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Crystal structure of 4-nitro-*N*-[(pyridin-2-yl)methylidene]aniline

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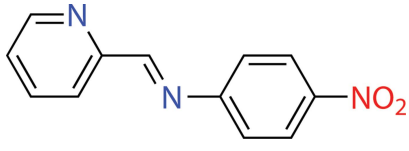
The title compound, $C_{12}H_9N_3O_2$, adopts an *E* conformation at the imine double bond. The pyridyl ring makes a dihedral angle of 47.78 (5)° with the benzene ring, indicating the molecule is twisted. In the crystal, molecules are π–π stacked into columns parallel to [100], with an interplanar separation of 3.8537 (8) Å, corresponding to the length of the *a* axis. The chains are further linked *via* weak C—H···O and C—H···N hydrogen bonds, forming two-dimensional sheets parallel to (010). The sheets interact by van der Waals interactions.

Keywords: crystal structure; hydrogen bonds; Schiff base; π–π stacking.

CCDC reference: 1423407

1. Related literature

For related crystal structures, see: Zheng & Lee (2012); Marjani *et al.* (2011); Tzimopoulos *et al.* (2010); Heinze & Bueno Toro (2004).



2. Experimental

2.1. Crystal data

$C_{12}H_9N_3O_2$
M_r = 227.22
Monoclinic, $P2_1/n$
a = 3.8573 (8) Å
b = 20.334 (4) Å
c = 13.629 (3) Å
β = 90.57 (3)°
V = 1068.9 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 296 K
0.22 × 0.14 × 0.14 mm

2.2. Data collection

Bruker D8 QUEST CMOS diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.983, T_{max} = 0.986
4963 measured reflections
2729 independent reflections
1389 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.146
S = 0.96
2729 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{i}	0.93	2.65	3.343 (3)	132
C6—H6···O2^{ii}	0.93	2.65	3.527 (2)	158
C11—H11···N1^{iii}	0.93	2.60	3.465 (2)	155

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

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2015* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5383).

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supporting information

Acta Cryst. (2015). E**71**, o760 [doi:10.1107/S2056989015016928]

Crystal structure of 4-nitro-*N*-[(pyridin-2-yl)methylidene]aniline

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S1. Synthesis and crystallization

At room temperature, 2-pyridinecarboxaldehyde (1.90 ml, 0.02 mol) was added to a benzene solution (100 ml) of 4-nitroaniline (2.76 g, 0.02 mol), with a few drops of acetic acid added as catalyst. The reaction mixture was stirred under reflux at 110 °C. After 6 h of reflux, the yellow solution was neutralized with Na_2CO_3 (2 mmol), filtered, and concentrated to dryness *in vacuo*. The residue was recrystallized from a mixture of CH_2Cl_2 and petroleum ether (2:1, *v*/*v*) to give light-yellow crystalline solid of (I).

S2. Refinement

The C–bound hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atom positions with a C—H distances of 0.93 Å, and with U_{iso}(H) = 1.2U_{eq}(C).

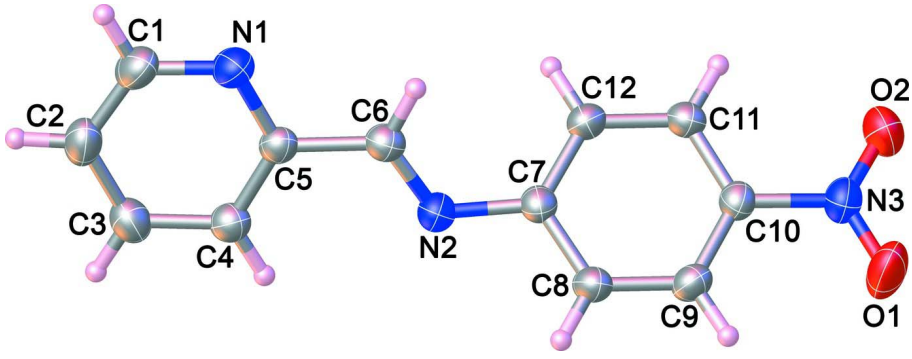

Figure 1

The molecular structure of (I), showing 35% probability displacement ellipsoids nd atom labels.

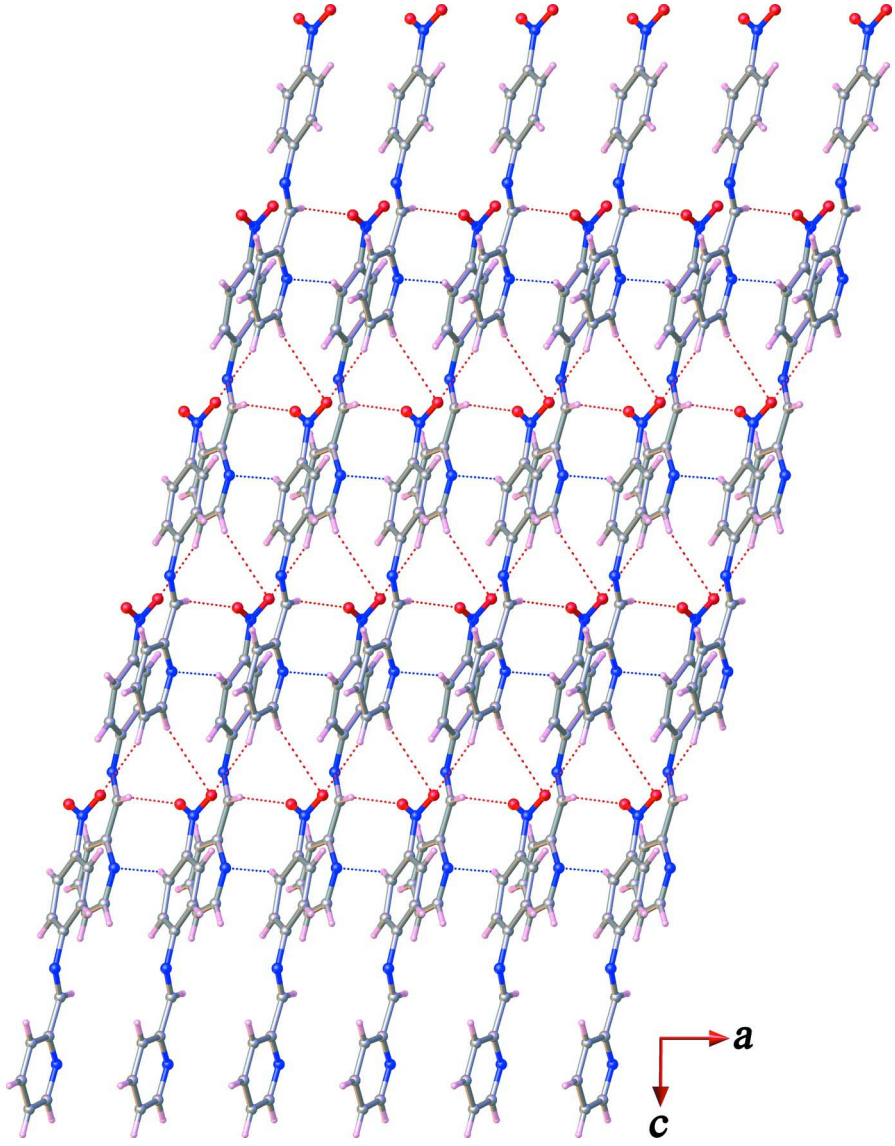

Figure 2

A packing view of (I) along (010). Hydrogen bonds are shown as dashed lines.

4-Nitro-*N*-[(pyridin-2-yl)methylidene]aniline

Crystal data

$C_{12}H_9N_3O_2$
$M_r = 227.22$
Monoclinic, $P2_1/n$
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$c = 13.629$ (3) Å
$\beta = 90.57$ (3)°
$V = 1068.9$ (4) Å^3
$Z = 4$
$F(000) = 472$
$D_x = 1.412$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\theta = 3.4$–25.0°
$\mu = 0.10$ mm^{-1}
$T = 296$ K
Block, light-yellow
0.22 × 0.14 × 0.14 mm

Data collection

Bruker D8 QUEST CMOS diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.983, T_{max} = 0.986
4963 measured reflections
2729 independent reflections
1389 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 28.8°, θ_{min} = 3.4°
h = −5→5
k = −27→26
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.146
S = 0.96
2729 reflections
154 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	1.1083 (5)	0.13951 (9)	0.12132 (11)	0.0956 (6)
O2	0.8270 (5)	0.22866 (8)	0.14401 (10)	0.0803 (5)
N1	0.7398 (4)	0.15745 (8)	0.80644 (11)	0.0590 (5)
N2	0.7157 (4)	0.09779 (7)	0.56225 (11)	0.0514 (4)
N3	0.9470 (5)	0.17696 (9)	0.17367 (11)	0.0593 (5)
C1	0.6529 (6)	0.14026 (10)	0.89705 (15)	0.0665 (6)
H1	0.7013	0.1697	0.9476	0.080*
C2	0.4961 (6)	0.08178 (10)	0.92062 (15)	0.0649 (6)
H2	0.4409	0.0721	0.9853	0.078*
C3	0.4229 (5)	0.03823 (10)	0.84726 (14)	0.0608 (5)
H3	0.3171	−0.0018	0.8611	0.073*
C4	0.5083 (5)	0.05437 (9)	0.75229 (13)	0.0515 (5)
H4	0.4605	0.0256	0.7008	0.062*
C5	0.6660 (5)	0.11411 (8)	0.73519 (12)	0.0460 (4)
C6	0.7641 (5)	0.13469 (8)	0.63552 (13)	0.0488 (5)
H6	0.8641	0.1758	0.6265	0.059*
C7	0.7881 (5)	0.12104 (8)	0.46689 (12)	0.0453 (4)
C8	0.9466 (5)	0.07832 (8)	0.40174 (13)	0.0508 (5)
H8	1.0149	0.0367	0.4228	0.061*
C9	1.0034 (5)	0.09701 (9)	0.30649 (13)	0.0506 (5)

H9	1.1141	0.0688	0.2632	0.061*
C10	0.8940 (5)	0.15815 (8)	0.27591 (12)	0.0459 (5)
C11	0.7340 (5)	0.20177 (8)	0.33848 (13)	0.0489 (5)
H11	0.6609	0.2428	0.3163	0.059*
C12	0.6854 (5)	0.18309 (8)	0.43442 (13)	0.0494 (5)
H12	0.5828	0.2122	0.4780	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1297 (16)	0.1088 (13)	0.0488 (9)	0.0354 (12)	0.0238 (9)	−0.0004 (9)
O2	0.1152 (14)	0.0682 (10)	0.0575 (9)	0.0082 (9)	0.0074 (8)	0.0176 (8)
N1	0.0777 (12)	0.0518 (9)	0.0473 (9)	0.0002 (8)	−0.0048 (8)	−0.0048 (7)
N2	0.0641 (11)	0.0471 (8)	0.0431 (9)	−0.0009 (7)	0.0031 (7)	−0.0005 (7)
N3	0.0723 (12)	0.0635 (11)	0.0421 (9)	−0.0019 (9)	0.0024 (8)	0.0009 (8)
C1	0.0924 (17)	0.0614 (13)	0.0455 (12)	0.0092 (12)	−0.0062 (11)	−0.0079 (9)
C2	0.0821 (16)	0.0690 (14)	0.0438 (11)	0.0121 (12)	0.0072 (10)	0.0064 (10)
C3	0.0689 (14)	0.0559 (11)	0.0576 (13)	−0.0003 (10)	0.0044 (10)	0.0096 (10)
C4	0.0591 (12)	0.0471 (11)	0.0483 (11)	0.0026 (9)	−0.0018 (8)	−0.0016 (8)
C5	0.0531 (11)	0.0421 (9)	0.0427 (10)	0.0063 (8)	−0.0015 (8)	−0.0017 (8)
C6	0.0544 (12)	0.0422 (9)	0.0497 (11)	−0.0014 (8)	−0.0001 (9)	0.0002 (8)
C7	0.0542 (11)	0.0413 (9)	0.0402 (10)	−0.0055 (8)	−0.0001 (8)	−0.0005 (7)
C8	0.0680 (13)	0.0385 (9)	0.0459 (10)	0.0044 (9)	−0.0015 (9)	−0.0013 (8)
C9	0.0595 (12)	0.0473 (10)	0.0449 (10)	0.0058 (9)	0.0026 (9)	−0.0085 (8)
C10	0.0529 (12)	0.0460 (10)	0.0390 (10)	−0.0046 (8)	0.0003 (8)	−0.0006 (8)
C11	0.0615 (12)	0.0375 (9)	0.0476 (11)	0.0013 (8)	0.0000 (8)	0.0000 (8)
C12	0.0608 (12)	0.0423 (10)	0.0452 (10)	0.0018 (9)	0.0053 (8)	−0.0055 (8)

Geometric parameters (Å, º)

O1—N3	1.219 (2)	C4—C5	1.380 (3)
O2—N3	1.216 (2)	C5—C6	1.474 (3)
N1—C1	1.330 (3)	C6—H6	0.9300
N1—C5	1.340 (2)	C7—C8	1.388 (2)
N2—C6	1.262 (2)	C7—C12	1.393 (2)
N2—C7	1.413 (2)	C8—H8	0.9300
N3—C10	1.461 (2)	C8—C9	1.372 (3)
C1—H1	0.9300	C9—H9	0.9300
C1—C2	1.374 (3)	C9—C10	1.376 (2)
C2—H2	0.9300	C10—C11	1.380 (2)
C2—C3	1.363 (3)	C11—H11	0.9300
C3—H3	0.9300	C11—C12	1.376 (3)
C3—C4	1.378 (3)	C12—H12	0.9300
C4—H4	0.9300		
C1—N1—C5	116.52 (17)	N2—C6—H6	119.2
C6—N2—C7	119.98 (15)	C5—C6—H6	119.2
O1—N3—C10	118.14 (17)	C8—C7—N2	118.10 (15)

O2—N3—O1	122.71 (16)	C8—C7—C12	119.28 (16)
O2—N3—C10	119.14 (17)	C12—C7—N2	122.47 (16)
N1—C1—H1	118.0	C7—C8—H8	119.8
N1—C1—C2	124.10 (19)	C9—C8—C7	120.47 (16)
C2—C1—H1	118.0	C9—C8—H8	119.8
C1—C2—H2	120.7	C8—C9—H9	120.5
C3—C2—C1	118.63 (19)	C8—C9—C10	119.04 (16)
C3—C2—H2	120.7	C10—C9—H9	120.5
C2—C3—H3	120.5	C9—C10—N3	118.69 (16)
C2—C3—C4	118.98 (19)	C9—C10—C11	122.07 (16)
C4—C3—H3	120.5	C11—C10—N3	119.24 (16)
C3—C4—H4	120.7	C10—C11—H11	120.8
C3—C4—C5	118.57 (17)	C12—C11—C10	118.40 (15)
C5—C4—H4	120.7	C12—C11—H11	120.8
N1—C5—C4	123.20 (17)	C7—C12—H12	119.6
N1—C5—C6	115.24 (16)	C11—C12—C7	120.71 (16)
C4—C5—C6	121.55 (16)	C11—C12—H12	119.6
N2—C6—C5	121.55 (16)		

O1—N3—C10—C9	−5.2 (3)	C3—C4—C5—C6	−179.92 (17)
O1—N3—C10—C11	175.38 (18)	C4—C5—C6—N2	−1.8 (3)
O2—N3—C10—C9	174.23 (18)	C5—N1—C1—C2	0.1 (3)
O2—N3—C10—C11	−5.2 (3)	C6—N2—C7—C8	139.41 (19)
N1—C1—C2—C3	−0.1 (3)	C6—N2—C7—C12	−45.1 (3)
N1—C5—C6—N2	178.44 (17)	C7—N2—C6—C5	175.13 (15)
N2—C7—C8—C9	175.98 (17)	C7—C8—C9—C10	−1.4 (3)
N2—C7—C12—C11	−174.32 (16)	C8—C7—C12—C11	1.1 (3)
N3—C10—C11—C12	179.77 (15)	C8—C9—C10—N3	−178.34 (16)
C1—N1—C5—C4	0.0 (3)	C8—C9—C10—C11	1.1 (3)
C1—N1—C5—C6	179.76 (17)	C9—C10—C11—C12	0.3 (3)
C1—C2—C3—C4	−0.1 (3)	C10—C11—C12—C7	−1.5 (3)
C2—C3—C4—C5	0.2 (3)	C12—C7—C8—C9	0.3 (3)
C3—C4—C5—N1	−0.2 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O1^{i}	0.93	2.89	3.510 (3)	125
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