organic compounds

3-Nitro-5-(4-pyridinio)benzoate

Xiao-Jun Zhao and Cheng-Jun Hao*

College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan 467000, People's Republic of China
Correspondence e-mail: haochengjun2008@163.com

The title compound, $C_{12}H_8N_2O_4$, crystallizes as a zwitterion in which the pyridyl N atom is protonated. The dihedral angle between the benzene and pyridinium rings is 27.9 (2)°. In the crystal, N—H···O hydrogen bonds link adjacent zwitterions into a three-dimensional structure.

Related literature

The title compound was reacted with $MgCl_2$ under hydrothermal conditions in an attempt to obtain a new coordination polymer as part of our investigation of pyridine caboxylate coordination polymers. For the advantages of hydrothermal synthesis, see: Feng *et al.* (2001); Tao *et al.* (2001). For the crystal structures of coordination polymers involving 4-pyridinecarboxylate ligands, see: Lu *et al.* (2003).
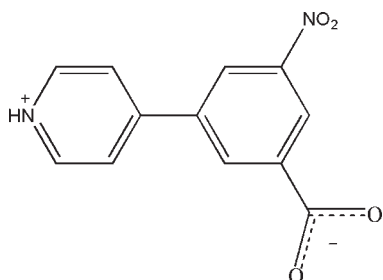
Experimental

Crystal data

$C_{12}H_8N_2O_4$	V = 4268.5 (7) Å^3
M_r = 244.20	Z = 16
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation
a = 16.1215 (14) Å	μ = 0.12 mm^{-1}
b = 37.126 (3) Å	T = 298 K
c = 7.1317 (8) Å	0.46 × 0.17 × 0.09 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	4377 measured reflections
	1023 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	621 reflections with $I > 2\sigma(I)$
T_{min} = 0.948, T_{max} = 0.990	R_{int} = 0.110

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048	1 restraint
$wR(F^2)$ = 0.118	H-atom parameters constrained
S = 1.02	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
1023 reflections	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
163 parameters	

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^i	0.86	1.74	2.592 (5)	172

Symmetry code: (i) $-x + \frac{3}{4}, y - \frac{1}{4}, z + \frac{1}{4}$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; 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: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2400).

References

Bruker (2007). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Feng, S. H. & Xu, R. R. (2001). *Acc. Chem. Res.* **34**, 239–247.
Lu, T. B. & Luck, R. L. (2003). *Inorg. Chim. Acta*, **351**, 345–355.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tao, J., Zhang, X. M., Tong, M. L. & Chen, X. M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 770–771.

supplementary materials

3-Nitro-5-(4-pyridinio)benzoate

X.-J. Zhao and **C.-J. Hao**

Comment

Hydrothermal synthesis has been successful in the preparation of new materials, because problems associated with ligand solubility were minimized and the reactivity of reactants was enhanced during the crystallization process in a heated sealed solution above ambient temperature and pressure (Feng *et al.*, 2001; Tao *et al.*, 2001). Thus, we have reacted 5-(4-pyridyl)-3-nitrobenzoic acid with $MgCl_2$ under hydrothermal conditions in an effort to obtain a new coordination polymer as part of further investigation of pyridine caboxylate coordination polymers (Lu *et al.*, 2003). In fact, no complex was formed, but we report here the crystal structure of the starting organic compound.

In the title compound, $C_{12}H_8N_2O_4$, the pyridyl N atom is protonated, and the compound is formally a zwitterion. The carboxyl group and the nitro group are approximately coplanar with the aromatic ring (Fig. 1), as indicated by the O2—C1—C2—C3 and O1—C1—C2—C3 torsion angles of 11.1 (8) ° and -170.2 (5) °, respectively; the O3—N1—C4—C3 and O4—N1—C4—C3 torsion angles are 1.0 (7) and -176.9 (5) °, respectively. Furthermore, the dihedral angle between the benzene ring and the pyridine ring is 27.9 (2) °. In the crystal packing, N—H···O hydrogen bonds stabilize the three-dimensional structure.

Experimental

A mixture of $MgCl_2$ (0.1 mmol, 0.01g), 5-(4-pyridyl)-3-nitrobenzoic acid (0.1 mmol, 0.025 g) and 10 ml of H_2O was loaded in a 20 ml Teflon-lined stainless steel vessel and heated at 303K for 3 days. Colourless crystals were obtained when the solution was slowly cooled to room temperature.

Refinement

H atoms were placed at calculated positions and were treated as riding on the parent C or N atoms with C—H = 0.93 Å, N—H = 0.86 Å, and with $U_{iso}(H) = 1.2\ U_{eq}(C, N)$. In the absence of significant anomalous scattering Friedel pairs were merged.
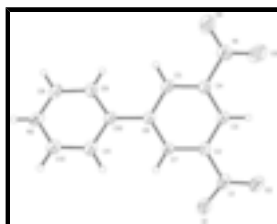
Figures

Fig. 1. The structure of the title compound, showing the atomic numbering scheme. Non-H atoms are shown with 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.
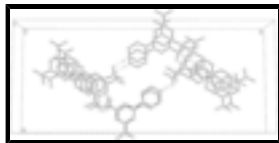
Fig. 2. View of the three-dimensional network constructed by N—H···O hydrogen bonding interactions (dashed lines). H atoms not involved in the hydrogen bonds are omitted for clarity.

3-Nitro-5-(4-pyridinio)benzoate

Crystal data

$C_{12}H_8N_2O_4$	$F(000) = 2016$
$M_r = 244.20$	$D_x = 1.520$ Mg m^{-3}
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: F 2 -2d	Cell parameters from 638 reflections
$a = 16.1215$ (14) Å	$\theta = 2.8–26.3°$
$b = 37.126$ (3) Å	$\mu = 0.12$ mm^{-1}
$c = 7.1317$ (8) Å	$T = 298$ K
$V = 4268.5$ (7) Å^3	Needle, colourless
$Z = 16$	$0.46 \times 0.17 \times 0.09$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	1023 independent reflections
Radiation source: fine-focus sealed tube	621 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.110$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	$h = -19 \rightarrow 11$
$T_{min} = 0.948$, $T_{max} = 0.990$	$k = -43 \rightarrow 43$
4377 measured reflections	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.048$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.118$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.170P]$ where $P = (F_o^2 + 2F_c^2)/3$
1023 reflections	$(\Delta/\sigma)_{max} < 0.001$
163 parameters	$\Delta\rho_{max} = 0.18$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.22$ e Å^{-3}

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 $F^2 > 2\text{sigma}(F^2)$ 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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
N1	−0.0034 (3)	0.07102 (12)	0.9143 (9)	0.0630 (15)
N2	0.3542 (3)	−0.05673 (10)	0.8083 (7)	0.0543 (14)
H2	0.3836	−0.0760	0.8109	0.065*
O1	0.3097 (2)	0.13480 (9)	0.5977 (7)	0.0701 (13)
O2	0.2043 (2)	0.16759 (9)	0.7037 (7)	0.0731 (14)
O3	−0.0420 (2)	0.09929 (10)	0.9147 (9)	0.0919 (17)
O4	−0.0331 (2)	0.04219 (10)	0.9681 (8)	0.0856 (17)
C1	0.2386 (4)	0.13874 (13)	0.6766 (9)	0.0526 (15)
C2	0.2001 (3)	0.10398 (12)	0.7393 (8)	0.0435 (14)
C3	0.1187 (3)	0.10352 (12)	0.7997 (8)	0.0486 (15)
H3	0.0881	0.1247	0.8046	0.058*
C4	0.0835 (3)	0.07138 (12)	0.8524 (9)	0.0474 (15)
C5	0.1277 (3)	0.03937 (12)	0.8486 (8)	0.0451 (14)
H5	0.1020	0.0179	0.8822	0.054*
C6	0.2104 (3)	0.03957 (11)	0.7944 (7)	0.0403 (12)
C7	0.2461 (3)	0.07216 (11)	0.7400 (8)	0.0428 (14)
H7	0.3015	0.0727	0.7035	0.051*
C8	0.2731 (3)	−0.05830 (13)	0.7825 (8)	0.0508 (15)
H8	0.2480	−0.0807	0.7685	0.061*
C9	0.2244 (3)	−0.02788 (12)	0.7757 (8)	0.0475 (14)
H9	0.1675	−0.0300	0.7580	0.057*
C10	0.2600 (3)	0.00589 (12)	0.7950 (8)	0.0420 (13)
C11	0.3461 (3)	0.00687 (12)	0.8235 (9)	0.0522 (15)
H11	0.3734	0.0288	0.8378	0.063*
C12	0.3890 (3)	−0.02476 (13)	0.8300 (9)	0.0575 (17)
H12	0.4459	−0.0238	0.8507	0.069*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.044 (3)	0.056 (3)	0.089 (4)	0.001 (2)	0.002 (3)	−0.004 (3)
N2	0.055 (3)	0.036 (2)	0.072 (4)	0.014 (2)	0.003 (3)	0.005 (3)

O1	0.063 (3)	0.041 (2)	0.106 (4)	−0.0047 (18)	0.024 (3)	0.005 (2)
O2	0.066 (3)	0.0369 (19)	0.116 (4)	0.0041 (18)	0.007 (3)	0.011 (3)
O3	0.063 (2)	0.065 (3)	0.149 (5)	0.020 (2)	0.030 (3)	0.006 (3)
O4	0.056 (2)	0.058 (2)	0.143 (5)	−0.009 (2)	0.019 (3)	0.012 (3)
C1	0.057 (4)	0.035 (3)	0.066 (4)	−0.003 (3)	0.001 (3)	0.011 (3)
C2	0.042 (3)	0.032 (2)	0.057 (4)	−0.001 (2)	−0.001 (3)	0.000 (2)
C3	0.046 (3)	0.030 (3)	0.070 (4)	0.003 (2)	−0.001 (3)	−0.002 (3)
C4	0.041 (3)	0.034 (3)	0.067 (4)	−0.001 (2)	0.000 (3)	0.000 (3)
C5	0.046 (3)	0.031 (3)	0.058 (4)	0.001 (2)	0.001 (3)	0.003 (3)
C6	0.040 (3)	0.031 (3)	0.049 (3)	−0.002 (2)	−0.001 (3)	0.000 (3)
C7	0.035 (3)	0.031 (2)	0.061 (4)	0.001 (2)	0.000 (3)	−0.001 (3)
C8	0.057 (4)	0.032 (3)	0.063 (4)	0.001 (2)	−0.003 (3)	0.008 (3)
C9	0.044 (3)	0.038 (3)	0.060 (4)	−0.004 (2)	0.001 (3)	0.001 (3)
C10	0.045 (3)	0.031 (3)	0.051 (4)	0.002 (2)	0.003 (3)	0.003 (2)
C11	0.051 (3)	0.035 (3)	0.070 (4)	−0.001 (2)	0.004 (3)	0.004 (3)
C12	0.049 (3)	0.042 (3)	0.082 (5)	0.005 (3)	0.005 (3)	0.008 (3)

Geometric parameters (Å, °)

N1—O3	1.220 (5)	C5—C6	1.388 (6)
N1—O4	1.233 (5)	C5—H5	0.9300
N1—C4	1.469 (7)	C6—C7	1.395 (6)
N2—C12	1.322 (6)	C6—C10	1.485 (6)
N2—C8	1.323 (6)	C7—H7	0.9300
N2—H2	0.8600	C8—C9	1.376 (6)
O1—C1	1.284 (6)	C8—H8	0.9300
O2—C1	1.221 (6)	C9—C10	1.386 (6)
C1—C2	1.500 (6)	C9—H9	0.9300
C2—C3	1.381 (7)	C10—C11	1.403 (6)
C2—C7	1.394 (6)	C11—C12	1.364 (6)
C3—C4	1.374 (6)	C11—H11	0.9300
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.386 (6)		
O3—N1—O4	123.2 (5)	C5—C6—C7	118.6 (4)
O3—N1—C4	118.6 (5)	C5—C6—C10	120.8 (4)
O4—N1—C4	118.1 (4)	C7—C6—C10	120.6 (4)
C12—N2—C8	118.4 (4)	C2—C7—C6	121.1 (4)
C12—N2—H2	120.8	C2—C7—H7	119.4
C8—N2—H2	120.8	C6—C7—H7	119.4
O2—C1—O1	125.0 (5)	N2—C8—C9	122.2 (5)
O2—C1—C2	121.3 (5)	N2—C8—H8	118.9
O1—C1—C2	113.7 (4)	C9—C8—H8	118.9
C3—C2—C7	119.6 (4)	C8—C9—C10	120.2 (4)
C3—C2—C1	119.8 (4)	C8—C9—H9	119.9
C7—C2—C1	120.7 (4)	C10—C9—H9	119.9
C4—C3—C2	119.3 (4)	C9—C10—C11	116.6 (4)
C4—C3—H3	120.4	C9—C10—C6	122.6 (4)
C2—C3—H3	120.4	C11—C10—C6	120.8 (4)
C3—C4—C5	121.8 (4)	C12—C11—C10	119.0 (5)

C3—C4—N1	119.0 (4)	C12—C11—H11	120.5
C5—C4—N1	119.2 (5)	C10—C11—H11	120.5
C4—C5—C6	119.6 (4)	N2—C12—C11	123.6 (5)
C4—C5—H5	120.2	N2—C12—H12	118.2
C6—C5—H5	120.2	C11—C12—H12	118.2
O2—C1—C2—C3	11.2 (9)	C3—C2—C7—C6	2.3 (9)
O1—C1—C2—C3	−170.0 (5)	C1—C2—C7—C6	−178.7 (5)
O2—C1—C2—C7	−167.8 (6)	C5—C6—C7—C2	−0.1 (8)
O1—C1—C2—C7	10.9 (8)	C10—C6—C7—C2	−179.8 (5)
C7—C2—C3—C4	−2.6 (8)	C12—N2—C8—C9	0.7 (9)
C1—C2—C3—C4	178.4 (5)	N2—C8—C9—C10	0.4 (9)
C2—C3—C4—C5	0.7 (8)	C8—C9—C10—C11	−0.8 (8)
C2—C3—C4—N1	−179.3 (6)	C8—C9—C10—C6	−178.2 (5)
O3—N1—C4—C3	0.9 (8)	C5—C6—C10—C9	25.9 (8)
O4—N1—C4—C3	−177.2 (6)	C7—C6—C10—C9	−154.3 (5)
O3—N1—C4—C5	−179.0 (6)	C5—C6—C10—C11	−151.4 (6)
O4—N1—C4—C5	2.8 (8)	C7—C6—C10—C11	28.4 (8)
C3—C4—C5—C6	1.5 (9)	C9—C10—C11—C12	0.2 (9)
N1—C4—C5—C6	−178.5 (5)	C6—C10—C11—C12	177.6 (5)
C4—C5—C6—C7	−1.8 (8)	C8—N2—C12—C11	−1.3 (10)
C4—C5—C6—C10	178.0 (5)	C10—C11—C12—N2	0.9 (10)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1[i]	0.86	1.74	2.592 (5)	172

Symmetry codes: (i) −*x*+3/4, *y*−1/4, *z*+1/4.

Fig. 1

Fig. 2