organic papers

2-Phenoxybenzoic acid at room temperature

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.164
Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title compound, $C_{13}H_{10}O_3$, the molecules form classical hydrogen-bonded carboxylic acid dimers [O···O = 2.651 (2) Å]. These dimers are linked by C—H···π and π–π interactions to give a three-dimensional network.

Comment

Benzoic acid is a compound that has an elegant simplicity to its molecular structure, but its derivatives display an enormous complexity and diversity of molecular structures. The latest version of the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002) contains 1883 structures with a benzoic acid derivative existing in the crystal structure as an isolated molecule; this does not include structures in which the molecules are either deprotonated or coordinated to metal ions. By contrast, the simple and readily available title compound, (I), is only observed in four crystal structures in the CSD, and in all of these it serves as a ligand. The 3- and 4-phenoxybenzoic acid structures are observed even less frequently, with zero and one structures of these compounds, respectively. Possibly the most closely related structure available in the CSD is that of 2-(2-carboxyphenoxy)benzoic acid (CSD refcode MIGPAT; Field & Venkataraman, 2002), which differs only by the presence of an extra carboxylic acid group on the second benzene ring.

(I)
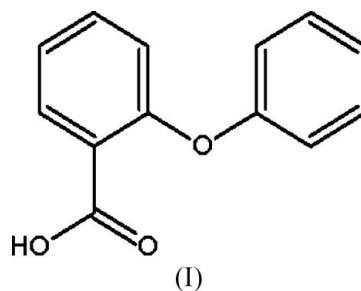
The molecular geometry observed in the structure of (I) is mostly unremarkable, with the principal features of note being the prolate displacement ellipsoid of atom O10, which is consistent with a large vibration perpendicular to the plane of the benzoic acid fragment (Fig. 1). This motion is not obviously propagated in the second benzene ring; in this portion, the displacement ellipsoids are surprisingly close to spherical, although large. These observations are most likely due to the combination of three movements: a typical in-plane rotational movement around the ring, the translational movement observed for O10 in the plane of this ring and perpendicular to the O10—C11 bond vector, and a rotational
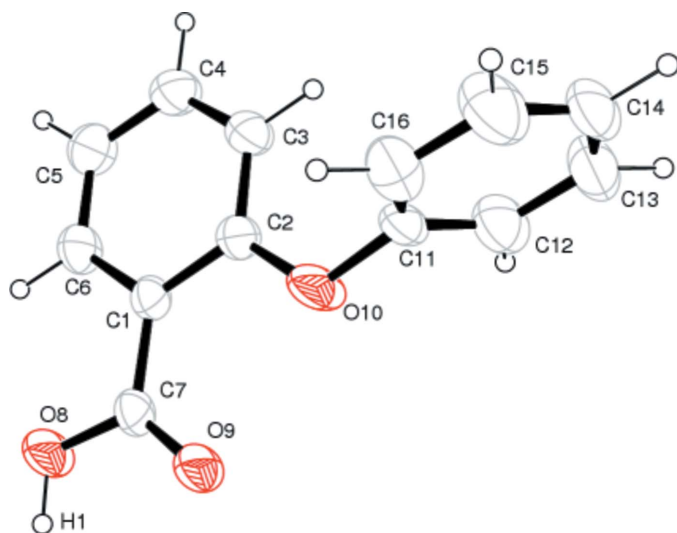
Figure 1
A drawing of the molecule of (I), showing the atomic numbering scheme. Ellipsoids for non-H atoms are shown at the 30% probability level. All H atoms take their number from the parent C atom, except for H1.
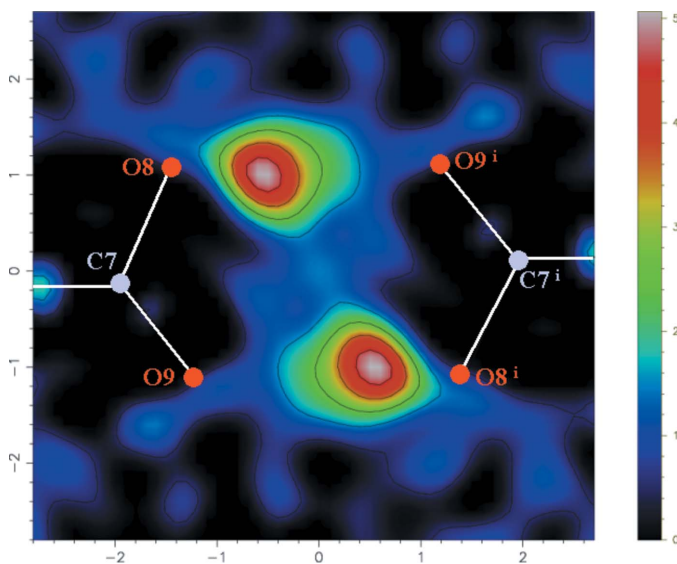

Figure 2
Fourier difference map section through the carboxylic acid dimer plane defined by atoms C7, O8, O9, C7^i, O8^i and O9^i [symmetry code: (i) $3 - x$, $1 - y$, $-z$]. There is clearly only a single peak associated with each hydrogen bond, corresponding to an ordered H atom.

Figure 3
Packing plots of (I), illustrating the principal contacts in the structure. (top) The hydrogen-bond dimers link together into ribbons via C—H···π contacts (shown in yellow). (bottom) These ribbons stack due to π–π interactions (shown in pale green).

movement around the O10—C11 bond vector. The average C—C bond length in this ring is slightly short, at 1.36 Å; this bond shortening can also be attributed to the effect of large thermal libration. The normals to the planes of the two benzene rings are nearly perpendicular, at 89.8 (2)°.

The molecules of (I) assemble to form a classical hydrogen-bonded dimer, in which the C7—O9 and C7—O8 bond lengths in the carboxylic acid group of 1.223 (2) and 1.3015 (18) Å, respectively, indicate a well ordered hydrogen bond. This is supported by the lack of H-atom disorder observed in the Fourier difference map (calculated with the program
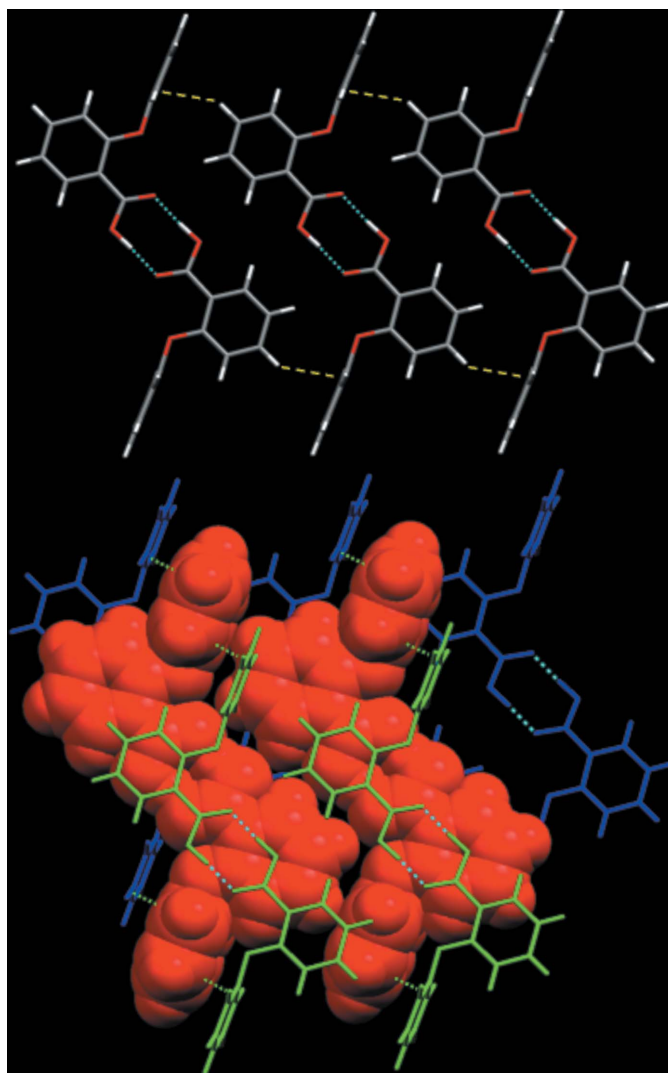
MAPVIEW, part of the *WinGX* suite; Farrugia, 1999) through the dimer group (Fig. 2). The single crystallographically unique hydrogen bond, *viz.* O8—H1···O9^i [symmetry code: (i) $3 - x$, $1 - y$, $-z$], exhibits a typical O···O separation for benzoic acid dimers of 2.651 (2) Å. The remainder of the contacts lie outside the sum of the van der Waals radii of the two atoms involved, but these very weak interactions can still be used to describe the remainder of the structure. The dimers assemble into extended ribbons through C—H···π inter-actions of 3.658 Å for C4—H4···C12^{ii} [symmetry code: (ii) x, $y - 1$, z] (Fig. 3a), and these ribbons form stacks defined by a π–π contact of 3.446 Å between atoms C13 and C16^{iii} [symmetry code: (iii) $x - 1$, y, z] (Fig. 3b). The stacks pack together with C—H···π interactions of 3.697 Å for C12—H12···C5^{iv} [symmetry code: (iv) $x - 1$, $y + 1$, z] (Fig. 4).

The most striking difference between the molecular struc-ture presented here and that of MIGPAT (Field & Venkata-
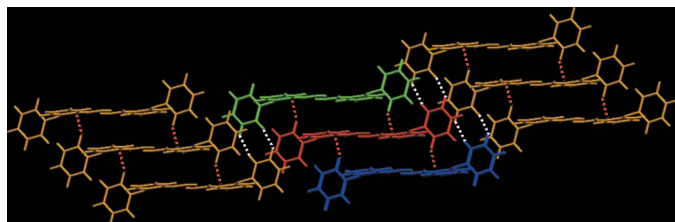
Figure 4
A packing plot of the entire structure. The stacks are linked by C—H···π interactions, shown in red.

raman, 2002) is the geometry of the carboxylic acid group. In the title compound, it is clear from the bond lengths that the C=O double bond is C7=O9, involving the O atom closest to the ether group. By contrast, the shorter C—O bond in MIGPAT is that further from the ether O atom, although the difference between the two bond lengths is much less than we report here. As the two chemically different carboxylic acids in MIGPAT are crystallographically identical, it is possible that there is some correlated structural disorder between the C—O and C=O bonds; this might explain the very similar C—O bond lengths in MIGPAT.

Experimental

The title compound was used as received from Aldrich. Crystals of diffraction quality were grown from an acetone solution.

Crystal data

$C_{13}H_{10}O_3$	$Z = 2$
$M_r = 214.22$	$D_x = 1.330$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 5.2736 (5)$ Å	Cell parameters from 8180
$b = 7.7366 (6)$ Å	reflections
$c = 13.6863 (10)$ Å	$\theta = 2-28°$
$\alpha = 89.184 (6)°$	$\mu = 0.10$ mm^{-1}
$\beta = 83.433 (6)°$	$T = 293$ K
$\gamma = 74.640 (6)°$	Block, colourless
$V = 534.84 (8)$ Å^3	$0.30 \times 0.15 \times 0.10$ mm

Data collection

Bruker APEX2 diffractometer	1516 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.028$
Absorption correction: multi-scan	$\theta_{max} = 28.5°$
(*SADABS*; Sheldrick, 1996)	$h = -6 \rightarrow 7$
$T_{min} = 0.98$, $T_{max} = 0.99$	$k = -10 \rightarrow 10$
8180 measured reflections	$l = -18 \rightarrow 18$
2565 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F^2) + 0.08$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$+ 0.08P]$
$wR(F^2) = 0.164$	where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$S = 0.93$	$(\Delta/\sigma)_{max} < 0.001$
2565 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
148 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.397 (2)	C13—C14	1.343 (4)
C1—C6	1.390 (2)	C14—C15	1.328 (4)
C1—C7	1.477 (2)	C15—C16	1.379 (3)
C2—O10	1.371 (2)	C3—C4	1.367 (3)
C2—C3	1.389 (3)	C4—C5	1.376 (3)
O10—C11	1.387 (2)	C5—C6	1.378 (3)
C11—C12	1.346 (3)	C7—O9	1.223 (2)
C11—C16	1.372 (4)	C7—O8	1.3015 (18)
C12—C13	1.373 (3)		
C2—C1—C6	117.52 (16)	C12—C13—C14	121.1 (2)
C2—C1—C7	122.57 (15)	C13—C14—C15	119.9 (2)
C6—C1—C7	119.91 (14)	C14—C15—C16	120.9 (3)
C1—C2—O10	117.58 (15)	C15—C16—C11	118.8 (2)
C1—C2—C3	120.32 (16)	C2—C3—C4	120.45 (17)
O10—C2—C3	122.08 (15)	C3—C4—C5	120.44 (19)
C2—O10—C11	119.76 (14)	C4—C5—C6	119.18 (18)
O10—C11—C12	119.5 (2)	C1—C6—C5	122.08 (17)
O10—C11—C16	120.0 (2)	C1—C7—O9	124.03 (14)
C12—C11—C16	120.14 (19)	C1—C7—O8	114.22 (15)
C11—C12—C13	119.2 (2)	O9—C7—O8	121.75 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H1···O9^i	0.90 (2)	1.75 (2)	2.651 (2)	175 (2)

Symmetry code: (i) $3 - x, 1 - y, -z$.

H atoms were positioned geometrically and refined as riding groups, with C—H = 1.0 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, except for atom H1, which was located in a Fourier difference map and refined with an O—H distance restraint of 0.90 (5) Å and a fixed $U_{iso}(H) = 0.05$ Å^2.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *CRYSTALS*.

This paper is the result of an optional undergraduate class project entitled 'Frontiers of Crystallography', designed to show some of the sort of research that can be undertaken in crystallography. The data collection, structure solution, refinement and post-refinement analysis of the unknown title structure were all undertaken in parallel by the undergraduate students, who are all co-authors, and the collated information has resulted in this paper.

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