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Kennedy, Alan R. and Silva De Moraes, Lygia (2016) A monoclinic polymorph of 2-(4-nitrophenyl)acetic acid. IUCr Data, 1. ISSN 2414-3146 , <http://dx.doi.org/10.1107/S2414314616019325>

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A monoclinic polymorph of 2-(4-nitrophenyl)acetic acid

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Received 19 November 2016

Accepted 2 December 2016

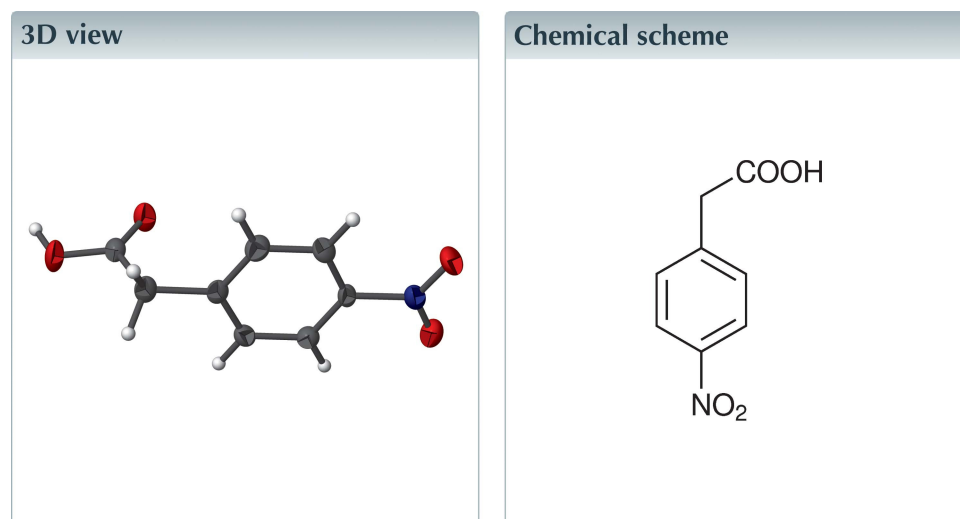
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; polymorphism; carboxylic acid; hydrogen bonding; nitro–nitro dipole interactions.

CCDC reference: 1520553

Structural data: full structural data are available from iucrdata.iucr.org

A new monoclinic form of 4-nitrophenylacetic acid, $C_8H_7NO_4$, (I), differs from the known orthorhombic form both in its molecular conformation and in its intermolecular contacts. The conformation is different as the plane of the carboxylic acid group in (I) is more nearly perpendicular to the plane of the aromatic ring [dihedral angle = $86.9(3)^\circ$] than in the previous form (74.5°). Both polymorphs display hydrogen-bonded $R_2^2(8)$ carboxylic acid dimeric pairs, but in (I), neighbouring dimers interact through nitro–nitro $N \cdots O$ dipole–dipole contacts rather than the nitro–carbonyl contacts found in the orthorhombic form.



Structure description

An orthorhombic polymorph of 4-nitrophenylacetic acid was crystallized from ethanol solution and structurally described by Grabowski *et al.* (1990). The new polymorph described herein, (I), features a molecular structure with a nitro group that is essentially coplanar with the aromatic ring [dihedral angle = $3.9(3)^\circ$] and a carboxylic acid group that approaches the perpendicular with respect to the aromatic ring [dihedral angle = $86.9(3)^\circ$], see Fig. 1. The previously known orthorhombic polymorph also features near coplanarity of the nitro and aromatic groups, but the carboxylic acid group lies further from the perpendicular (74.5°).

In the crystal structure of (I), strong $O-H \cdots O$ hydrogen bonds (Table 1) occur between carboxylic acid groups, creating the classic dimeric $R_2^2(8)$ motif (Fig. 2). This motif is also present in the orthorhombic polymorph. A difference is that in (I) these dimers interconnect through nitro-to-nitro dipole-to-dipole contacts [$O3 \cdots N1^{ii}$ 2.923(3) Å, symmetry code: (ii) $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$] to form an extended chain (Wozniak *et al.*, 1994). However, in the orthorhombic form of 4-nitrophenylacetic acid, the nitro group forms nitro-to-carbonyl dipole–dipole contacts instead. A similar set of inter-

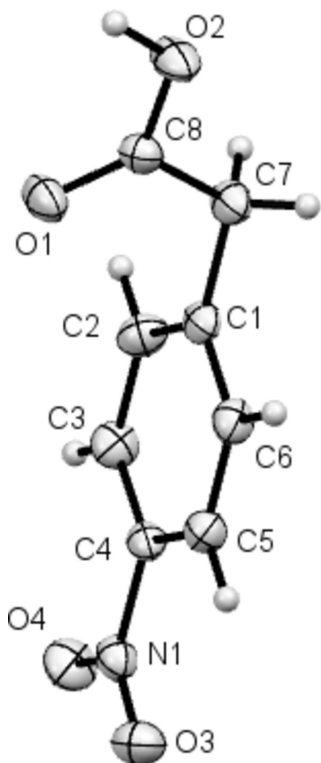


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

molecular contacts to that found in (I) is found in the polymorph of 4-nitrobenzoic acid described by Groth (1980). Interestingly, that structure also has a unit cell that is similar to that found for (I) ($a = 5.403$, $b = 5.153$, $c = 24.692$ Å, $\beta = 96.89^\circ$, space group $P2_1/c$).

Synthesis and crystallization

The crystallization of 4-nitrophenylacetic acid occurred during an attempt to synthesize a salt form of *N*-methylephedrine by reaction with the acid (Kennedy *et al.*, 2011): 1.27 mmol of 4-nitrophenylacetic acid was dissolved in 5 ml of deionized water and the added to a slurry of 1 mmol of base in 5 ml of deionized water. The resulting solution was stirred at 323 K

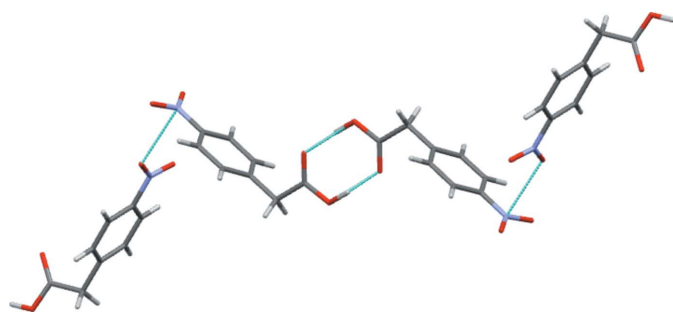


Figure 2
The crystal structure of (I) displays the classic $R_2^2(8)$ carboxylic acid dimeric hydrogen-bonding motif. Neighbouring dimers interact through nitro-to-nitro contacts to form a chain.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2O \cdots O1^i$	0.99 (4)	1.69 (4)	2.672 (2)	170 (3)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_7NO_4$
M_r	181.15
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	6.1364 (5), 5.1034 (4), 25.458 (3)
β (°)	95.937 (8)
V (Å ³)	792.98 (13)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.12
Crystal size (mm)	0.32 × 0.18 × 0.13
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Eos
Absorption correction	Multi-scan <i>CrysAlis PRO</i> (Agilent, 2014)
T_{min}, T_{max}	0.880, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15530, 1814, 1076
R_{int}	0.090
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.054, 0.130, 1.06
No. of reflections	1814
No. of parameters	122
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.24, -0.26

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

for 30 minutes and filtered. The solution was then put into a test tube and left to slowly evaporate and to cool to room temperature: monoclinic 4-nitrophenylacetic acid in the form of colourless tablets crystallized on the walls of the test tube.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The financial support of a PhD studentship by CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and the advice of GSK are gratefully acknowledged.

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full crystallographic data

IUCrData (2016). **1**, x161932 [<https://doi.org/10.1107/S2414314616019325>]

A monoclinic polymorph of 2-(4-nitrophenyl)acetic acid

Alan R. Kennedy and Lygia Silva de Moraes

2-(4-Nitrophenyl)acetic acid

Crystal data

$C_8H_7NO_4$

$M_r = 181.15$

Monoclinic, $P2_1/c$

$a = 6.1364$ (5) Å

$b = 5.1034$ (4) Å

$c = 25.458$ (3) Å

$\beta = 95.937$ (8)°

$V = 792.98$ (13) Å³

$Z = 4$

$F(000) = 376$

$D_x = 1.517$ Mg m⁻³

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

Cell parameters from 2414 reflections

$\theta = 3.2$ – 28.7 °

$\mu = 0.12$ mm⁻¹

$T = 150$ K

Tablet, colourless

$0.32 \times 0.18 \times 0.13$ mm

Data collection

Oxford Diffraction Xcalibur Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.0727 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

CrysAlis PRO (Agilent, 2014)

$T_{\min} = 0.880$, $T_{\max} = 1.000$

15530 measured reflections

1814 independent reflections

1076 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.090$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.2$ °

$h = -7 \rightarrow 7$

$k = -6 \rightarrow 6$

$l = -33 \rightarrow 32$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.130$

$S = 1.06$

1814 reflections

122 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.2348P]$

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

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

$\Delta\rho_{\max} = 0.24$ e Å⁻³

$\Delta\rho_{\min} = -0.26$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.1037 (3)	0.8022 (4)	0.03062 (7)	0.0364 (5)
O3	0.8335 (3)	-0.2053 (3)	0.23833 (7)	0.0349 (5)
O4	1.0830 (3)	-0.1662 (4)	0.18470 (7)	0.0371 (5)
O1	0.2209 (3)	0.3888 (3)	0.03653 (7)	0.0337 (5)
N1	0.9081 (3)	-0.1028 (4)	0.20049 (8)	0.0274 (5)
C4	0.7826 (4)	0.1092 (5)	0.17228 (9)	0.0229 (5)
C1	0.5454 (4)	0.5029 (5)	0.11899 (9)	0.0243 (6)
C6	0.4753 (4)	0.3949 (5)	0.16427 (9)	0.0267 (6)
H6	0.3449	0.4582	0.1770	0.032*
C8	0.2380 (4)	0.6189 (5)	0.04973 (9)	0.0252 (6)
C5	0.5924 (4)	0.1965 (5)	0.19118 (9)	0.0265 (6)
H5	0.5431	0.1218	0.2220	0.032*
C3	0.8571 (4)	0.2132 (5)	0.12774 (9)	0.0288 (6)
H3	0.9886	0.1511	0.1155	0.035*
C2	0.7366 (4)	0.4104 (5)	0.10109 (10)	0.0297 (6)
H2	0.7858	0.4833	0.0701	0.036*
C7	0.4160 (4)	0.7176 (5)	0.08958 (10)	0.0284 (6)
H7A	0.3497	0.8298	0.1154	0.034*
H7B	0.5173	0.8280	0.0713	0.034*
H2O	-0.009 (7)	0.741 (8)	0.0027 (16)	0.099 (13)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0362 (11)	0.0257 (10)	0.0427 (11)	0.0049 (9)	-0.0178 (9)	0.0012 (9)
O3	0.0359 (11)	0.0336 (11)	0.0346 (10)	0.0010 (9)	0.0003 (8)	0.0081 (9)
O4	0.0291 (10)	0.0390 (12)	0.0430 (11)	0.0141 (9)	0.0033 (8)	-0.0006 (9)
O1	0.0353 (11)	0.0213 (10)	0.0416 (11)	-0.0006 (8)	-0.0095 (8)	-0.0026 (8)
N1	0.0262 (12)	0.0240 (12)	0.0307 (12)	0.0026 (10)	-0.0032 (9)	-0.0034 (10)
C4	0.0213 (12)	0.0217 (13)	0.0242 (13)	0.0034 (11)	-0.0050 (9)	-0.0015 (11)
C1	0.0237 (13)	0.0225 (13)	0.0250 (13)	-0.0016 (11)	-0.0056 (10)	-0.0032 (10)
C6	0.0236 (13)	0.0296 (14)	0.0264 (13)	0.0053 (11)	0.0005 (10)	-0.0038 (11)
C8	0.0250 (14)	0.0241 (14)	0.0260 (13)	0.0009 (11)	0.0008 (10)	0.0032 (11)
C5	0.0276 (13)	0.0268 (13)	0.0251 (13)	0.0008 (12)	0.0021 (10)	-0.0004 (11)
C3	0.0214 (13)	0.0337 (15)	0.0315 (14)	0.0054 (12)	0.0038 (10)	-0.0002 (12)
C2	0.0264 (14)	0.0349 (15)	0.0277 (14)	-0.0013 (12)	0.0026 (11)	0.0045 (12)
C7	0.0277 (14)	0.0244 (13)	0.0309 (14)	-0.0004 (11)	-0.0071 (11)	-0.0026 (11)

Geometric parameters (\AA , $^\circ$)

O2—C8	1.307 (3)	C1—C7	1.506 (3)
O2—H2O	0.99 (4)	C6—C5	1.382 (3)
O3—N1	1.226 (3)	C6—H6	0.9500
O4—N1	1.228 (2)	C8—C7	1.499 (3)
O1—C8	1.223 (3)	C5—H5	0.9500

N1—C4	1.472 (3)	C3—C2	1.384 (3)
C4—C3	1.372 (3)	C3—H3	0.9500
C4—C5	1.382 (3)	C2—H2	0.9500
C1—C2	1.385 (3)	C7—H7A	0.9900
C1—C6	1.386 (3)	C7—H7B	0.9900
C8—O2—H2O	114 (2)	C6—C5—C4	118.6 (2)
O3—N1—O4	123.7 (2)	C6—C5—H5	120.7
O3—N1—C4	118.6 (2)	C4—C5—H5	120.7
O4—N1—C4	117.7 (2)	C4—C3—C2	118.7 (2)
C3—C4—C5	121.9 (2)	C4—C3—H3	120.7
C3—C4—N1	119.0 (2)	C2—C3—H3	120.7
C5—C4—N1	119.1 (2)	C3—C2—C1	120.9 (2)
C2—C1—C6	119.0 (2)	C3—C2—H2	119.5
C2—C1—C7	120.4 (2)	C1—C2—H2	119.5
C6—C1—C7	120.6 (2)	C8—C7—C1	113.7 (2)
C5—C6—C1	120.9 (2)	C8—C7—H7A	108.8
C5—C6—H6	119.6	C1—C7—H7A	108.8
C1—C6—H6	119.6	C8—C7—H7B	108.8
O1—C8—O2	123.5 (2)	C1—C7—H7B	108.8
O1—C8—C7	123.0 (2)	H7A—C7—H7B	107.7
O2—C8—C7	113.5 (2)		
O3—N1—C4—C3	-175.6 (2)	C5—C4—C3—C2	-0.3 (4)
O4—N1—C4—C3	4.7 (3)	N1—C4—C3—C2	179.2 (2)
O3—N1—C4—C5	3.9 (3)	C4—C3—C2—C1	0.4 (4)
O4—N1—C4—C5	-175.8 (2)	C6—C1—C2—C3	0.0 (4)
C2—C1—C6—C5	-0.5 (4)	C7—C1—C2—C3	180.0 (2)
C7—C1—C6—C5	179.5 (2)	O1—C8—C7—C1	-10.7 (3)
C1—C6—C5—C4	0.6 (4)	O2—C8—C7—C1	169.3 (2)
C3—C4—C5—C6	-0.2 (4)	C2—C1—C7—C8	93.1 (3)
N1—C4—C5—C6	-179.7 (2)	C6—C1—C7—C8	-86.9 (3)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H2O...O1 ⁱ	0.99 (4)	1.69 (4)	2.672 (2)	170 (3)

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