

Christopher Glidewell,^{a*} John N. Low,^b Janet M. S. Skakle^b and James L. Wardell^c^aSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cInstituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil

Correspondence e-mail: cg@st-andrews.ac.uk

Key indicators

Single-crystal X-ray study

T = 291 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

Disorder in main residue

R factor = 0.050

wR factor = 0.130

Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.2-Methoxycarbonyl-4-nitroacetanilide: π -stacked chains linked in pairs by C—H...O hydrogen bondsMolecules of the title compound, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_5$, lie on mirror planes in space group *Ibam*. The molecules are linked into [001] chains by an aromatic π - π stacking interaction, and pairs of these chains are linked by a single C—H...O hydrogen bond.

Received 15 April 2004

Accepted 19 April 2004

Online 24 April 2004

Comment

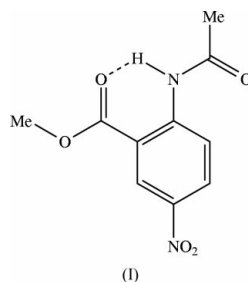
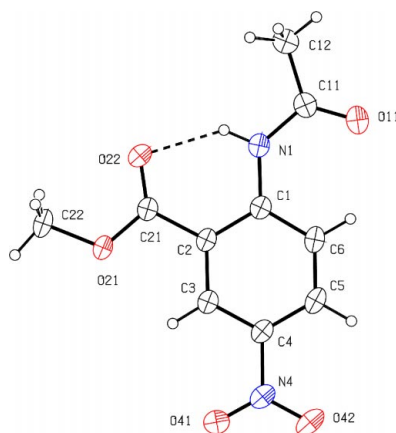
The title compound (I) (Fig. 1), crystallizes in the uncommon space group *Ibam* with $Z' = 0.5$: all of the atoms apart from the methyl H atoms lie on a mirror plane, chosen for the reference molecule as that at $z = 0.5$. Each of the H atoms in the methyl groups is disordered over two sites with equal occupancy. The inter-bond angles at N1, at C11 and at C21 (Table 1) show marked deviations from 120° , possibly indicative of repulsive non-bonded intramolecular contacts (Table 2). The bond distances show no unusual values.The molecules of compound (I) are linked into chains by a single aromatic π - π stacking interaction, and these chains are

Figure 1

The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only one orientation is shown for each methyl group.

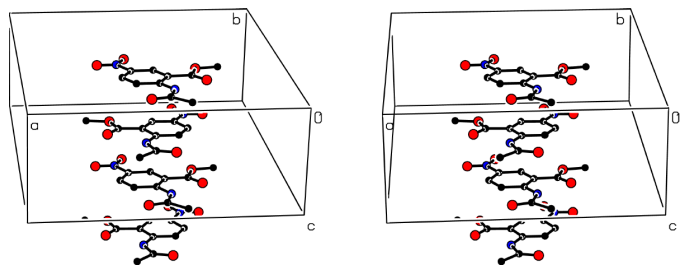


Figure 2
Stereoview of part of the crystal structure of compound (I), showing the formation of a π -stacked chain along [001]. For the sake of clarity, the H atoms have all been omitted.

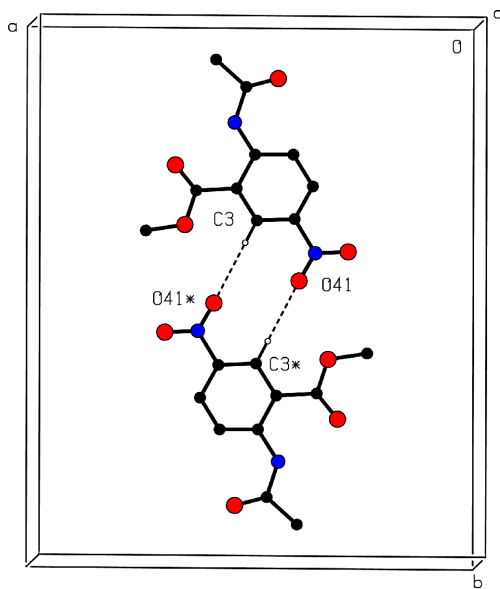


Figure 3
Part of the crystal structure of compound (I), showing the formation of the $R_2^2(10)$ motif which links the [001] chains into pairs. For the sake of clarity, the H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 0.5)$.

weakly linked in pairs by a C—H \cdots O hydrogen bond. The reference molecule at $(x, y, 0.5)$ forms π -stacking interactions with the two molecules at $(1-x, y, 0)$ and $(1-x, y, 1)$. The common interplanar spacing is $c/2$ and the ring-centroid separation is $3.634(2)$ Å, corresponding to a near-ideal centroid offset of $1.341(2)$ Å. Propagation of this interaction thus produces a chain running parallel to the [001] direction and generated by the c -glide plane at $x = 0.5$ (Fig. 2). Four chains of this type run through each unit cell; two are generated by the c -glide plane at $x = 0.5$ and lie wholly within the domain $0.25 < y < 0.75$, while the two others generated by the c -glide plane at $x = 0.0$ lie within the domain $-0.25 < x < 0.25$.

Within each domain of x , the pairs of [001] chains in the domains $0 < y < 0.5$ and $0.5 < y < 1.0$ are linked by a single C—H \cdots O hydrogen bond which, although it is rather long, is effectively linear (Table 2). Atom C3 in the molecule at $(x, y, 0.5)$ acts as donor to nitro atom O41 in the molecule at $(1-x, 1-y, 0.5)$, so forming an $R_2^2(10)$ motif generated by the twofold rotation axis along $(0.5, 0.5, z)$ (Fig. 3).

Experimental

2-Carboxymethylacetanilide was nitrated using fuming nitric acid at 273 K, following a published procedure (Adams *et al.*, 1954). The reaction mixture was poured on to ice and the resulting solid (I) was collected. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in acetone (m.p. 447–449 K).

Crystal data

$C_{10}H_{10}N_2O_5$
 $M_r = 238.20$
Orthorhombic, *Ibam*
 $a = 16.4482(14)$ Å
 $b = 19.9095(17)$ Å
 $c = 6.7549(6)$ Å
 $V = 2212.1(3)$ Å³
 $Z = 8$
 $D_x = 1.430$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 1384 reflections
 $\theta = 2.1$ – 27.5°
 $\mu = 0.12$ mm⁻¹
 $T = 291(2)$ K
Prism, colourless
 $0.43 \times 0.18 \times 0.13$ mm

Data collection

Bruker SMART 1000 CCD area detector diffractometer
 φ - ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.930$, $T_{\max} = 0.985$
7820 measured reflections

1384 independent reflections
828 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\max} = 27.5^\circ$
 $h = -21 \rightarrow 21$
 $k = -24 \rightarrow 25$
 $l = -8 \rightarrow 6$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.130$
 $S = 1.01$
1384 reflections
105 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 0.1650P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.17$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³

Table 1

Selected bond angles ($^\circ$).

C1—N1—C11	129.6 (2)	C2—C21—O21	111.55 (19)
N1—C11—O11	122.8 (2)	C2—C21—O22	125.9 (2)
N1—C11—C12	114.1 (2)	O21—C21—O22	122.5 (2)
O11—C11—C12	123.1 (2)	C21—O21—C22	117.2 (2)

Table 2

Geometric parameters (Å, $^\circ$) for hydrogen bonds and short intramolecular contacts.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O22	0.86	1.98	2.691 (2)	139
C3—H3 \cdots O41 ⁱ	0.93	2.51	3.440 (3)	180
C3—H3 \cdots O21	0.93	2.32	2.660 (3)	101
C6—H6 \cdots O11	0.93	2.23	2.854 (3)	124

Symmetry code: (i) $1-x, 1-y, z$.

All of the non-H atoms lie on mirror planes and the reference molecule was chosen to lie on the mirror plane at $z = 0.5$. The H atoms were located in difference maps and then treated as riding atoms, with C—H distances 0.93 (aromatic) or 0.95 Å (methyl) and an N—H distance of 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl groups. Each methyl group was modelled using six H-atom sites, each with 0.5 occupancy, offset by 60° intervals.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT-Plus (Bruker, 2000); data reduction: SAINT-Plus; program(s) used to solve structure: OSCAIL (McArdle, 2003) and SHELXS97 (Shel-

drick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Aberdeen using a Bruker SMART 1000 CCD diffractometer; the authors thank the University of Aberdeen for funding the purchase of the diffractometer. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

References

- Adams, R., Young, T. E. & Short, R. W. P. (1954). *J. Am. Chem. Soc.* **76**, 1114–1118.
- Bruker (2000). *SMART* (Version 5.624), *SAINT-Plus* (Version 6.02A) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Acta Cryst. (2004). E60, o852–o854 [https://doi.org/10.1107/S1600536804009195]

2-Methoxycarbonyl-4-nitroacetanilide: π -stacked chains linked in pairs by C—H \cdots O hydrogen bonds

Christopher Glidewell, John N. Low, Janet M. S. Skakle and James L. Wardell

2-Methoxycarbonyl-4-nitroacetanilide

Crystal data

C₁₀H₁₀N₂O₅

$M_r = 238.20$

Orthorhombic, *Ibam*

Hall symbol: -I 2 2c

$a = 16.4482$ (14) Å

$b = 19.9095$ (17) Å

$c = 6.7549$ (6) Å

$V = 2212.1$ (3) Å³

$Z = 8$

$F(000) = 992$

$D_x = 1.430$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1384 reflections

$\theta = 2.1$ – 27.5°

$\mu = 0.12$ mm⁻¹

$T = 291$ K

Prism, colourless

$0.43 \times 0.18 \times 0.13$ mm

Data collection

Bruker SMART 1000 CCD area detector
diffractometer

Radiation source: fine-focus sealed X-ray tube

Graphite monochromator

φ - ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2000)

$T_{\min} = 0.930$, $T_{\max} = 0.985$

7820 measured reflections

1384 independent reflections

828 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -21 \rightarrow 21$

$k = -24 \rightarrow 25$

$l = -8 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.130$

$S = 1.01$

1384 reflections

105 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 0.165P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.17$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O11	0.45219 (11)	0.10453 (9)	0.5000	0.0744 (6)	
O21	0.66067 (10)	0.37614 (9)	0.5000	0.0692 (6)	

O22	0.68212 (10)	0.26564 (8)	0.5000	0.0616 (6)	
O41	0.40462 (14)	0.47898 (12)	0.5000	0.1634 (16)	
O42	0.29482 (11)	0.42449 (11)	0.5000	0.0958 (8)	
N1	0.54959 (11)	0.18637 (9)	0.5000	0.0489 (5)	
N4	0.36872 (14)	0.42739 (12)	0.5000	0.0729 (8)	
C1	0.50391 (14)	0.24555 (11)	0.5000	0.0416 (6)	
C2	0.54480 (12)	0.30844 (11)	0.5000	0.0408 (5)	
C3	0.49928 (13)	0.36756 (12)	0.5000	0.0470 (6)	
C4	0.41495 (13)	0.36446 (12)	0.5000	0.0490 (6)	
C5	0.37413 (14)	0.30371 (13)	0.5000	0.0507 (6)	
C6	0.41814 (14)	0.24511 (12)	0.5000	0.0504 (6)	
C11	0.52385 (16)	0.12038 (12)	0.5000	0.0512 (6)	
C12	0.59167 (17)	0.07005 (13)	0.5000	0.0689 (8)	
C21	0.63546 (13)	0.31282 (11)	0.5000	0.0450 (6)	
C22	0.74801 (15)	0.38759 (15)	0.5000	0.0832 (10)	
H1	0.6015	0.1919	0.5000	0.059*	
H3	0.5254	0.4090	0.5000	0.056*	
H5	0.3176	0.3026	0.5000	0.061*	
H6	0.3908	0.2042	0.5000	0.061*	
H12A	0.6364	0.0871	0.4236	0.103*	0.50
H12B	0.5729	0.0287	0.4428	0.103*	0.50
H12C	0.6092	0.0621	0.6335	0.103*	0.50
H22A	0.7726	0.3620	0.6046	0.125*	0.50
H22B	0.7587	0.4345	0.5202	0.125*	0.50
H22C	0.7704	0.3738	0.3752	0.125*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.0529 (12)	0.0586 (11)	0.1116 (18)	-0.0126 (8)	0.000	0.000
O21	0.0310 (8)	0.0527 (10)	0.1239 (18)	-0.0032 (7)	0.000	0.000
O22	0.0367 (9)	0.0546 (10)	0.0936 (16)	0.0063 (8)	0.000	0.000
O41	0.0541 (13)	0.0527 (14)	0.383 (5)	0.0054 (10)	0.000	0.000
O42	0.0394 (11)	0.0895 (15)	0.158 (3)	0.0176 (10)	0.000	0.000
N1	0.0394 (10)	0.0479 (11)	0.0593 (14)	-0.0033 (8)	0.000	0.000
N4	0.0402 (12)	0.0643 (15)	0.114 (2)	0.0088 (11)	0.000	0.000
C1	0.0381 (12)	0.0490 (12)	0.0376 (14)	-0.0013 (9)	0.000	0.000
C2	0.0325 (11)	0.0494 (12)	0.0404 (14)	-0.0020 (9)	0.000	0.000
C3	0.0358 (12)	0.0497 (12)	0.0556 (16)	-0.0024 (10)	0.000	0.000
C4	0.0351 (12)	0.0541 (14)	0.0580 (17)	0.0029 (10)	0.000	0.000
C5	0.0314 (11)	0.0679 (16)	0.0527 (17)	-0.0019 (11)	0.000	0.000
C6	0.0369 (13)	0.0590 (15)	0.0554 (17)	-0.0090 (10)	0.000	0.000
C11	0.0522 (15)	0.0485 (14)	0.0530 (16)	-0.0055 (11)	0.000	0.000
C12	0.0604 (16)	0.0521 (16)	0.094 (2)	0.0014 (12)	0.000	0.000
C21	0.0365 (12)	0.0479 (13)	0.0504 (16)	-0.0031 (10)	0.000	0.000
C22	0.0301 (13)	0.0730 (18)	0.147 (3)	-0.0092 (13)	0.000	0.000

Geometric parameters (Å, °)

C1—N1	1.397 (3)	O21—C22	1.454 (3)
C1—C6	1.411 (3)	C22—H22A	0.96
C1—C2	1.421 (3)	C22—H22B	0.96
N1—C11	1.380 (3)	C22—H22C	0.96
N1—H1	0.86	C3—C4	1.388 (3)
C11—O11	1.220 (3)	C3—H3	0.93
C11—C12	1.499 (4)	C4—C5	1.383 (3)
C12—H12A	0.96	C4—N4	1.466 (3)
C12—H12B	0.96	N4—O41	1.185 (3)
C12—H12C	0.96	N4—O42	1.217 (3)
C2—C3	1.395 (3)	C5—C6	1.373 (3)
C2—C21	1.494 (3)	C5—H5	0.93
C21—O22	1.213 (3)	C6—H6	0.93
C21—O21	1.327 (3)		
N1—C1—C6	122.2 (2)	O21—C22—H22A	109.5
N1—C1—C2	119.24 (19)	O21—C22—H22B	109.5
C6—C1—C2	118.6 (2)	H22A—C22—H22B	109.5
C1—N1—C11	129.6 (2)	O21—C22—H22C	109.5
C11—N1—H1	115.2	H22A—C22—H22C	109.5
C1—N1—H1	115.2	H22B—C22—H22C	109.5
N1—C11—O11	122.8 (2)	C4—C3—C2	119.9 (2)
N1—C11—C12	114.1 (2)	C4—C3—H3	120.0
O11—C11—C12	123.1 (2)	C2—C3—H3	120.0
C11—C12—H12A	109.5	C5—C4—C3	121.6 (2)
C11—C12—H12B	109.5	C5—C4—N4	119.7 (2)
H12A—C12—H12B	109.5	C3—C4—N4	118.7 (2)
C11—C12—H12C	109.5	O41—N4—O42	122.6 (2)
H12A—C12—H12C	109.5	O41—N4—C4	118.8 (2)
H12B—C12—H12C	109.5	O42—N4—C4	118.5 (2)
C3—C2—C1	119.3 (2)	C6—C5—C4	119.1 (2)
C3—C2—C21	119.1 (2)	C6—C5—H5	120.4
C1—C2—C21	121.58 (19)	C4—C5—H5	120.4
C2—C21—O21	111.55 (19)	C5—C6—C1	121.5 (2)
C2—C21—O22	125.9 (2)	C5—C6—H6	119.3
O21—C21—O22	122.5 (2)	C1—C6—H6	119.3
C21—O21—C22	117.2 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O22	0.86	1.98	2.691 (2)	139
C3—H3 \cdots O41 ⁱ	0.93	2.51	3.440 (3)	180
C3—H3 \cdots O21	0.93	2.32	2.660 (3)	101
C6—H6 \cdots O11	0.93	2.23	2.854 (3)	124

Symmetry code: (i) $-x+1, -y+1, z$.