

Hydrogen bonding in C-methylated nitroanilines: the three-dimensional framework structure of 2-methyl-4-nitroaniline

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Molecules of 2-methyl-4-nitroaniline, C₇H₈N₂O₂, act as double donors and as double acceptors of N—H···O hydrogen bonds [N···O 3.117 (3) and 3.239 (3) Å; N—H···O 169 and 136°]. The molecules are thereby linked into a three-dimensional framework.

Comment

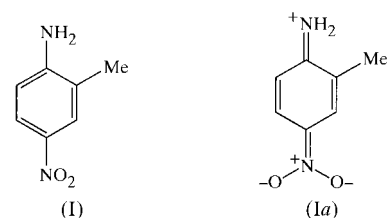
The introduction of C-methyl groups into 2- or 3-nitroanilines gives rise to patterns of supramolecular aggregation very different from those observed in the unsubstituted analogues (Cannon *et al.*, 2001). In this paper, we report the structure of 2-methyl-4-nitroaniline, (I), where again the supramolecular structure is markedly different from that found in 4-nitroaniline itself [Cambridge Structural Database (CSD) refcode (Allen & Kennard, 1993) NANILIO2 (Tonogaki *et al.*, 1993)]. Compound (I) is listed in the CSD (BAJCIY; Lipscomb *et al.*, 1981), but there are no atomic coordinates recorded either in the CSD or in the original report, nor does this report discuss the supramolecular aggregation. It seems clear, however, from both the cell dimensions and the space group that the structure reported here is for the same polymorph of (I) as BAJCIY.

The molecules of (I) (Fig. 1) lie in general positions and each acts as a double donor and as a double acceptor of N—H···O hydrogen bonds. The three-dimensional structure is readily analysed in terms of two independent C(8) chain motifs (Bernstein *et al.*, 1995). The amino N1 atom at (x, y, z) acts as a hydrogen-bond donor, *via* H1B, to O2 in the molecule at (½ + x, -y, 1 + z), while N1 at (½ + x, -y, 1 + z) in turn acts as donor to O2 at (1 + x, y, 2 + z); this hydrogen bond thus produces a zigzag chain running parallel to the [102] direction

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and generated by the glide plane at y = 0. At the same time, N1 at (x, y, z) also acts as donor, this time *via* H1A, to O1 in the molecule at (½ + x, ½ + y, ½ + z), so producing by translation a chain running parallel to the [111] direction; the glide plane at y = 0 generates an entirely similar chain parallel to [1̄1̄1]. The combination of the [102] and [111] chains generates continuous sheets parallel to (2̄11) and built from a single type of R₈⁸(54) ring (Fig. 2); similarly, the combination of the [102] and [1̄1̄1] chains generates continuous sheets parallel to (211̄). Every intersection between the stacked sheets generates a [102] chain, and the molecules are thus linked into a continuous three-dimensional framework.



The structure of (I) thus differs from that of 4-nitroaniline itself (Tonogaki *et al.*, 1993) in two ways. In 4-nitroaniline, the molecules are linked by N—H···O hydrogen bonds into two-dimensional sheets, which are weakly linked by aromatic π - π -stacking interactions; in compound (I), the hydrogen-bonded structure is three-dimensional and there are no π - π -stacking interactions. The structure of (I) also differs from those of the isomeric compounds 4-methyl-2-nitroaniline, (II), and 4-methyl-3-nitroaniline, (III), in both of which the supramolecular structure is one-dimensional; the supramolecular structure of (II) consists of chains, while that of (III) contains both simple chains and molecular ladders (Cannon *et al.*, 2001). Thus, very simple nitroanilines can have supramolecular structures in one, two or three dimensions.

The C—NH₂ bond in (I) (Table 1) is marginally longer than the analogous bonds in both (II) and 3,4-dimethyl-2-nitroaniline, (IV), in each of which Z' = 2 (Cannon *et al.*, 2001) [range 1.341 (5)–1.347 (4) Å, mean 1.345 (5) Å], but significantly shorter than those in (III), where Z' = 4 [range 1.370 (2)–1.380 (2) Å, mean 1.376 (2) Å]. Likewise, the C—NO₂ bond in (I) is slightly longer than those in (II) and (IV) [range 1.413 (4)–1.437 (5) Å, mean 1.426 (3) Å], but much shorter than those in (III) [range 1.465 (2)–1.469 (2) Å, mean 1.467 (2) Å]. Despite this, the C—C bond lengths in the aromatic ring of (I) indicate only a modest contribution from the quinonoid form (Ia).

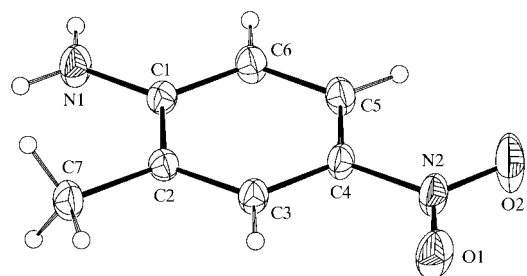


Figure 1

The molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

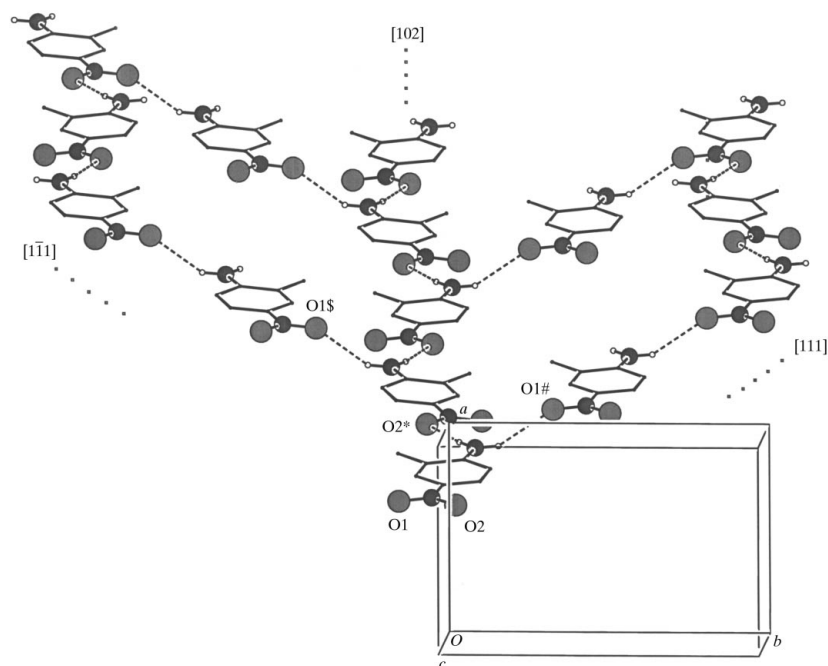


Figure 2
Part of the crystal structure of (I) showing the intersection of [102] chains with [111] and $[1\bar{1}1]$ chains. Atoms marked with an asterisk (*), hash (#) or dollar (\$) sign are at the symmetry positions $(\frac{1}{2} + x, -y, 1 + z)$, $(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$ and $(1 + x, -\frac{1}{2} - y, \frac{3}{2} + z)$, respectively. H atoms bonded to C atoms have been omitted for clarity.

Experimental

A sample of compound (I) was obtained from Aldrich. Crystals suitable for single-crystal X-ray diffraction were grown from a solution in ethanol.

Crystal data

| | |
|-------------------------------|---|
| $C_7H_8N_2O_2$ | $D_x = 1.391 \text{ Mg m}^{-3}$ |
| $M_r = 152.15$ | Mo $K\alpha$ radiation |
| Monoclinic, Ia | Cell parameters from 1316 reflections |
| $a = 7.6113(5) \text{ \AA}$ | $\theta = 3.04\text{--}32.54^\circ$ |
| $b = 11.6304(7) \text{ \AA}$ | $\mu = 0.104 \text{ mm}^{-1}$ |
| $c = 8.2286(5) \text{ \AA}$ | $T = 150(2) \text{ K}$ |
| $\beta = 94.050(2)^\circ$ | Block, orange |
| $V = 726.60(8) \text{ \AA}^3$ | $0.30 \times 0.20 \times 0.20 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|--|--|
| Bruker SMART 1000 CCD diffractometer | 1037 reflections with $I > 2\sigma(I)$ |
| φ and ω scans with κ offsets | $R_{\text{int}} = 0.032$ |
| Absorption correction: multi-scan (SADABS; Bruker, 1997) | $\theta_{\text{max}} = 32.54^\circ$ |
| $T_{\text{min}} = 0.969$, $T_{\text{max}} = 0.979$ | $h = -11 \rightarrow 11$ |
| 4272 measured reflections | $k = -17 \rightarrow 14$ |
| 1316 independent reflections | $l = -12 \rightarrow 12$ |
| | Intensity decay: negligible |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | $w = 1/[\sigma^2(F_o^2) + (0.0735P)^2]$ |
| $wR(F^2) = 0.113$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.995$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 1316 reflections | $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$ |
| 101 parameters | $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$ |

Compound (I) is monoclinic and the systematic absences permitted Cc and $C2/c$ as possible space groups. The unit-cell dimensions were consistent with $Z = 4$, so space group Cc was chosen and confirmed by the successful structure solution and refinement. Before the final refinement, the space-group setting was transformed

Table 1

Selected geometric parameters (\AA).

| | | | |
|-------|-----------|-------|-----------|
| C1—C2 | 1.415 (2) | C1—N1 | 1.358 (2) |
| C2—C3 | 1.381 (2) | C4—N2 | 1.433 (2) |
| C3—C4 | 1.398 (2) | N2—O1 | 1.233 (2) |
| C4—C5 | 1.387 (3) | N2—O2 | 1.231 (2) |
| C5—C6 | 1.377 (3) | C2—C7 | 1.505 (2) |
| C6—C1 | 1.405 (2) | | |

from the standard setting Cc , in which $\beta = 139.104(2)^\circ$, to the non-standard setting Ia , in which $\beta = 94.050(2)^\circ$. H atoms were treated as riding with $N-H = 0.86 \text{ \AA}$ and $C-H = 0.93$ (aromatic) or 0.96 \AA (methyl). In the absence of any significant anomalous scatterers, Friedel equivalents were merged before refinement. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *XPREP* (Bruker, 1997); cell refinement: *XPREP*; data reduction: *XPREP*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97* and *WordPerfect* macro *PRP-KAPPA* (Ferguson, 1999).

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------|-------|-------------|-------------|---------------|
| $N1-H1A\cdots O1^i$ | 0.86 | 2.56 | 3.239 (3) | 136 |
| $N1-H1B\cdots O2^{ii}$ | 0.86 | 2.27 | 3.117 (3) | 169 |

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

X-ray data were collected at Aberdeen using a Bruker SMART 1000 CCD diffractometer. The authors thank Dr W. T. A. Harrison for all his help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1442). Services for accessing these data are described at the back of the journal.

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