

2-Hydroxy-5-[(*E*)-(4-methoxyphenyl)-  
diazanyl]benzoic acidT. S. Basu Baul,<sup>a</sup> S. Dhar<sup>a</sup> and E. R. T. Tiekink<sup>b\*</sup><sup>a</sup>Chemical Laboratory, Regional Sophisticated Instrumentation Centre, North Eastern Hill University, Bijnai Complex, Shillong 793 003, India, and <sup>b</sup>Department of Chemistry, The University of Adelaide, Australia 5005  
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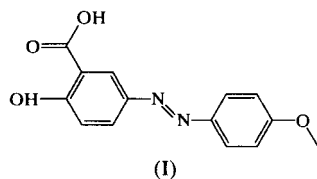
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The title compound, C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>, shows an *E* conformation about the diazenyl N atoms. The crystal structure features layers of molecules with the primary connection between the layers afforded by carboxylic acid dimer motifs; no evidence for extensive  $\pi$ - $\pi$  stacking between the layers was found.

## Comment

Organotin compounds containing carboxylate ligands similar to that derived from the title compound have received considerable attention recently (Basu Baul & Tiekink, 1998, 1999; Willem *et al.*, 1998). These systems have provided a large number of X-ray quality crystals enabling systematic analyses and hence conclusions to be drawn as to the reasons why different motifs (Tiekink, 1991, 1994) are found for tri-organotin carboxylates (Willem *et al.*, 1998). A key feature of some of these structures is the presence of  $\pi$ - $\pi$  interactions that serve to stabilize the crystal structure. Surprisingly, relatively little is known about the structural chemistry of diazo-carboxylic acid derivatives themselves (Moreiras *et al.*, 1980; van der Sluis & Spek, 1990) and in order to ascertain the reasons why  $\pi$ - $\pi$  stacking is observed in some organotin derivatives but not in others, the structure of the title compound, (I) (Fig. 1 and Table 1), was investigated.



The conformation about the diazo group is *E* and derived interatomic parameters are as expected. The molecule is basically planar, although there is a slight twist about the diazenyl group, as seen in the N1–N2–C8–C9 and N2–N1–C6–C5 torsion angles of 176.4 (2) and 8.5 (3)°, respectively. The dihedral angle between the two aromatic rings is

5.43 (7)°. The carboxylic acid group is coplanar with the C2–C7 ring [O1–C1–C2–C3–178.2 (2)°], which facilitates the formation of an intramolecular hydrogen-bonding contact, such that O3···O2 is 2.630 (2) Å (see Table 2). Intermolecular hydrogen-bonding interactions are also present.

The structure may be described as a hydrogen-bonded array in the *ac* plane that is stacked along *b*; however, the layers are not flat, there being significant corrugation within them. The arrangement of molecules within the layer is best described as being based on the coronene motif (Desiraju & Gavezzotti, 1989). The layers are stabilized in part by weak hydrogen-bonding interactions between the hydroxyl-H atom and a symmetry-related methoxy-O atom, such that O3···O4<sup>i</sup> is 3.003 (2) Å [symmetry code: (i)  $\frac{1}{2} + x, y, \frac{1}{2} - z$ ]. Contacts of 3.522 (2) Å occurring between translationally related C1 and C5<sup>ii</sup> atoms throughout the layer are also noted [symmetry code: (ii)  $x, y, 1 + z$ ]. Connections between the layers are afforded by carboxylic acid dimer formation [O1···O2<sup>iii</sup>

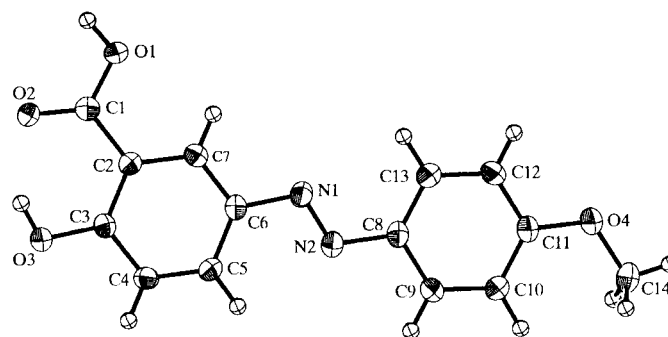


Figure 1

The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids shown at the 50% probability level (ORTEP; Johnson, 1976).

2.631 (2) Å; symmetry code: (iii)  $2 - x, -y, 2 - z$ ]. No evidence was found for extensive  $\pi$ - $\pi$  interactions in the lattice. However, between layers, centrosymmetrically related pairs of benzoic acid fragments approach each other at distances indicative of  $\pi$ - $\pi$  interactions. The closest contact of 3.295 (2) Å occurs between C1 and C3<sup>iv</sup>, and the average separation between the least-squares planes through each of the O<sub>2</sub>CC<sub>6</sub> fragments is 3.24 Å [symmetry code: (iv)  $2 - x, -y, 1 - z$ ]. Presumably,  $\pi$ - $\pi$  interactions involving the methoxyphenyl fragment and hence, the whole molecule, are precluded by the bulky nature of the methyl group. Finally, evidence for a C–H···ring interaction between the layers is also noted, such that C5–H4···Cp<sup>v</sup> (where Cp is the centroid of the C2–C7 ring) is 2.78 Å and the angle at H4 is 139° [symmetry code: (v)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ].

## Experimental

Diazo-coupling of *p*-methoxyaniline and *o*-hydroxybenzoic acid in alkaline solution yielded the title compound in 52% yield. Recrystallization from benzene solution gave orange–red crystals (m.p. 482–483 K).

## Crystal data

$C_{14}H_{12}N_2O_4$   
 $M_r = 272.26$   
 Orthorhombic,  $Pbca$   
 $a = 24.902$  (6) Å  
 $b = 15.109$  (6) Å  
 $c = 6.674$  (2) Å  
 $V = 2511$  (1) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.440$  Mg m<sup>-3</sup>

## Data collection

Rigaku AFC-7R diffractometer  
 $\omega$  scans  
 6617 measured reflections  
 2894 independent reflections  
 1800 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.030$   
 $\theta_{max} = 27.52^\circ$

## Refinement

Refinement on  $F$   
 $R = 0.034$   
 $wR = 0.033$   
 $S = 1.650$   
 1800 reflections  
 181 parameters

Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 6.4$ – $9.6^\circ$   
 $\mu = 0.107$  mm<sup>-1</sup>  
 $T = 173$  K  
 Trigonal plate, orange-red  
 $0.45 \times 0.24 \times 0.19$  mm

$h = 0 \rightarrow 32$   
 $k = -1 \rightarrow 19$   
 $l = -8 \rightarrow 8$   
 3 standard reflections  
 every 400 reflections  
 intensity decay:  $-1.39\%$

H-atom parameters not refined  
 $w = 1/[\sigma^2(F_o) + 0.00001|F_o|^2]$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.20$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.311 (2)	O4–C14	1.427 (3)
O2–C1	1.241 (2)	N1–N2	1.260 (2)
O3–C3	1.355 (2)	N1–C6	1.432 (2)
O4–C11	1.367 (2)	N2–C8	1.424 (2)
C11–O4–C14	117.1 (2)	O1–C1–O2	122.7 (2)
N2–N1–C6	112.2 (2)	O1–C1–C2	115.2 (2)
N1–N2–C8	115.1 (2)	O2–C1–C2	122.1 (2)

All H atoms were located from a difference map and refined but were fixed in the final cycles of refinement (O–H 0.86 and 0.90 Å; C–H 0.95–1.03 Å).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997–1999); program(s) used to solve

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H1 <sup>i</sup> ···O2 <sup>i</sup>	0.90	1.73	2.631 (2)	176
O3–H2 <sup>i</sup> ···O2	0.86	1.87	2.630 (2)	146
O3–H2 <sup>ii</sup> ···O4 <sup>ii</sup>	0.86	2.46	3.003 (2)	122

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

structure: *SIR97* (Altomare *et al.*, 1997); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1403). Services for accessing these data are described at the back of the journal.

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