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2-(4-Nitrophenoxy)benzoic acid: a three-dimensional hydrogen-bonded framework in a triclinic structure having $Z' = 3$

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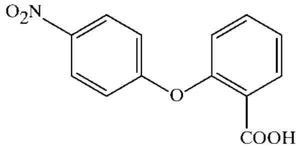
The title compound, $C_{13}H_9NO_5$, crystallizes in space group $P\overline{1}$, with $Z' = 3$. The molecules are linked by O—H···O hydrogen bonds [H···O = 1.79–1.81 Å, O···O = 2.625 (3)–2.648 (3) Å and O—H···O = 172–176°] into two types of $R_2^2(8)$ dimer, only one of which is centrosymmetric. An extensive series of soft hydrogen bonds, of C—H···O and C—H···π(arene) types, links the dimers into a three-dimensional framework.

Comment

Persulfate oxidation of substituted 2-aryloxybenzoic acids yields asymmetrically substituted bis(salicylates), whose formation has been ascribed to the 2-4 coupling of phenoxyl radicals (Thomson & Wylie, 1966). We report here the molecular and supramolecular structure of one such precursor compound, namely 2-(4-nitrophenoxy)benzoic acid, (I).



(I)

Compound (I) crystallizes in the triclinic space group $P\overline{1}$, with $Z' = 3$ (Fig. 1). In each of the three independent molecules, the two aryl rings are both rotated away from the plane of the central C/O/C fragment, as shown by the leading torsion angles (Table 1). Likewise, each of the nitro and carboxy groups is rotated away from the plane of the adjacent aryl ring. Comparison of the corresponding values for the three molecules is sufficient to rule out the possibility of any additional symmetry.

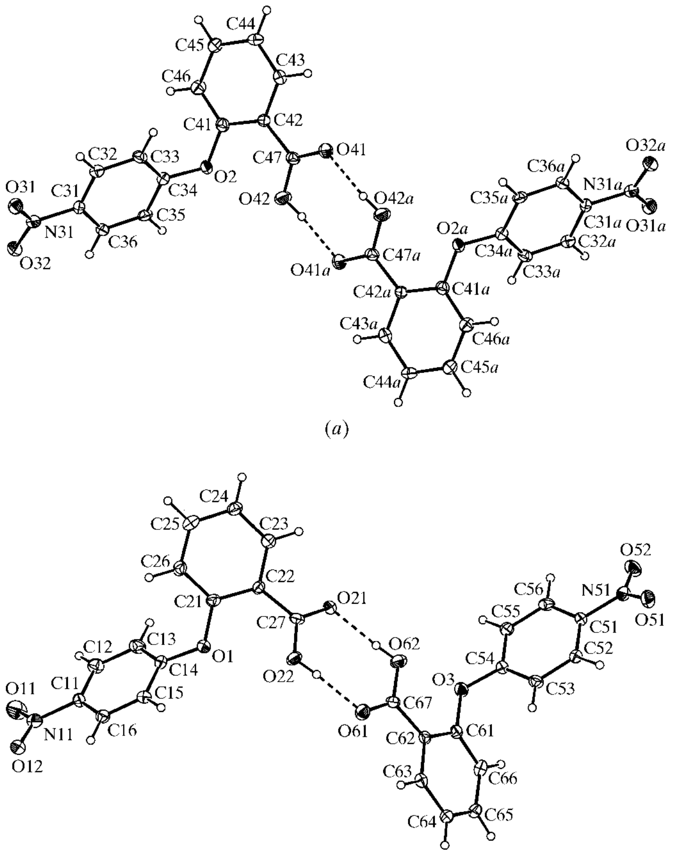


Figure 1
The independent molecules of (I), showing the atom-labelling scheme and the dimers formed by the O—H···O hydrogen bonding. (*a*) The centrosymmetric dimer formed by the type 2 molecules, where atoms labelled with the suffix *a* are at the symmetry position $(1 - x, 1 - y, 1 - z)$. (*b*) The dimer formed by the type 1 and type 3 molecules. Displacement ellipsoids are drawn at the 30% probability level.

The C—O distances within the carboxy groups are consistent with the fully ordered locations of the carboxy H atoms as deduced from difference maps. In each molecule, the central C—O—C angle has a value significantly larger than the idealized tetrahedral angle. The remaining bond lengths and angles show no unusual values.

Molecules of types 1 and 3, containing atoms O1 and O3, respectively (Fig. 1*a*), are linked into hydrogen-bonded dimers by two independent O—H···O hydrogen bonds, both of which are short for their type and nearly linear (Table 2). By contrast, molecules of type 2, containing atom O2 (Fig. 1*b*), are linked by pairs of O—H···O hydrogen bonds into centrosymmetric $R_2^2(8)$ (Bernstein *et al.*, 1995) dimers. With the centrosymmetric dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, the centroid of the non-centrosymmetric dimer is at approximately (0.265, 0.225, 0.416), thus precluding the possibility of any additional inversion centres.

The two types of dimer are linked by an extensive series of soft hydrogen bonds (Braga *et al.*, 1995; Desiraju & Steiner, 1999) into a continuous three-dimensional framework of considerable complexity. However, the descriptive analysis of the framework formation is eased by the adoption of the

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substructure approach (Gregson *et al.*, 2000). The dimeric units formed by the O—H···O hydrogen bonds are linked by the three strongest C—H···O hydrogen bonds (the first three such entries in Table 2, all having C—H···O angles greater than 160°) into two distinct types of chain running parallel to the [001] direction. These chains are then linked by two weaker C—H···O hydrogen bonds (the fourth and fifth such entries in Table 2, with C—H···O angles of ~140° but with H···O distances shorter than 2.50 Å). The resulting framework is further reinforced, albeit weakly, by the remaining C—H···O hydrogen bonds (which have H···O distances slightly longer than 2.50 Å) and by a single C—H···π(arene) hydrogen bond.

The centrosymmetric dimers formed by the type 2 molecules are linked by a single C—H···O hydrogen bond. Atom C46 in the molecule at (x, y, z), which forms part of the centrosymmetric dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), acts as a hydrogen-bond donor to nitro atom O31 in the type 2 molecule at ($1 - x$, $1 - y$, $2 - z$), which forms part of the corresponding dimer centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{3}{2}$). Propagation of this hydrogen bond then generates a chain of rings running parallel to [001] containing $R_2^2(8)$ rings centred at ($\frac{1}{2}$, $\frac{1}{2}$, $n + \frac{1}{2}$) (n = zero or integer) and $R_2^2(20)$ rings centred at ($\frac{1}{2}$, $\frac{1}{2}$, n) (n = zero or integer) (Fig. 2).

Molecules of types 1 and 3 are also linked into a [001] chain, but this is more complex than that formed by the type 2 molecules and its formation involves two C—H···O hydrogen bonds. In the first such interaction, atom C26 in the type 1 molecule at (x, y, z) acts as a hydrogen-bond donor to nitro atom O51 in the type 3 molecule at (x, y, $-1 + z$), so linking the dimers formed by molecules 1 and 3 into a $C_2^2(18)[R_2^2(8)]$ chain of rings (Fig. 3).

In the second of these interactions, atom C13 in the type 1 molecule at (x, y, z) acts as a donor to nitro atom O52 in the type 3 molecule at ($1 - x$, $-y$, $1 - z$), thereby generating a centrosymmetric four-molecule aggregate centred at ($\frac{1}{2}$, 0, $\frac{1}{2}$) and containing two $R_2^2(8)$ rings and one $R_4^4(40)$ ring (Fig. 3). The effect of the $R_4^4(40)$ motif is to link the $C_2^2(18)[R_2^2(8)]$ chains of rings into pairs, forming a complex chain enclosing $R_4^4(20)$ rings centred at ($\frac{1}{2}$, 0, n) (n = zero or integer) alternating with $R_4^4(40)$ rings centred at ($\frac{1}{2}$, 0, $n + \frac{1}{2}$) (n = zero or integer) (Fig. 3).

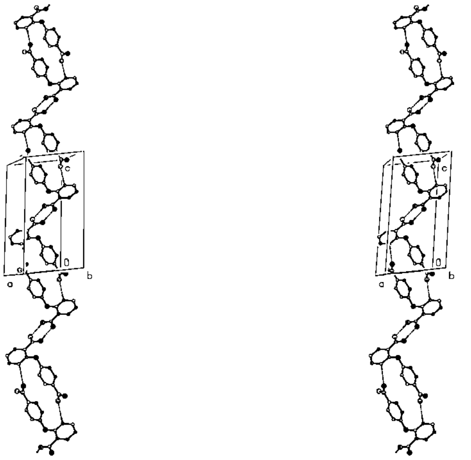

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a [001] chain of $R_2^2(8)$ and $R_2^2(20)$ rings formed by type 2 molecules only. For clarity, H atoms not involved in the motif shown have been omitted.

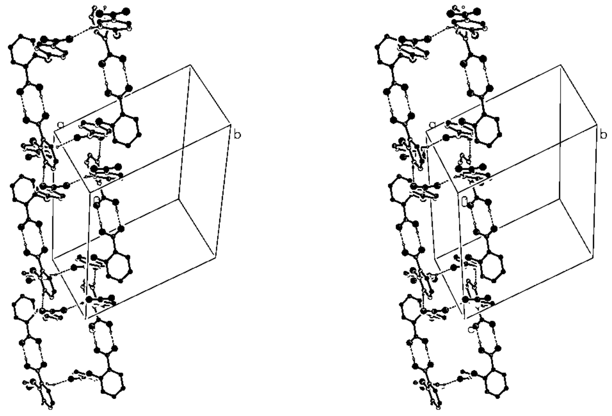

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a complex chain along [001] containing $R_2^2(8)$, $R_4^4(20)$ and $R_4^4(40)$ rings and built from type 1 and type 3 molecules only. For clarity, H atoms not involved in the motif shown have been omitted.

There are thus chains of type 2 molecules running along ($\frac{1}{2}$, $\frac{1}{2}$, z), and chains containing type 1 and type 3 molecules running along ($\frac{1}{2}$, 0, z). Two further C—H···O hydrogen bonds suffice to link these two types of chain into a single framework. Atom C16 in the type 1 molecule at (x, y, z), which lies in the chain along ($\frac{1}{2}$, 0, z), acts as a hydrogen-bond donor to nitro atom O32 in the type 2 molecule at ($-1 + x$, y, $-1 + z$), which forms part of the chain along ($-\frac{1}{2}$, $\frac{1}{2}$, z). Finally, atom C52 in the type 3 molecule at (x, y, z) acts as a donor to nitro atom O31 in the type 2 molecule at ($1 - x$, $1 - y$, $2 - z$), which lies in the chain along ($\frac{1}{2}$, $\frac{1}{2}$, z). Propagation of these two hydrogen bonds by translation and inversion links all of the [001] chain, and the three remaining hydrogen bonds simply reinforce the resulting framework.

The pattern of the C—H···O hydrogen bonds is itself sufficient to preclude any possible additional symmetry; for example, the nitro O atoms in the type 1 molecule, O11 and O12, do not act as hydrogen-bond acceptors, while both of the O atoms in the type 3 molecule, O51 and O52, are acceptors of C—H···O hydrogen bonds.

In addition to the hydrogen bonds, there is a short dipolar interaction involving the type 3 molecules only. The C61—O3 bonds in the molecules at (x, y, z) and ($-x$, $-y$, $1 - z$) are antiparallel; the corresponding O···C$^{\rm vii}$ and O···O$^{\rm vii}$ distances [symmetry code: (vii) $-x$, $-y$, $1 - z$] are 2.978 (4) and 2.758 (3) Å, respectively, and the C—O···C$^{\rm vii}$ angle is 112.7 (2)°. In this respect, this interaction is reminiscent of the type II interaction between antiparallel pairs of carbonyl groups (Allen *et al.*, 1998).

Experimental

A sample of (I) was prepared by the Ullmann reaction of 2-chlorobenzoic acid with 4-nitrophenol, according to the procedure published by Thomson & Wylie (1966). Crystals suitable for single-

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crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol (m.p. 435–437 K).

Crystal data

$C_{13}H_9NO_5$
$M_r = 259.21$
Triclinic, $P\bar{1}$
$a = 7.8495\ (6)$ Å
$b = 14.0847\ (15)$ Å
$c = 17.2325\ (18)$ Å
$\alpha = 113.187\ (4)^\circ$
$\beta = 98.515\ (6)^\circ$
$\gamma = 96.400\ (7)^\circ$
$V = 1701.5\ (3)$ Å^3

$Z = 6$
$D_x = 1.518$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7578 reflections
$\theta = 2.9$–27.5°
$\mu = 0.12$ mm^{-1}
$T = 120\ (2)$ K
Lath, colourless
$0.15 \times 0.06 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.966$, $T_{\max} = 0.998$
14 193 measured reflections
7578 independent reflections

2621 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.122$
$\theta_{\max} = 27.5^\circ$
$h = -9 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.149$
$S = 0.87$
7578 reflections
517 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C27—O21	1.226 (4)	C27—O22	1.314 (4)
C47—O41	1.245 (4)	C47—O42	1.297 (4)
C67—O61	1.234 (4)	C67—O62	1.297 (4)
C14—O1—C21	120.1 (3)	C54—O3—C61	118.4 (3)
C34—O2—C41	119.2 (3)		
C13—C14—O1—C21	43.0 (5)	C12—C11—N11—O11	8.5 (5)
C33—C34—O2—C41	−20.9 (5)	C32—C31—N31—O31	−11.9 (5)
C53—C54—O3—C61	−9.5 (5)	C52—C51—N51—O51	−19.2 (5)
C14—O1—C21—C22	−153.2 (3)	C21—C22—C27—O21	150.2 (4)
C34—O2—C41—C42	129.4 (3)	C41—C42—C47—O41	−169.0 (3)
C54—O3—C61—C62	115.8 (4)	C61—C62—C67—O61	170.8 (3)

Crystals of (I) are triclinic; space group $P\bar{1}$ was selected and confirmed by the subsequent structure analysis. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 Å and O—H distances of 0.84 Å, and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C) or $1.5U_{\rm eq}$(O). All H atoms were fully ordered. Examination of the refined structure using ADDSYM in *PLATON* (Spek, 2003) revealed no possible additional symmetry. The quality of the crystals obtained was always poor and this fact may underlie both the low proportion (35%) of the reflections labelled 'observed', even at 120 (2) K, and the fairly high merging index (0.12).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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

*Cg*1 is the centroid of the C61–C66 ring in the type 3 molecule; soft hydrogen bonds are listed in the order in which they are discussed in the *Comment* section.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O22—H22$\cdots$O61	0.84	1.79	2.625 (3)	175
O42—H42$\cdots$O41$^{\rm i}$	0.84	1.81	2.648 (3)	172
O62—H62$\cdots$O21	0.84	1.80	2.637 (3)	176
C46—H46$\cdots$O31$^{\rm ii}$	0.95	2.49	3.413 (5)	163
C26—H26$\cdots$O51$^{\rm iii}$	0.95	2.36	3.268 (5)	161
C13—H13$\cdots$O52$^{\rm iv}$	0.95	2.50	3.422 (5)	163
C16—H16$\cdots$O32$^{\rm v}$	0.95	2.48	3.241 (5)	138
C52—H52$\cdots$O31$^{\rm ii}$	0.95	2.35	3.153 (5)	142
C32—H32$\cdots$O51$^{\rm ii}$	0.95	2.54	3.388 (5)	149
C44—H44$\cdots$O22$^{\rm vi}$	0.95	2.53	3.370 (5)	147
C55—H55$\cdots$*Cg*1$^{\rm vii}$	0.95	2.87	3.745 (4)	154

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, 2-z$; (iii) $x, y, z-1$; (iv) $1-x, -y, 1-z$; (v) $x-1, y, z-1$; (vi) $-x, 1-y, 1-z$; (vii) $-x, -y, 1-z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1719). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Baalham, C. A., Lommerse, J. P. M. & Raithby, P. R. (1998). *Acta Cryst.* B**54**, 320–329.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Braga, D., Grepioni, F., Birdha, K., Pedireddi, V. R. & Desiraju, G. R. (1995). *J. Am. Chem. Soc.* **117**, 3156–3166.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 86–89. Oxford University Press.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* B**56**, 39–57.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
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). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Thomson, R. H. & Wylie, A. G. (1966). *J. Chem. Soc. C*, pp. 321–324.

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