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3-Nitrophenylacetic acid: a three-dimensional hydrogen-bonded framework structure containing substructures in zero, one and two dimensions

Solange M. S. V. Wardell,[a] James L. Wardell,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Instituto de Tecnologia em Fármacos, Far-Manguinhos, FIOCRUZ, 21041-250 Rio de Janeiro, RJ, Brazil, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife, KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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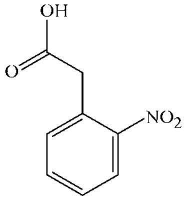
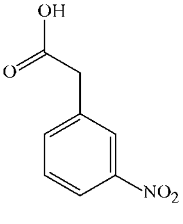
In the title compound, $C_8H_7NO_4$, the molecules are linked into a three-dimensional framework structure by a combination of O—H···O, C—H···O(carbonyl) and C—H···O(nitro) hydrogen bonds. Comparisons are made between the supramolecular structures of the three isomeric nitrophenylacetic acids.

Comment

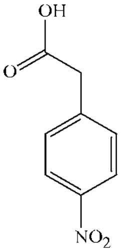
We have recently reported the structure of 2-nitrophenylacetic acid, (I) (Wardell *et al.*, 2006), and here we report the structure of the isomeric compound 3-nitrophenylacetic acid, (II). The structure of 4-nitrophenylacetic acid, (III), was reported some years ago (Grabowski *et al.*, 1990), and the structure determination for (II) now permits a comparison of all three isomers, (I)–(III).



(I)



(II)



(III)

The exocyclic substituents in compound (II) are both twisted out of the plane of the aryl ring (Fig. 1 and Table 1), so that the molecules are chiral. However, the space group accommodates equal numbers of the two enantiomeric forms. The C—O bond distances are consistent with full ordering of the acidic H atom, as deduced from difference maps.

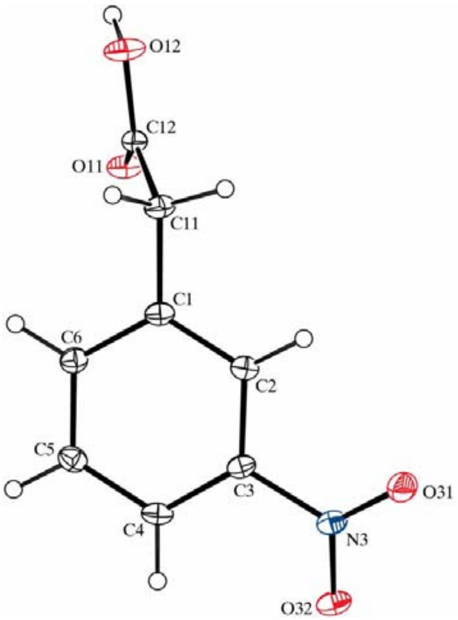


Figure 1
A molecule of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

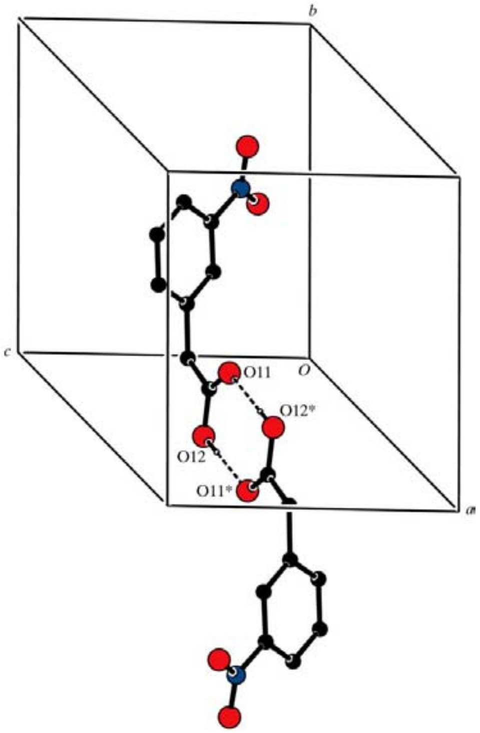


Figure 2
Part of the crystal structure of (II), showing the formation of an $R_2^2(8)$ dimer centred at $(\frac{1}{2}, 0, \frac{1}{2})$. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, -y, 1 - z)$.

The molecules of (II) are linked by a combination of O—H···O, C—H···O(carbonyl) and C—H···O(nitro) hydrogen bonds (Table 2) into a three-dimensional framework structure, whose formation is readily analysed in terms of a series of

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substructures of lower dimensionality: a finite zero-dimensional dimer unit, which can be regarded as the basic building unit within the structure, and two independent substructures, one of which is one-dimensional and the other of which is two-dimensional, which result from different modes of linkage of the dimers.

Hydroxyl atom O12 in the molecule at (x, y, z) acts as hydrogen-bond donor to carbonyl atom O11 in the molecule at ($1 - x$, $-y$, $1 - z$), so generating by inversion a dimer characterized by the usual $R_2^2(8)$ (Bernstein *et al.*, 1995) motif (Fig. 2). This dimer can be regarded as the basic building unit within the structure, from which the other two substructures are built. The one-dimensional substructure involves a C—H$\cdots$O(carbonyl) hydrogen bond: aryl atom C6 in the molecule at (x, y, z), part of the dimer centred at ($\frac{1}{2}$, 0, $\frac{1}{2}$), acts as hydrogen-bond donor to carbonyl atom O11 in the molecule at ($1 - x, y, \frac{3}{2} - z$), which is part of the dimer centred at ($\frac{1}{2}$, 0, 1). Propagation by inversion and rotation then generates a chain of $R_2^2(8)$ rings generated by inversion alternating with $R_2^2(12)$ rings generated by rotation, running parallel to the [001] direction (Fig. 3).

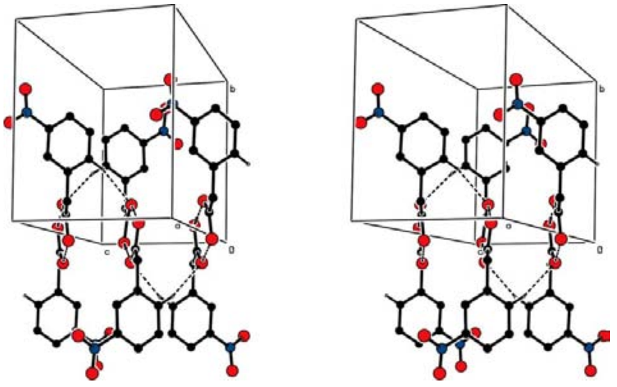

Figure 3
A stereoview of part of the crystal structure of (II), showing the formation of a chain of $R_2^2(8)$ and $R_2^2(12)$ rings along [001]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

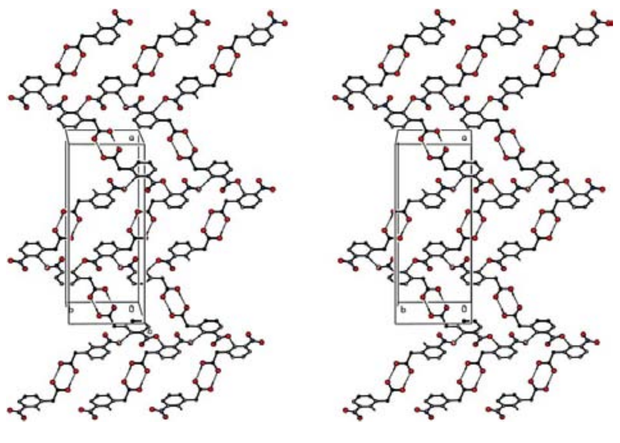

Figure 4
A stereoview of part of the crystal structure of (II), showing the formation of a sheet of $R_2^2(8)$ and $R_6^6(40)$ rings parallel to ($10\overline{1}$). For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

The two-dimensional substructure of compound (II) involves a C—H$\cdots$O(nitro) hydrogen bond. The aryl atoms C2 in the molecules at (x, y, z) and ($1 - x$, $-y$, $1 - z$), which comprise the $R_2^2(8)$ dimer centred at ($\frac{1}{2}$, 0, $\frac{1}{2}$), act as hydrogen-bond donors to the nitro atoms O32 in the molecules at ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$) and ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), respectively, which themselves form parts of the dimers centred at (0, $-\frac{1}{2}$, 0) and (1, $\frac{1}{2}$, 1). Similarly, nitro atoms O32 in the molecules at (x, y, z) and ($1 - x$, $-y$, $1 - z$) accept hydrogen bonds from atoms C2 in the molecules at ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) and ($\frac{1}{2} + x$, $-\frac{1}{2} - y$, $\frac{1}{2} + z$), respectively, which form parts of the dimers centred at (0, $\frac{1}{2}$, 0) and (1, $-\frac{1}{2}$, 1). Hence, each dimer is linked in this manner to four adjacent dimers, and propagation of this C—H$\cdots$O(nitro) hydrogen bond then generates a sheet parallel to ($10\overline{1}$) built of alternating $R_2^2(8)$ and $R_6^6(40)$ rings (Fig. 4). The combination of [001] chains and ($10\overline{1}$) sheets suffices to generate a single continuous three-dimensional framework structure.

It is of interest to compare briefly the supramolecular structure of (II) with those of the two isomers, (I) and (III). In 2-nitropheylacetic acid, (I), the molecules are linked into sheets of $R_2^2(8)$ and $R_4^4(18)$ rings by one O—H$\cdots$O hydrogen bond and two independent C—H$\cdots$O hydrogen bonds, both of which involve nitro O atoms as acceptors (Wardell *et al.*, 2006). Thus, although the hydrogen bonds deployed in the structures of (I) and (II) are similar, differing principally in the identity of one of the acceptors, the dimensionality of the resulting structures differs. In 4-nitrophenylacetic acid, (III) (Grabowski *et al.*, 1990), the centrosymmetric $R_2^2(8)$ dimers are linked into sheets by an aromatic π–π stacking interaction but, in contrast with the structures of (I) and (II), C—H$\cdots$O hydrogen bonds are absent (Wardell *et al.*, 2006). Hence, significant changes in the supramolecular structures of isomers (I)–(III) result from a simple shift of a single substituent between the various sites on the aryl ring, posing a keen test for the predictability of structures from first principles.

Experimental

A commercial sample (Aldrich) of 3-nitrophenylacetic acid was recrystallized from water.

Crystal data

$C_8H_7NO_4$
$M_r = 181.15$
Monoclinic, $C2/c$
$a = 21.9690$ (6) Å
$b = 9.2901$ (7) Å
$c = 7.9642$ (2) Å
$\beta = 106.216$ (2)°
$V = 1560.78$ (13) Å^3

$Z = 8$
$D_x = 1.542$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.62 × 0.07 × 0.05 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.957$, $T_{\max} = 0.994$

16903 measured reflections
1798 independent reflections
1426 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 27.6°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.108$
$S = 1.03$
1798 reflections
119 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.8287P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C12—O11	1.2194 (16)	C12—O12	1.3216 (15)
C2—C3—N3—O31	14.78 (17)	C1—C11—C12—O12	172.54 (11)
C2—C1—C11—C12	117.89 (13)		

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O12—H12⋯O11^{i}	0.84	1.86	2.6980 (13)	175
C2—H2⋯O32^{ii}	0.95	2.49	3.4099 (16)	164
C6—H6⋯O11^{iii}	0.95	2.52	3.4474 (17)	166

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y, -z+\frac{3}{2}$.

The systematic absences permitted *Cc* and *C*2/*c* as possible space groups; *C*2/*c* was selected and confirmed by the successful structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH$_2$) and O—H distances of 0.84 Å, and with U_{iso}H = 1.2U_{eq}(C) or 1.5U_{eq}(O).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3059). Services for accessing these data are described at the back of the journal.

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