

3-Nitrophthalic acid: $C(4)$ and $R_2^2(8)$ motifs of $O-H \cdots O$ hydrogen bonds generate sheets which are linked by $C-H \cdots O$ hydrogen bonds

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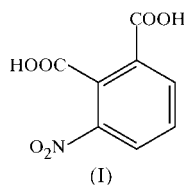
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In molecules of 3-nitrophthalic acid, $C_8H_5NO_6$, the 2-carboxyl group, which is the central of the three substituents, is almost orthogonal to the arene ring, while the other two substituents are effectively coplanar with the ring. The molecules are linked by two $O-H \cdots O$ hydrogen bonds [$H \cdots O = 1.86$ and 1.89 \AA , $O \cdots O = 2.6983(13)$ and $2.6809(12) \text{ \AA}$, and $O-H \cdots O = 172$ and 155°] into sheets containing alternating $R_2^2(8)$ and $R_6^6(36)$ rings; these sheets are linked into a three-dimensional framework by a single $C-H \cdots O$ hydrogen bond [$H \cdots O = 2.41 \text{ \AA}$, $C \cdots O = 3.2663(15) \text{ \AA}$ and $C-H \cdots O = 150^\circ$].

Comment

The $O-H \cdots O$ hydrogen bonds in simple carboxylic acids exhibit two main patterns, namely formation of $R_2^2(8)$ (Bernstein *et al.*, 1995) rings, often centrosymmetric, as exemplified by benzoic acid (Sim *et al.*, 1955; Feld *et al.*, 1981; Wilson *et al.*, 1996), and formation of $C(4)$ chains, as exemplified by acetic



acid (Jones & Templeton, 1958; Nahrungbauer, 1970; Jönsson, 1971). We report here the molecular and supramolecular structure of 3-nitrophthalic acid, (I), in which the two independent carboxyl groups are involved in different supramolecular synthons, one forming an $R_2^2(8)$ ring and the other a $C(4)$ chain.

The molecular conformation of (I) (Fig. 1 and Table 1) is dominated by the avoidance of steric clashing between adjacent substituents; thus, while the nitro group and the carboxyl group containing atom C11 are both nearly coplanar with the aryl ring, the carboxyl group containing C21, which lies between the other two substituents, is almost orthogonal to the ring. While there are no significant differences between corresponding C—O distances in the two carboxyl substituents, the C2—C21 bond is somewhat longer than C1—C11, suggesting a reduction in conjugation. Accordingly, the internal C—C—C angle at C2 has a value more typical of an electron-source substituent rather than an electron-sink substituent (Domenicano & Murray-Rust, 1979).

Molecules of (I) are linked into a single three-dimensional framework by a combination of two $O-H \cdots O$ hydrogen bonds and one $C-H \cdots O$ hydrogen bond (Table 2), and the formation of the framework is readily analysed using the substructure approach (Gregson *et al.*, 2000). Carboxyl atom

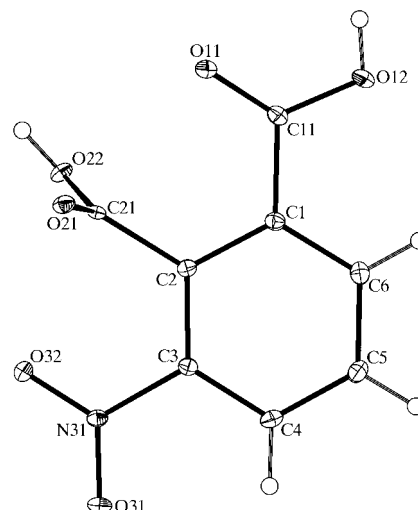


Figure 1

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

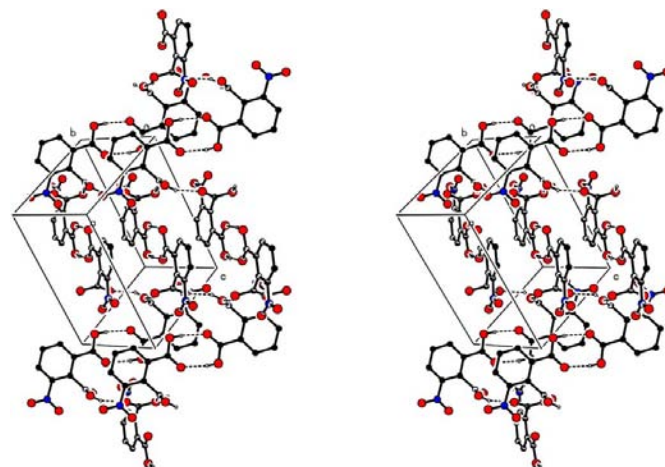


Figure 2

Stereoview of part of the crystal structure of (I), showing the formation of a $(10\bar{1})$ sheet of $R_2^2(8)$ and $R_6^6(36)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

O22 in the molecule at (x, y, z) acts as hydrogen-bond donor to carboxyl atom O21 in the molecule at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, while O22 at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, in turn, acts as donor to O21 at $(x, -1 + y, z)$; this hydrogen bond thus produces a $C(4)$ chain running parallel to the $[010]$ direction and generated by

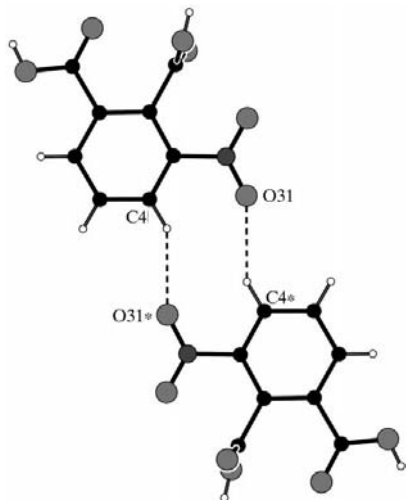


Figure 3
Part of the crystal structure of (I), showing the $R_2^2(10)$ motif which links the $(10\bar{1})$ sheets. For the sake of clarity, the unit-cell box has been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x, 2 - y, 1 - z)$.

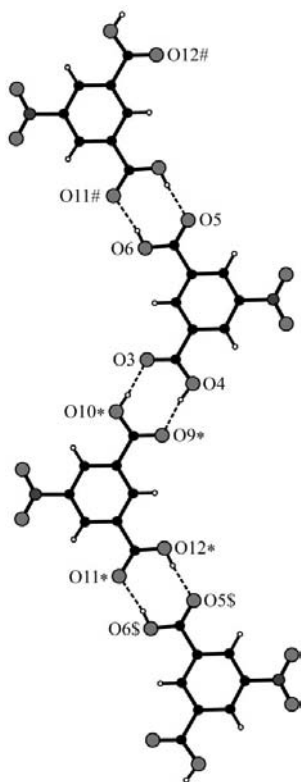


Figure 4
Part of the crystal structure of COFDUW10 (Domenicano *et al.*, 1990), showing the formation of a chain of $R_2^2(8)$ rings along $[01\bar{1}]$. For the sake of clarity, the unit-cell box has been omitted; the atom labels and symmetry positions are those used in the original report (Domenicano *et al.*, 1990). Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(\frac{1}{2} + x, -y, z)$, $(\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z)$ and $(x, \frac{1}{2} + y, -\frac{1}{2} + z)$, respectively.

the 2_1 screw axis along $(\frac{1}{4}, y, \frac{1}{4})$. A second, antiparallel, chain, related to the first by inversion, runs through the cell around the 2_1 screw axis along $(\frac{3}{4}, -y, \frac{3}{4})$.

There is a short non-bonded contact between the negatively polarized carbonyl atom O21 in the molecule at (x, y, z) and the positively polarized atom N31 in the molecule at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$. The geometry of this interaction (Fig. 2) resembles that of the perpendicular interaction between pairs of carbonyl groups (Allen *et al.*, 1998). The $O \cdots N$ distance is 2.807 (2) Å, well below the sum of the van der Waals radii for N and O of 3.05 Å (Bondi, 1964), and hence this interaction must be regarded as attractive, reinforcing the formation of the chain along $[010]$.

Carboxyl atom O12 in the molecule at (x, y, z) acts as hydrogen-bond donor to O11 in the molecule at $(1 - x, -y, 1 - z)$, so generating a centrosymmetric $R_2^2(8)$ motif. The molecules at (x, y, z) and $(1 - x, -y, 1 - z)$ lie in the spiral chains along $(\frac{1}{4}, y, \frac{1}{4})$ and $(\frac{3}{4}, -y, \frac{3}{4})$, respectively. Hence, the combination of the $C(4)$ and $R_2^2(8)$ motifs generates a sheet, parallel to $(10\bar{1})$, containing $R_2^2(8)$ and $R_6^6(36)$ rings, alternating in a checkerboard fashion (Fig. 2). Just one sheet of this type passes through each unit cell.

Finally, atom C4 in the molecule at (x, y, z) , which lies in the $(10\bar{1})$ sheet passing through $(\frac{1}{4}, y, \frac{1}{4})$, acts as hydrogen-bond donor to nitro atom O31 in the molecule at $(-x, 2 - y, 1 - z)$, which lies in the sheet passing through $(-\frac{3}{4}, y, \frac{1}{4})$. Propagation of this interaction, *via* the $R_2^2(10)$ motif (Fig. 3), thus links together all of the $(10\bar{1})$ sheets to form a single framework.

Of the six possible isomeric nitrophthalic acids, only the structure of 5-nitroisophthalic acid, (II), has been reported (Domenicano *et al.*, 1990) prior to the present report on (I). However, that report (Domenicano *et al.*, 1990) was concerned solely with the intramolecular dimensions, in particular the internal angles of the arene ring, and gave no discussion whatsoever of the supramolecular structure. We have now analysed the supramolecular structure of (II) using coordinates retrieved from the Cambridge Structural Database (CSD; Allen, 2002) for (II) (CSD refcode COFDUW10). Compound (II) was refined in space group $A2/c$ (*cf.* $C2/c$) with $Z' = 2$, but with a disconnected asymmetric unit. The supramolecular structure is determined by four distinct $O-H \cdots O$ hydrogen bonds, which link the molecules into a chain of $R_2^2(8)$ rings running parallel to the $[01\bar{1}]$ direction (Fig. 4). However, the $C(4)$ motif apparent in (I) is absent from (II).

Experimental

A sample of commercial 3-nitrophthalic acid (Aldrich) was crystallized by slow evaporation of a solution in ethanol.

Crystal data

$C_8H_5NO_6$
 $M_r = 211.13$
 Monoclinic, $P2_1/n$
 $a = 9.4972$ (2) Å
 $b = 6.9014$ (2) Å
 $c = 12.3077$ (3) Å
 $\beta = 92.0599$ (11)°
 $V = 806.17$ (3) Å³
 $Z = 4$

$D_x = 1.740$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1827 reflections
 $\theta = 3.4$ – 27.5°
 $\mu = 0.15$ mm⁻¹
 $T = 120$ (2) K
 Block, brown
 $0.35 \times 0.30 \times 0.18$ mm

Table 1

Selected geometric parameters (Å, °).

C11—O11	1.2169 (16)	C21—O21	1.2160 (15)
C11—O12	1.3171 (15)	C21—O22	1.3130 (14)
C1—C11	1.4977 (16)	C2—C21	1.5148 (16)
C2—C1—C6	120.41 (11)	C2—C3—C4	122.89 (11)
C1—C2—C3	117.19 (11)		
C2—C1—C11—O11	6.30 (18)	C2—C3—N31—O32	3.48 (15)
C1—C2—C21—O21	−92.11 (14)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O12—H12...O11 ⁱ	0.84	1.86	2.6983 (13)	172
O22—H22...O21 ⁱⁱ	0.84	1.89	2.6809 (12)	155
C4—H4...O31 ⁱⁱⁱ	0.95	2.41	3.2663 (15)	150

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

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.945$, $T_{\max} = 0.972$
 9456 measured reflections

1827 independent reflections
 1641 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -8 \rightarrow 8$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.087$
 $S = 1.07$
 1827 reflections
 138 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 0.4307P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{Å}^{-3}$

Compound (I) is monoclinic, and the space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were treated as riding atoms, with C—H distances of 0.95 Å and O—H distances of 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); 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: SK1616). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Allen, F. H., Baalham, C., Lommerse, J. P. M. & Raithby, P. R. (1998). *Acta Cryst.* **B54**, 320–329.
 Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.
 Domenicano, A., Schultz, G., Hargittai, I., Colapietro, M., Portalone, G., George, P. & Bock, C. W. (1990). *Struct. Chem.* **1**, 107–122.
 Feld, R., Lehmann, M. S., Muir, K. W. & Speakman, J. C. (1981). *Z. Kristallogr.* **157**, 215–231.
 Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
 Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* **B56**, 39–57.
 Jones, R. E. & Templeton, D. H. (1958). *Acta Cryst.* **11**, 484–487.
 Jönsson, P.-G. (1971). *Acta Cryst.* **B27**, 893–898.
 Nahrungbauer, I. (1970). *Acta Chem. Scand.* **24**, 453–462.
 Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sim, G. A., Robertson, J. M. & Goodwin, T. A. (1955). *Acta Cryst.* **8**, 157–164.
 Spek, A. L. (2002). *PLATON*. Version of December 2002. Utrecht University, The Netherlands.
 Wilson, C. C., Shankland, N. & Florence, A. J. (1996). *J. Chem. Soc. Faraday Trans.* **92**, 5051–5057.