

2-Methyl-6-nitroaniline

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Key indicators

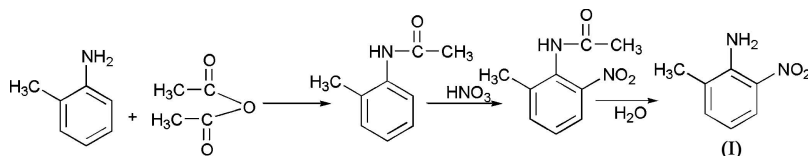
Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.037
 wR factor = 0.107
Data-to-parameter ratio = 11.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_7\text{H}_8\text{N}_2\text{O}_2$, the molecules are linked through $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds, forming an extended supramolecule, which contributes to the stability of the structure in the solid state. There are two molecules in the asymmetric unit.

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Comment

The syntheses of new intentionally designed crystal structures are part of a major strand of modern chemistry (Belloni *et al.*, 2005; Tynan *et al.*, 2005). Metal complexes of Schiff bases have attracted much attention because they can be utilized as model compounds for the active centres in various enzymes and proteins (Kahwa *et al.*, 1986; Santos *et al.*, 2001). One of the aims of crystal engineering is to establish control over the preparation of crystalline solid materials so that their subsequent architecture and properties are predictable. In order to investigate a crystal structure with strong intermolecular bonding that might provide useful information in the field of crystal engineering, we report here the synthesis and the molecular and crystal structures of the title compound (I).



A view of the two molecules of the asymmetric unit of (I) is shown in Fig. 1, and selected bond lengths and angles are reported in Table 1. They are all within the normal ranges for such values. The molecules are linked through $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds (Table 2), forming a supramolecule which leads to a stable crystal structure. Fig. 2 shows a portion of this extensively hydrogen-bonded supramolecular assembly.

Experimental

o-Methylaniline (107 ml, 0.1 mol) was added to a solution of acetic anhydride (600 ml, 0.1 mol) and the mixture was stirred vigorously at 320 K for 1 h. Upon cooling to 273 K, a solid appeared as a paste. Concentrated nitric acid (127 ml) was then added and the temperature maintained at 283–288 K. Fuming nitric acid (70 ml) was added and stirring continued for 10 min. The mixture was poured into ice-water (3 l) and the solvent was removed. The residue was refluxed with hydrochloric acid (2 mol l⁻¹; 500 ml) for 3 h (Rabjohn, 1963). The solvent was removed and the residue recrystallized from ethanol. The product was isolated and then dried *in vacuo* to give pure (I) in 65% yield. Yellow single crystals suitable for X-ray analysis were

obtained by slow evaporation of an *N,N*-dimethylformamide solution of (I).

Crystal data

$C_7H_8N_2O_2$
 $M_r = 152.15$
 Monoclinic, $P2_1/c$
 $a = 8.9844$ (16) Å
 $b = 11.359$ (2) Å
 $c = 14.785$ (3) Å
 $\beta = 103.814$ (2)°
 $V = 1465.1$ (5) Å³
 $Z = 8$

$D_x = 1.380$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2333 reflections
 $\theta = 2.9$ – 23.4 °
 $\mu = 0.10$ mm⁻¹
 $T = 294$ (2) K
 Block, yellow
 $0.22 \times 0.16 \times 0.14$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.968$, $T_{max} = 0.986$
 7772 measured reflections

2589 independent reflections
 1931 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.014$
 $\theta_{max} = 25.0$ °
 $h = -9 \rightarrow 10$
 $k = -13 \rightarrow 13$
 $l = -15 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.107$
 $S = 1.04$
 2589 reflections
 217 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.1509P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.11$ e Å⁻³
 $\Delta\rho_{min} = -0.17$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1–N1	1.2316 (17)	N2–H2A	0.92 (2)
O2–N1	1.2368 (17)	N2–H2B	0.84 (2)
O3–N3	1.2208 (19)	N3–C13	1.434 (2)
O4–N3	1.2393 (19)	N4–C14	1.349 (2)
N1–C4	1.4312 (18)	N4–H4A	1.02 (3)
N2–C3	1.346 (2)	N4–H4B	0.902 (19)
O1–N1–O2	120.81 (13)	O3–N3–O4	120.65 (15)
O1–N1–C4	119.33 (13)	O3–N3–C13	119.87 (16)
O2–N1–C4	119.86 (12)	O4–N3–C13	119.47 (15)
C3–N2–H2A	116.4 (13)	N2–C3–C4	123.94 (14)
C3–N2–H2B	121.4 (14)	N2–C3–C2	119.31 (14)
H2A–N2–H2B	122.0 (19)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4–H4B \cdots O1	0.902 (19)	2.341 (19)	3.161 (2)	151.2 (16)
N4–H4A \cdots O4	1.02 (3)	1.84 (2)	2.616 (2)	130 (2)
N2–H2B \cdots O4 ⁱ	0.84 (2)	2.38 (2)	3.151 (2)	152.6 (18)
N2–H2A \cdots N1	0.92 (2)	2.55 (2)	2.915 (2)	103.8 (14)
N2–H2A \cdots O2	0.92 (2)	1.90 (2)	2.607 (2)	131.4 (17)

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

All C-bound H atoms were positioned geometrically and refined using the riding-model approximation, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to N and O atoms were located in a difference Fourier map and refined freely.

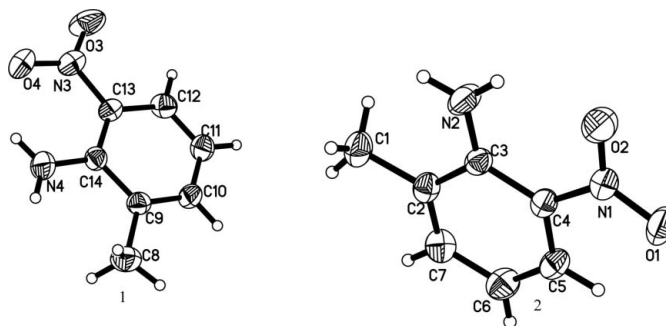


Figure 1

The asymmetric unit of the title compound, (I), with 30% probability displacement ellipsoids.

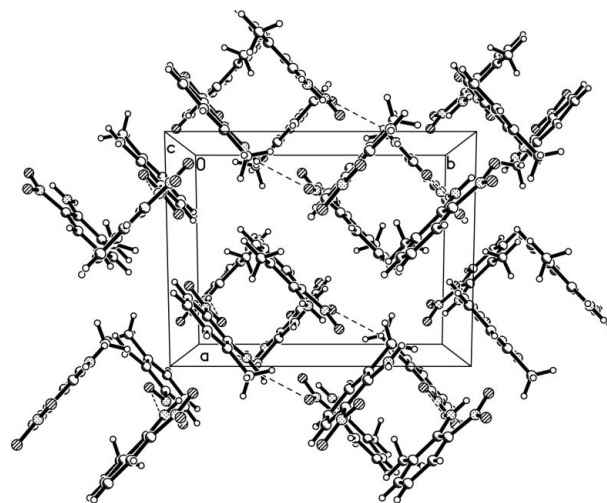


Figure 2

A view down the c axis of a portion of the crystal structure of (I), showing the extensive intermolecular hydrogen-bonding interactions (dashed lines).

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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