3-(1,2,2-Triiodoethenyl)benzoic acid

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The title compound, $C_9H_5I_3O_2$, has a layered structure exhibiting O—H$\cdots$O hydrogen bonds, as well as C—I$\cdots$C and C—I$\cdots$O halogen bonding. The C atoms of the ethenyl group are disordered over two sets of sites with refined occupancies of 0.545 (18) and 0.455 (18).

3D view
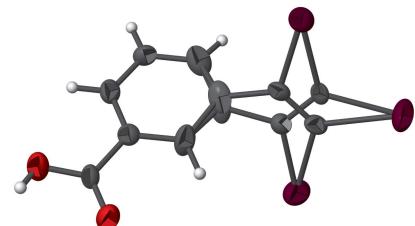
Chemical scheme
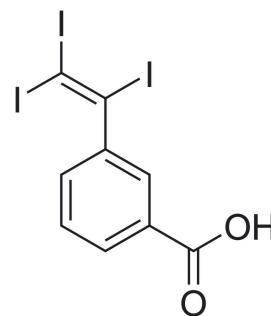
Structure description

Upon analyzing the crystals obtained from recrystallizing 3-iodoethynylbenzoic acid from acetonitrile, a trace quantity of 3-(1,2,2-triiodoethenyl)benzoic acid (Fig. 1) was observed. The crystal structure of 3-(1,2,2-triiodoethenyl)benzoic acid has a disordered ethenyl group, with the disorder akin to that reported for 1,2,2-triiodovinylbenzene (Berger *et al.*, 2016). While the iodine atoms' coordinates are well ordered, the carbon atoms occupy two sets of sites.

In the crystal, the carboxylic acid group interacts with the carboxylic acid group from an adjacent molecule *via* O—H$\cdots$O hydrogen bonds (see Table 1), forming inversion dimers. One of the iodine atoms participates in a C—I$\cdots$O halogen bond [$d_{I\cdots O}$ = 3.174 (6) Å, $\theta_{C-I\cdots O}$ = 159.3 (6)° for C9—I2$\cdots$O2, 161.3 (4)° for C9′—I2$\cdots$O2] and a second iodine atom participates in a halogen bond (Table 2) to the carbon atom on the benzene ring [$d_{I\cdots C}$ = 3.511 (7) Å, $\theta_{C-I\cdots C}$ = 165.0 (5)° for C9′—I1$\cdots$C4 and 164.5 (6)° for C8—I1$\cdots$C4]. As a result of the disorder of the carbon atoms and the dependence of the halogen-bond angle on the position of the carbon atoms, two sets of bond angles can be obtained from the crystal structure. Sheets of inversion dimers are stacked to give the crystal of 3-(1,2,2-triiodoethenyl)benzoic acid. Overall, as shown in Fig. 2, the structure is convoluted as a result of co-present hydrogen and halogen bonds, in addition to disorder.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1⋯O2[i]	0.82 (7)	1.83 (8)	2.614 (7)	159 (9)

Symmetry code: (i) $-x + 2, -y + 1, -z + 2$.

Table 2
Halogen-bond geometry (Å, °).

$C-I\cdots X$	$I\cdots X$	$C-I\cdots X$
C9—I2⋯O2[i]	3.174 (6)	159.3 (6)
C9′—I2⋯O2[i]	3.174 (6)	161.3 (4)
C8—I1⋯C4[ii]	3.511 (7)	164.5 (6)
C9′—I1⋯C4[ii]	3.511 (7)	165.0 (5)

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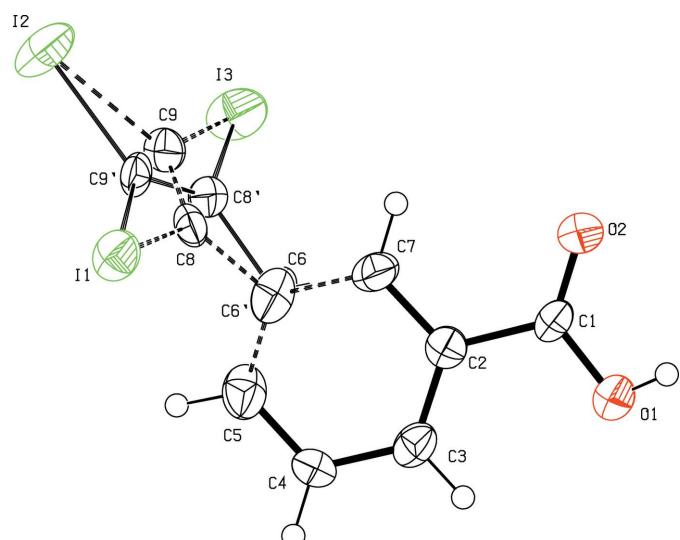

Figure 1
The molecular structure of 3-(1,2,2-triiodoethenyl)benzoic acid, with displacement ellipsoids drawn at the 50% probability level.

Synthesis and crystallization

Crystals of 3-(1,2,2-triiodoethenyl)benzoic acid were obtained as a trace impurity during the recrystallization of 3-iodo-

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_9H_5I_3O_2$
M_r	525.83
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	4.7121 (9), 18.752 (4), 13.856 (3)
β (°)	92.379 (5)
V (Å^3)	1223.3 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.64
Crystal size (mm)	0.48 × 0.16 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.485, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9164, 3033, 1539
R_{int}	0.065
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.078, 0.99
No. of reflections	3033
No. of parameters	159
No. of restraints	97
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.14, −1.11

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *CIFTAB* (Sheldrick, 1997).

ethynylbenzoic acid from acetonitrile. The synthesis of 3-iodoethynylbenzoic acid has been reported elsewhere (Szell *et al.*, 2018).

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3. The triiodoethenyl fragment is disordered over two positions with a 0.545 (18): 0.455 (18)
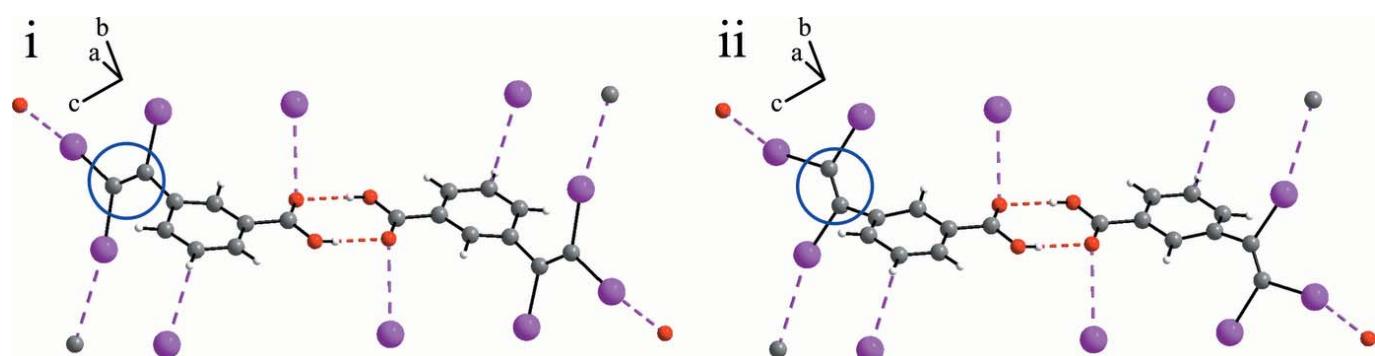

Figure 2
The crystal packing of 3-(1,2,2-triiodoethenyl)benzoic acid, showing O—H⋯O hydrogen bonds and the C—I⋯O and C—I⋯C halogen bonds as dashed lines. The disorder positions in the ethenyl group are also indicated.

occupancy ratio. It was refined using restraints applied to the atomic displacement parameters, bond distances and angles [RIGU, SAME in *SHELXL* (Sheldrick, 2015*b*)]. No additional restraints or constraints were applied.

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full crystallographic data

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3-(1,2,2-Triiodoethenyl)benzoic acid

Crystal data

$C_9H_5I_3O_2$	$F(000) = 936$
$M_r = 525.83$	$D_x = 2.855$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.7121$ (9) Å	Cell parameters from 2073 reflections
$b = 18.752$ (4) Å	$\theta = 2.6$–27.2°
$c = 13.856$ (3) Å	$\mu = 7.64$ mm^{-1}
$\beta = 92.379$ (5)°	$T = 200$ K
$V = 1223.3$ (4) Å^3	Prism, colourless
$Z = 4$	$0.48 \times 0.16 \times 0.06$ mm

Data collection

Bruker APEXII CCD diffractometer	3033 independent reflections
φ and ω scans	1539 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$R_{int} = 0.065$
	$\theta_{max} = 28.4°$, $\theta_{min} = 1.8°$
$T_{min} = 0.485$, $T_{max} = 0.746$	$h = -6 \rightarrow 6$
9164 measured reflections	$k = -24 \rightarrow 24$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.040$	
$wR(F^2) = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 0.1535P]$
$S = 0.99$	where $P = (F_o^2 + 2F_c^2)/3$
3033 reflections	$(\Delta/\sigma)_{max} = 0.001$
159 parameters	$\Delta\rho_{max} = 1.14$ e Å^{-3}
97 restraints	$\Delta\rho_{min} = -1.10$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The hydrogen atom bonded to the oxygen atom was located in the difference Fourier map and refined freely while the remaining hydrogen atoms were placed in idealized positions.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	0.47571 (12)	0.38729 (3)	0.47397 (4)	0.04455 (17)	
I2	0.23490 (14)	0.21161 (3)	0.51879 (4)	0.0605 (2)	
I3	0.07423 (13)	0.26225 (3)	0.75867 (4)	0.05472 (19)	
O1	0.7327 (13)	0.5516 (3)	0.9400 (4)	0.0463 (16)	
O2	0.8689 (11)	0.4380 (3)	0.9237 (4)	0.0427 (14)	
C1	0.7188 (16)	0.4891 (4)	0.8996 (5)	0.0317 (18)	
C2	0.5060 (15)	0.4839 (4)	0.8176 (5)	0.0316 (18)	
C3	0.3394 (15)	0.5406 (4)	0.7888 (5)	0.0364 (19)	
H3	0.357931	0.584600	0.822475	0.044*	
C4	0.1446 (15)	0.5348 (4)	0.7116 (5)	0.037 (2)	
H4	0.028550	0.574332	0.692924	0.045*	
C5	0.1209 (16)	0.4713 (5)	0.6623 (6)	0.046 (2)	
H5	−0.032421	0.464049	0.616701	0.055*	
C7	0.4797 (16)	0.4205 (4)	0.7676 (6)	0.047 (2)	
H7	0.568537	0.378584	0.792825	0.057*	
C6	0.321 (6)	0.4178 (10)	0.6791 (17)	0.038 (6)	0.455 (18)
C8	0.318 (4)	0.3591 (11)	0.6082 (13)	0.032 (4)	0.455 (18)
C9	0.237 (4)	0.2952 (12)	0.6235 (14)	0.032 (4)	0.455 (18)
C6′	0.259 (5)	0.4101 (8)	0.6977 (15)	0.040 (6)	0.545 (18)
C8′	0.228 (3)	0.3326 (9)	0.6600 (12)	0.033 (4)	0.545 (18)
C9′	0.284 (3)	0.3147 (9)	0.5707 (12)	0.030 (4)	0.545 (18)
H1	0.881 (17)	0.550 (4)	0.973 (6)	0.06 (3)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0602 (4)	0.0418 (3)	0.0321 (3)	−0.0075 (3)	0.0067 (3)	0.0011 (3)
I2	0.0916 (5)	0.0355 (3)	0.0558 (4)	−0.0137 (3)	0.0181 (3)	−0.0144 (3)
I3	0.0790 (5)	0.0431 (4)	0.0438 (3)	−0.0026 (3)	0.0223 (3)	0.0041 (3)
O1	0.050 (4)	0.037 (4)	0.051 (4)	0.002 (3)	−0.014 (3)	−0.010 (3)
O2	0.050 (4)	0.030 (3)	0.048 (3)	0.003 (3)	−0.008 (3)	−0.002 (3)
C1	0.038 (5)	0.027 (5)	0.030 (4)	−0.005 (4)	0.002 (4)	−0.007 (4)
C2	0.033 (5)	0.032 (5)	0.030 (4)	−0.002 (4)	0.003 (4)	0.001 (4)
C3	0.045 (5)	0.033 (5)	0.031 (4)	−0.003 (4)	0.007 (4)	−0.006 (4)
C4	0.041 (5)	0.032 (5)	0.038 (5)	0.008 (4)	−0.005 (4)	0.004 (4)
C5	0.031 (5)	0.060 (5)	0.046 (5)	0.003 (4)	−0.001 (4)	−0.013 (4)
C7	0.043 (5)	0.031 (5)	0.067 (6)	0.009 (4)	−0.014 (4)	−0.015 (4)
C6	0.012 (11)	0.054 (9)	0.049 (8)	−0.007 (8)	0.008 (8)	−0.017 (8)
C8	0.034 (11)	0.036 (7)	0.024 (7)	0.000 (7)	−0.009 (7)	0.003 (5)
C9	0.039 (11)	0.037 (8)	0.021 (9)	0.002 (8)	0.006 (9)	0.002 (6)
C6′	0.019 (11)	0.047 (6)	0.054 (10)	0.002 (6)	0.004 (9)	−0.023 (6)
C8′	0.041 (9)	0.031 (7)	0.028 (7)	0.002 (7)	−0.002 (6)	−0.001 (5)
C9′	0.033 (9)	0.030 (7)	0.027 (7)	−0.010 (7)	−0.007 (6)	−0.003 (6)

Geometric parameters (Å, º)

I1—C8	2.098 (19)	C3—H3	0.9500
I1—C9′	2.137 (16)	C4—C5	1.375 (10)
I2—C9′	2.072 (16)	C4—H4	0.9500
I2—C9	2.14 (2)	C5—C6	1.391 (15)
I3—C8′	2.054 (17)	C5—C6′	1.398 (14)
I3—C9	2.14 (2)	C5—H5	0.9500
O1—C1	1.299 (8)	C7—C6′	1.406 (14)
O1—H1	0.82 (7)	C7—C6	1.410 (15)
O2—C1	1.229 (8)	C7—H7	0.9500
C1—C2	1.488 (9)	C6—C8	1.48 (2)
C2—C3	1.371 (9)	C8—C9	1.28 (3)
C2—C7	1.379 (9)	C6′—C8′	1.55 (2)
C3—C4	1.385 (9)	C8′—C9′	1.32 (3)
C1—O1—H1	103 (6)	C6—C7—H7	120.0
O2—C1—O1	124.6 (7)	C5—C6—C7	116.8 (13)
O2—C1—C2	121.2 (7)	C5—C6—C8	116.1 (11)
O1—C1—C2	114.1 (7)	C7—C6—C8	126.6 (12)
C3—C2—C7	119.0 (7)	C9—C8—C6	126 (2)
C3—C2—C1	122.1 (7)	C9—C8—I1	120.2 (17)
C7—C2—C1	118.9 (7)	C6—C8—I1	114.1 (17)
C2—C3—C4	121.2 (7)	C8—C9—I2	124.6 (17)
C2—C3—H3	119.4	C8—C9—I3	122.4 (17)
C4—C3—H3	119.4	I2—C9—I3	112.9 (10)
C5—C4—C3	119.3 (7)	C5—C6′—C7	116.6 (12)
C5—C4—H4	120.4	C5—C6′—C8′	128.1 (11)
C3—C4—H4	120.4	C7—C6′—C8′	114.7 (10)
C4—C5—C6	120.1 (9)	C9′—C8′—C6′	122.4 (17)
C4—C5—C6′	120.7 (9)	C9′—C8′—I3	123.4 (14)
C4—C5—H5	119.9	C6′—C8′—I3	114.1 (13)
C6—C5—H5	119.9	C8′—C9′—I2	122.7 (14)
C2—C7—C6′	120.9 (8)	C8′—C9′—I1	122.1 (13)
C2—C7—C6	120.1 (9)	I2—C9′—I1	114.9 (8)
C2—C7—H7	120.0		
O2—C1—C2—C3	−179.1 (7)	C5—C6—C8—I1	72 (3)
O1—C1—C2—C3	−0.6 (10)	C7—C6—C8—I1	−116 (3)
O2—C1—C2—C7	−0.4 (11)	C6—C8—C9—I2	179.8 (13)
O1—C1—C2—C7	178.1 (7)	I1—C8—C9—I2	−2 (2)
C7—C2—C3—C4	0.7 (11)	C6—C8—C9—I3	2 (3)
C1—C2—C3—C4	179.4 (6)	I1—C8—C9—I3	179.9 (8)
C2—C3—C4—C5	−0.8 (11)	C4—C5—C6′—C7	−18 (3)
C3—C4—C5—C6	−11 (2)	C4—C5—C6′—C8′	171.7 (18)
C3—C4—C5—C6′	9.6 (18)	C2—C7—C6′—C5	17 (3)
C3—C2—C7—C6′	−9.3 (18)	C2—C7—C6′—C8′	−170.5 (13)
C1—C2—C7—C6′	172.0 (16)	C5—C6′—C8′—C9′	59 (3)

C3—C2—C7—C6	11 (2)	C7—C6′—C8′—C9′	−112 (2)
C1—C2—C7—C6	−168.0 (18)	C5—C6′—C8′—I3	−118 (2)
C4—C5—C6—C7	21 (3)	C7—C6′—C8′—I3	71 (2)
C4—C5—C6—C8	−166.2 (17)	C6′—C8′—C9′—I2	−178.6 (11)
C2—C7—C6—C5	−22 (3)	I3—C8′—C9′—I2	−2 (2)
C2—C7—C6—C8	167 (2)	C6′—C8′—C9′—I1	9 (2)
C5—C6—C8—C9	−109 (3)	I3—C8′—C9′—I1	−174.8 (7)
C7—C6—C8—C9	62 (4)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2[i]	0.82 (7)	1.83 (8)	2.614 (7)	159 (9)

Symmetry code: (i) −x+2, −y+1, −z+2.