—C5	120.2 (2)
C10—C9—C8	110.8 (2)	N1—C4—H4	119.9
C10—C9—H9	124.6	C5—C4—H4	119.9
C8—C9—H9	124.6	C4—C5—C1	119.5 (2)
C9—C10—N2	126.6 (2)	C4—C5—H5	120.3
C9—C10—S	114.08 (17)	C1—C5—H5	120.3

N2—C10—S	119.34 (17)		
O1—C6—C7—C8	7.6 (4)	O4—N2—C10—C9	−176.1 (2)
O2—C6—C7—C8	−172.7 (2)	O3—N2—C10—S	−178.2 (2)
O1—C6—C7—S	−172.45 (18)	O4—N2—C10—S	2.3 (3)
O2—C6—C7—S	7.3 (3)	C7—S—C10—C9	0.4 (2)
C10—S—C7—C8	−0.19 (19)	C7—S—C10—N2	−178.2 (2)
C10—S—C7—C6	179.87 (19)	C5—C1—C2—C3	0.3 (4)
C6—C7—C8—C9	179.9 (2)	C4—N1—C3—C2	0.1 (4)
S—C7—C8—C9	−0.1 (3)	C1—C2—C3—N1	−0.2 (4)
C7—C8—C9—C10	0.3 (3)	C3—N1—C4—C5	0.0 (4)
C8—C9—C10—N2	178.0 (2)	N1—C4—C5—C1	0.1 (4)
C8—C9—C10—S	−0.5 (3)	C2—C1—C5—C4	−0.2 (4)
O3—N2—C10—C9	3.4 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H6···O2	0.86	1.74	2.594 (3)	176
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