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Hydrogen bonding in *C*-methylated nitroanilines: a room-temperature monoclinic polymorph of 4-methyl-3-nitroaniline with $Z' = 2$

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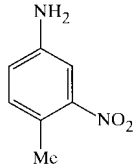
The title compound, $C_7H_8N_2O_2$, is monoclinic (space group $P2_1/n$) at 295 (2) K with $Z' = 2$. The two types of molecule form independent $C(7)$ chains, and the structure is related to that of the low-temperature triclinic polymorph, where $Z' = 4$ in $P\overline{1}$, by a simple displacive transformation.

Comment

When crystallized from ethanol, 4-methyl-3-nitroaniline, (I), is triclinic $P\overline{1}$ at 150 (2) K with $Z' = 4$ (Cannon *et al.*, 2001). Of the four independent molecules, two form individual chains built from N—H···O hydrogen bonds, while the other two types combine to form molecular ladders. At ambient temperatures, however, this material is monoclinic $P2_1/n$ with $Z' = 2$. The unit-cell dimensions and the atomic coordinates indicate that the low-temperature triclinic and ambient-temperature monoclinic polymorphs are related by a simple displacive phase transformation.



(I)

The molecular dimensions of the two independent molecules in the monoclinic polymorph (Fig. 1) are very similar (Table 1) and the C—C bond lengths show a significant deviation of the aryl rings from regular hexagons; this feature was also observed in the triclinic polymorph. The two molecules do, however, differ markedly in the twist of the nitro groups out of the plane of the adjacent rings (Table 1); this difference alone precludes the possibility of any further symmetry.

Each molecule acts as a single donor and single acceptor in N—H···O hydrogen bonds (Table 2); thus, half of the N—H bonds and half of the O atoms do not participate in the hydrogen bonding, so that the sole motif of supramolecular aggregation is the formation of $C(7)$ chains (Bernstein *et al.*, 1995). Molecules of type 1 and 2, containing atoms N11 and N21, respectively, each act as hydrogen-bond donors to another molecule of the same type, so generating by translation two distinct chains, both running parallel to the [100] direction and each containing just one type of molecule (Fig. 2). Four chains of each type run through each unit cell, but there are no N—H···O or C—H···O hydrogen bonds between adjacent chains, nor are there any aromatic π–π-stacking interactions.

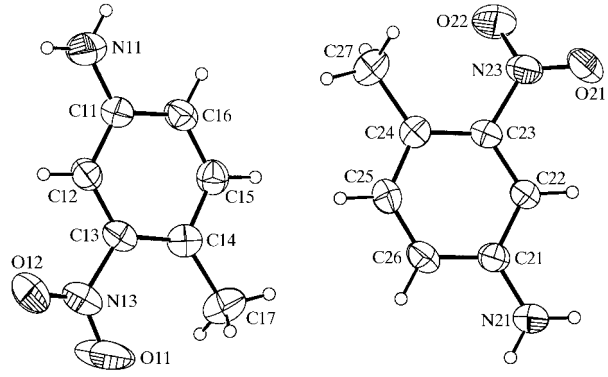


Figure 1
The two independent molecules in (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

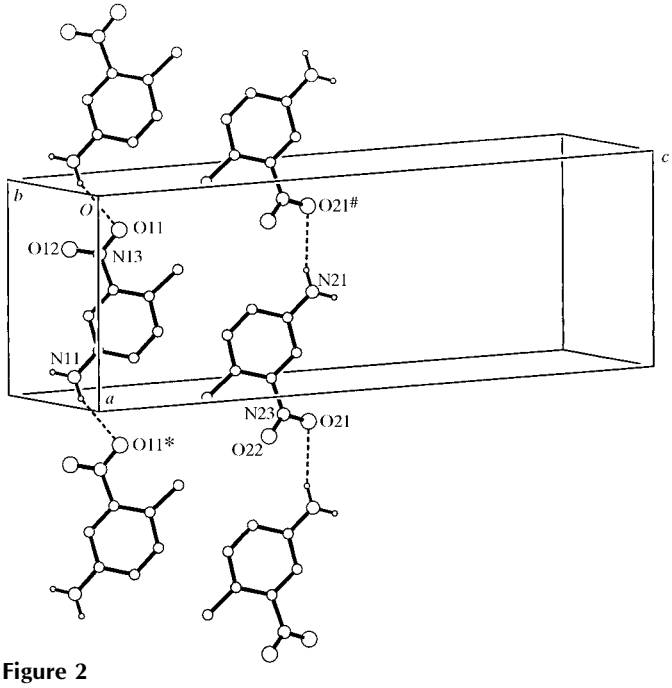


Figure 2
Part of the crystal structure of (I) showing the two independent $C(7)$ chains. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(-1 + x, y, z)$, respectively.

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The unit-cell dimensions of the triclinic and monoclinic polymorphs of (I) are very similar and the triclinic unit cell can be derived from the present monoclinic cell by means of the transformation (010, $\bar{1}00$, 001). Subject to this transformation and an origin shift, the atomic coordinates of the two forms indicate that triclinic molecules of types 1 and 2 (Cannon *et al.*, 2001) map into the monoclinic type 2 molecules at (x, y, z) and ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$), respectively, while triclinic molecules 3 and 4 map into the monoclinic type 1 molecules at ($-x$, $-y$, $-z$) and ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$), respectively. It is noteworthy that the conformations of the various molecules, as judged by the C—C—N—O torsion angles (Table 1) and particularly by the dihedral angles between the aryl rings and the C—NO_2 groups, faithfully follow this mapping. Thus, in the triclinic polymorph, molecules 1 and 2 have nitro-group twists of 31.91 (8) and 28.99 (8)°, respectively, comparable with the 32.5 (2)° twist in monoclinic type 2 molecules, while triclinic type 3 and 4 molecules have nitro-group twists of 7.91 (8) and 3.92 (8)°, respectively, compared with a twist of 7.5 (2)° in monoclinic type 1 molecules. These observations all point to a simple displacive phase transformation between the triclinic and monoclinic polymorphs.

Table 1
Selected geometric parameters (Å, °).

C11—C12	1.381 (4)	C21—C22	1.380 (4)
C12—C13	1.371 (4)	C22—C23	1.383 (4)
C13—C14	1.402 (4)	C23—C24	1.402 (3)
C14—C15	1.390 (4)	C24—C25	1.384 (4)
C15—C16	1.364 (4)	C25—C26	1.370 (4)
C16—C11	1.395 (4)	C26—C21	1.399 (3)
C11—N11	1.374 (4)	C21—N21	1.374 (4)
C13—N13	1.471 (4)	C23—N23	1.465 (3)
N13—O11	1.201 (4)	N23—O21	1.219 (3)
N13—O12	1.195 (4)	N23—O22	1.215 (3)
C14—C17	1.497 (4)	C24—C27	1.503 (4)
C12—C13—N13—O11	172.5 (4)	C22—C23—N23—O21	−31.5 (3)
C12—C13—N13—O12	−8.4 (4)	C22—C23—N23—O22	148.3 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11B···O11^{i}	0.86	2.41	3.181 (5)	150
N21—H21B···O21^{ii}	0.86	2.45	3.285 (4)	163

Symmetry codes: (i) $1+x, y, z$; (ii) $x-1, y, z$.

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. The same phase was obtained by recrystallization from CH_2Cl_2.

Crystal data

$C_7H_8N_2O_2$
M_r = 152.16
Monoclinic, $P2_1/n$
a = 8.2473 (7) Å
b = 7.5676 (7) Å
c = 23.7798 (16) Å
β = 91.717 (5)°
V = 1483.5 (2) Å^3
Z = 8
D_x = 1.363 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3128 reflections
θ = 3.2–27.5°
μ = 0.10 mm^{-1}
T = 295 (2) K
Plate, orange
0.36 × 0.18 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.951, T_{max} = 0.985
11 137 measured reflections
3128 independent reflections
1517 reflections with $I > 2\sigma(I)$
R_{int} = 0.105
θ_{max} = 27.5°
$h = -10 \rightarrow 10$
$k = -9 \rightarrow 9$
$l = -30 \rightarrow 28$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.204
S = 1.01
3128 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1003P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ was uniquely assigned from the systematic absences. H atoms were treated as riding atoms with C—H distances of 0.93 (aromatic) or 0.96 Å (methyl), and an N—H distance of 0.86 Å. The crystal quality was not high and, as expected, only *ca* 50% of the reflections were labelled 'observed' at ambient temperature.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997) and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1075). Services for accessing these data are described at the back of the journal.

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