

## 4-Methyl-2-nitroaniline

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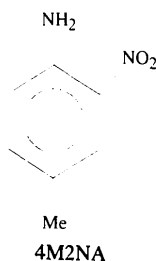
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### Abstract

The crystal structure of the title compound (C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>) has been determined by single-crystal X-ray diffraction at room temperature. The molecule is not planar, with dihedral angles of 18.0(36)° between the amino group and the aromatic ring, and 3.3(2)° between the nitro group and the ring. The molecular geometry is stabilized by an intramolecular hydrogen bond. The crystal packing involves two intermolecular hydrogen bonds that induce the formation of infinite polar chains.

### Comment

The formation of weak hydrogen bonds seems to have a decisive influence on the molecular organization of nitroanilines (Panunto, Urbánczyk-Lipkowska, Johnson & Etter, 1987). It has been proposed that N—H...O three-centre interactions between the amino and nitro groups are responsible for the formation of polar chains, not only in the solid state but also in solution, even when the interactions are longer than the sum of the van der Waals radii. Therefore, the appropriate selection and location of substituents might provide a means of obtaining non-centrosymmetric materials. The obtention of non-centrosymmetric crystals is essential for non-linear optical behaviour. An exceptionally large linear electro-optical effect (Lipscomb, Garito & Narang, 1981) and second-harmonic coefficient (Levine, Bethea, Thurmond, Lynch & Bernstein, 1979) have been observed in 2-methyl-4-nitroaniline (MNA). For a deeper understanding of the parameters that govern the molecular aggregation and the macroscopic properties of nitroanilines, the structures of 4-methyl-2-nitroaniline (4M2NA), an isomer of MNA, has been solved from diffractometric X-ray single-crystal data.



A view of the molecule with atomic labelling and displacement ellipsoids is shown in Fig. 1. The aromatic ring is essentially planar. This is confirmed by the small value of the total puckering amplitude (Cremer & Pople, 1975),  $QT = 0.008(3)$ . The amino group is rotated out of the ring plane; the dihedral angle between the amino group and the mean plane of the ring is 18.0(3.6)°. The nitro group is slightly twisted out of the mean ring plane by 3.3(2)°. The amino and nitro N atoms are displaced out of the ring plane by 0.035(4) and 0.034(3) Å, respectively.

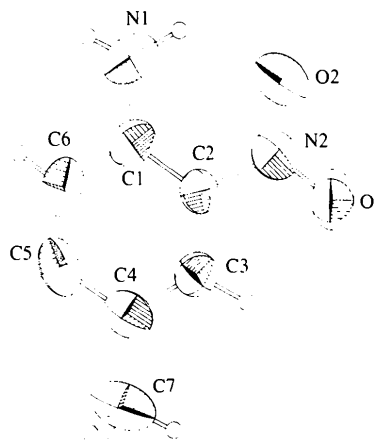


Fig. 1. An ORTEP (Johnson, 1976) view of the molecule showing the atomic labelling and 50% probability ellipsoids.

The C1—N1 bond length, 1.354(4) Å, is similar to that in MNA, 1.353(3) Å (Lipscomb, Garito & Narang, 1981) and in 2,4-dinitroaniline, 1.352(5) Å (Prasad, Gabe & Le Page, 1981), but shorter than the value found in 2-methyl-5-nitroaniline (2M5NA) (Ellena, Punte & Rivero, 1996), 1.369(6) Å. The C—NO<sub>2</sub> bond length, 1.434(3) Å, is similar to that in 2,4-dinitroaniline, 1.442(5) Å. Although this bond length is slightly larger than that found in MNA, 1.422(3) Å, it is shorter than the mean value, 1.471(2) Å, observed by Domenicano *et al.* (1989) for the C—N bond length in nitrobenzene derivatives, for which the substituents were chosen to avoid conjugation. The C—NH<sub>2</sub> and C—NO<sub>2</sub> bond lengths in 4M2NA indicate conjugation between the amino and nitro substituents. A comparison between the geometry of the title compound and that of *o*-nitroaniline has not been considered owing to the poor quality of the *o*-nitroaniline data (Dhaneshwar, Tavale & Pant, 1978). An analysis of the nitro group geometry shows that the N—O bond lengths, N2—O1 = 1.232(3) and N2—O2 = 1.235(3) Å, are slightly larger than the mean value obtained by Domenicano *et al.* (1989), 1.223(3) Å, and larger than the mean value obtained from 334 nitrobenzene derivatives surveyed from the 1987 release of the CSD (Allen, Kennard & Taylor, 1983), 1.218(11) Å. The bond angle O1—N2—O2, 121.1(3)°, is smaller than the mean values, 123.7(9)° (Allen *et al.*, 1983) and

124.3 (1)° (Domenicano *et al.*, 1989), but larger than the average, 118.9°, obtained for 44 nitroaniline NO<sub>2</sub> groups involved in three-centre hydrogen bonds (Panunto *et al.*, 1987). In 4M2NA, the molecular geometry is stabilized by an intramolecular hydrogen bond between the NH<sub>2</sub> and the *o*-NO<sub>2</sub> groups [H11···O2 = 1.91 (4) Å].

The additivity of the effect of the substituents on the molecular geometry was analyzed using the angular parameters of Domenicano & Murray-Rust (1979). In 4M2NA, the value of the non-additivity parameters, NAP (Krygowsky, 1990) {NAP = Σ[(θ<sub>exp</sub> - θ<sub>calc</sub>)<sup>2</sup>]<sup>1/2</sup>, where θ are endocyclic angles, and σ = [Σ(σ<sub>calc</sub> + σ<sub>exp</sub>)<sup>2</sup>]<sup>1/2</sup>} is 7.1 (σ = 1.7). This value shows a strong interaction between the substituents, in accordance with the above-mentioned intramolecular hydrogen bond.

The molecules of 4M2NA exhibit a centrosymmetric organization. The title compound, like other nitroanilines (Panunto *et al.*, 1987), has an amino proton situated between both O atoms of the nitro group, inducing the formation of infinite chains with three-centre interactions (bifurcated hydrogen bonds). The amino proton that is not locked in a three-centre interaction forms the intramolecular hydrogen bond. The interchain interactions are weak (C7—H73···O1). The packing arrangement of chains in 4M2NA, similar to that observed in *o*-nitroaniline, is shown in Fig. 2.

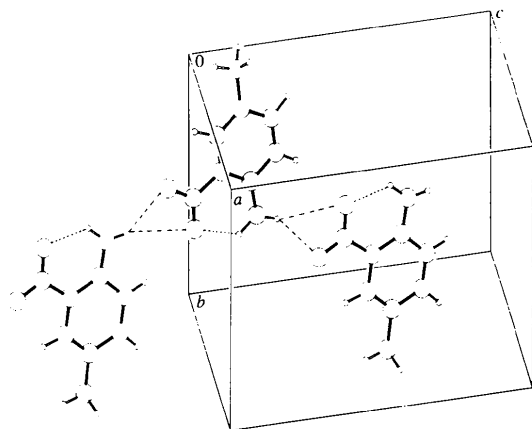


Fig. 2. The packing arrangement of chains in the 4-methyl-2-nitroaniline crystal.

**Experimental**

The title compound was acquired from a commercial source (Janssen). The crystal used for data collection was obtained by slow evaporation from an acetone-saturated solution at 298 K.

*Crystal data*

C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 152.15  
 Monoclinic  
 C2/c  
*a* = 13.401 (4) Å  
*b* = 9.103 (2) Å  
*c* = 12.375 (8) Å  
 β = 103.84 (3)°

Mo *K*α radiation  
 λ = 0.71073 Å  
 Cell parameters from 16 reflections  
 θ = 9–18.5°  
 μ = 0.104 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism

*V* = 1465.7 (11) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.379 Mg m<sup>-3</sup>

0.3 × 0.2 × 0.12 mm  
 Orange

*Data collection*

CAD-4 diffractometer  
 θ/2θ scans  
 Absorption correction: none  
 1428 measured reflections  
 1428 independent reflections  
 791 observed reflections  
 [*I* > 2σ(*I*)]

θ<sub>max</sub> = 27.96°  
*h* = -17 → 17  
*k* = 0 → 12  
*l* = 0 → 16  
 1 standard reflection  
 frequency: 100 min  
 intensity decay: 3%

*Refinement*

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.0533  
*wR*(*F*<sup>2</sup>) = 0.0937  
*S* = 1.380  
 1077 reflections  
 119 parameters  
 All H-atom parameters refined except methyl H atoms (riding)  
*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + 1.25*P*]  
 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.007

Δρ<sub>max</sub> = 0.145 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.152 e Å<sup>-3</sup>  
 Extinction correction: SHELXL93 (Sheldrick, 1993)  
 Extinction coefficient: 0.00063 (8)  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
O1	0.1015 (2)	0.1897 (3)	1.1253 (2)	0.0910 (8)
O2	0.1164 (2)	-0.0065 (3)	1.0340 (2)	0.0855 (8)
N2	0.1118 (2)	0.1286 (3)	1.0397 (2)	0.0651 (7)
N1	0.1303 (3)	0.0084 (4)	0.8276 (3)	0.0867 (10)
C2	0.1190 (2)	0.2184 (3)	0.9467 (2)	0.0498 (7)
C1	0.1270 (2)	0.1545 (3)	0.8469 (2)	0.0593 (8)
C6	0.1358 (3)	0.2548 (5)	0.7637 (3)	0.0745 (10)
C5	0.1361 (3)	0.4010 (5)	0.7782 (3)	0.0745 (10)
C4	0.1275 (2)	0.4630 (3)	0.8797 (3)	0.0645 (9)
C3	0.1183 (2)	0.3694 (3)	0.9615 (2)	0.0569 (8)
C7	0.1301 (3)	0.6265 (4)	0.8942 (3)	0.0964 (13)

Table 2. Geometric parameters (Å, °)

O1—N2	1.232 (3)	C1—C6	1.401 (4)
O2—N2	1.235 (3)	C6—C5	1.343 (5)
N2—C2	1.434 (3)	C5—C4	1.406 (4)
N1—C1	1.354 (4)	C4—C3	1.351 (4)
C2—C3	1.387 (4)	C4—C7	1.498 (4)
C2—C1	1.392 (4)		
O1—N2—O2	121.1 (3)	C2—C1—C6	114.7 (3)
O1—N2—C2	118.4 (3)	C5—C6—C1	123.0 (3)
O2—N2—C2	120.5 (3)	C6—C5—C4	121.3 (3)
C3—C2—C1	122.4 (3)	C3—C4—C5	117.2 (3)
C3—C2—N2	117.1 (3)	C3—C4—C7	122.7 (3)
C1—C2—N2	120.6 (3)	C5—C4—C7	120.1 (3)
N1—C1—C2	125.4 (3)	C4—C3—C2	121.4 (3)
N1—C1—C6	119.9 (3)		

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N1—H11···O2	0.96 (4)	1.91 (4)	2.609 (4)	127 (3)
N1—H12···O1 <sup>i</sup>	0.83 (4)	2.28 (4)	3.034 (4)	150 (3)
N1—H12···O2 <sup>i</sup>	0.83 (4)	2.80 (4)	3.593 (5)	160 (4)

Symmetry code: (i) *x*, -*y*, *z* - ½.

The structure was solved by direct methods with *SHELXS86* (Sheldrick, 1985). The Fourier map obtained showed all non-H atoms. All H atoms were found on successive Fourier difference maps. The model, including the H atoms, was refined by full-matrix least squares on  $F^2$  by means of *SHELXL93* (Sheldrick, 1993). Isotropic thermal parameters were used in the first steps and anisotropic ones afterwards, except for the H atoms, which were refined isotropically with overall isotropic temperature factors for the H atoms of the benzene ring, and the amino and the methyl groups. The methyl H atoms were refined riding over the bonded C atoms. Calculations were carried out on a 386 PC using the programs *SHELXS86*, *SHELXL93*, *PLUTON* (Spek, 1990) and *PARST* (Nardelli, 1983).

Data collection: *CAD-4* (Enraf–Nonius, 1993). Cell refinement: *CAD-4*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86*. Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *PLUTON*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1996). **C52**, 2076–2078

## 9-Benzyl-7-[(*E*)-2-butenyl]-2,3-dihydro-6-hydroxy-1,3-dimethylpyrimido[2,1-*f*]-purine-4,8(1*H*,9*H*)-dione

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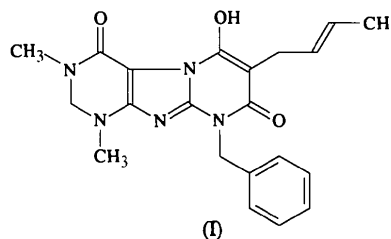
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## Abstract

The two independent molecules of C<sub>21</sub>H<sub>23</sub>N<sub>5</sub>O<sub>3</sub> in the asymmetric unit of the title compound possess similar conformations. In each molecule, an almost planar purine ring is fused to a reduced pyrimidine ring. The dihedral angles between the fused-ring plane and phenyl-ring plane of the molecules are different [115.5(2)° for molecule (1) and 68.0(1)° for molecule (2)]. The O14...O13 distances of 2.478(5) Å for molecule (1) and 2.467(5) Å for molecule (2) indicate the presence of intramolecular hydrogen bonding.

## Comment

The title compound, (I), is a member of a series of substituted 2,3-dihydro-6-hydroxypyrimido[2,1-*f*]purine-4,8(1*H*,9*H*)-diones, which exhibit anti-inflammatory activity (Kaminski *et al.*, 1989) in the adjuvant-induced arthritis rat model. It is of interest to study the effect of substituents on the molecular geometry and conformation responsible for biological activity. The crystal structure analysis of (I) was undertaken in order to establish its structure and connectivity in the solid state and forms part of a wider investigation (Das *et al.*, 1994) of those compounds.



The molecular structure of (I) consists of an almost planar purine ring fused to a reduced pyrimidine ring,