# organic compounds

# 4-Ethynyl-1,2-methylenedioxybenzene at 150 K

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The title compound, $C_9H_6O_2$, contains two moderate C—H$\cdots$O hydrogen bonds. That involving the terminal alkyne gives rise to chains along the $b$ axis. The other hydrogen bond occurs over a centre of symmetry, leading to dimers. The combination of the two interactions gives rise to rings, each comprising six molecules, which are part of infinite sheets in the $bc$ plane.

## Comment

The packing of simple aromatic compounds has attracted interest (Desiraju & Kishan, 1989; Weiss *et al.*, 1997). It has been demonstrated by Sarma & Desiraju (1986) that the effects of heteroatoms (principally O or Cl) either within the aromatic ring or peripheral to it can be structure determining. A low number of heteroatoms means that structures tend to adopt herring-bone motifs; benzene, with none, is the archetypal example (Bacon *et al.*, 1964). On the other hand, higher numbers of heteroatoms can lead to stacked motifs, *e.g.* pyranthrone (Sarma & Desiraju, 1986). Desiraju & Kishan (1989) demonstrated this principle with structural studies on 3,4-(methylenedioxy)cinnamic acid and [3,4-(methylenedioxy)phenyl]propiolic acid. Therefore, we decided to examine the structural motifs present in the related compound 4-ethynyl-1,2-methylenedioxybenzene, (I).

(I)
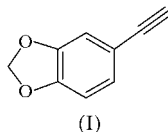
Compound (I) lies in a general position (Fig. 1), but with the non-H atoms coplanar to within 0.008 Å. All molecular geometry parameters lie within the normal ranges (Allen *et al.*, 1987).

The most significant feature of (I) is the presence of two intermolecular C—H$\cdots$O hydrogen bonds (Table 1). The first occurs over a centre of symmetry so that the aromatic H2 atom acts as a donor to O9[ii] [symmetry code: (ii) $1 - x, 1 - y, -z$], generating a dimeric centrosymmetric $R_2^2(8)$ motif (Fig. 2).

The second intermolecular hydrogen bond involves the alkynyl H8 atom, which acts as a donor to *n*-glide-related O9[i] [symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$]. This generates $C(7)$ chains along the $y$ axis, leading to herring-bone chains in the $ab$ plane. The top half of each dimer is related to the bottom half of the neighbouring dimer by this C—H$\cdots$O interaction (Fig. 2). Therefore, the dimers are related to each other in a zigzag manner along the $b$ direction within the $bc$ plane. The
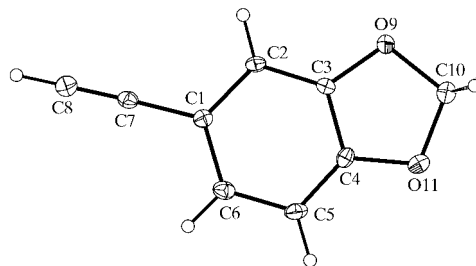


**Figure 1**
A view of the structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

combination of the two hydrogen bonds generates a six-molecule $R_6^4(28)$ ring as part of an infinite two-dimensional sheet (Fig. 2). There is also a possible C5—H5$\cdots$O11[iii] interaction [symmetry code: (iii) $-x, 1 - y, 1 - z$] between dimers related by a centre of symmetry in the middle of the $R_6^4(28)$ ring.
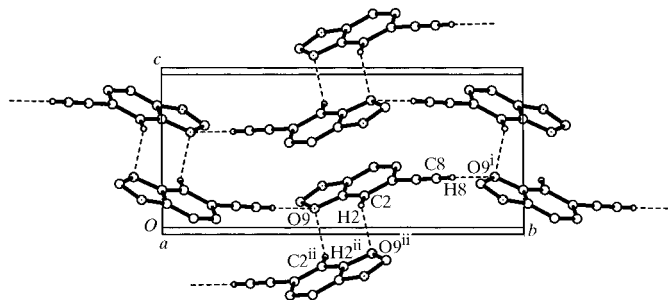


**Figure 2**
The packing diagram of (I) showing part of an infinite two-dimensional sheet in the $bc$ plane. The component dimeric units and six-molecule rings are visible [symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$].

## Experimental

Compound (I) (Pelter *et al.*, 1990) was prepared according to the method of Corey & Fuchs (1972). 3,4-(Methylenedioxy)benzaldehyde was firstly transformed to the dibromoalkene by treatment with carbon tetrabromide, triphenylphosphine and zinc; subsequent treatment with butyllithium generated the title alkyne, (I), which exists as a supercooled oil at room temperature. The sample was placed in a sealed capillary and cooled *in situ* on the diffractometer using an Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986). The crystal was grown by repeated cycling of the temperature across the freezing point of the compound (260 K).

*Crystal data*

$C_9H_6O_2$
$M_r = 146.14$
Monoclinic, $P2_1/n$
$a = 6.318\ (3)$ Å
$b = 15.867\ (10)$ Å
$c = 7.571\ (4)$ Å
$\beta = 115.03\ (3)°$
$V = 687.7\ (7)$ Å$^3$
$Z = 4$

$D_x = 1.411$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 40
  reflections
$\theta = 10.2–12.6°$
$\mu = 0.100$ mm$^{-1}$
$T = 150\ (2)$ K
Needle, pale yellow
$0.19 \times 0.11 \times 0.08$ mm

*Data collection*

Stoe Stadi-4 four-circle diffract-
  ometer
$\omega/\theta$ scans
5424 measured reflections
1356 independent reflections
729 reflections with $I > 2\sigma(I)$
$R_{int} = 0.196$

$\theta_{max} = 26.04°$
$h = -7 \rightarrow 7$
$k = -19 \rightarrow 19$
$l = -9 \rightarrow 9$
3 standard reflections
  frequency: 60 min
  intensity decay: 9.6%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.086$
$wR(F^2) = 0.163$
$S = 1.153$
1356 reflections
100 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 1.6470P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å$^{-3}$
$\Delta\rho_{min} = -0.35$ e Å$^{-3}$

**Table 1**
Geometry of hydrogen bonds and short intermolecular contacts (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| C8—H8$\cdots$O9$^i$ | 0.95 | 2.58 | 3.526 (7) | 178 |
| C2—H2$\cdots$O9$^{ii}$ | 0.95 | 2.53 | 3.344 (7) | 143 |
| C5—H5$\cdots$O11$^{iii}$ | 0.95 | 2.70 | 3.529 (7) | 146 |

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$; (iii) $-x, 1 - y, 1 - z$.

All H atoms were clearly defined in difference maps and were then treated as riding, with C—H = 0.95 or 0.99 Å. Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice. The high value of $R_{int}$ is attributed to the presence, within the region of the capillary irradiated by the X-ray beam, of additional crystallites of (I), the presence of which is an unavoidable consequence of the crystal-growth method.

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97 and *PLATON*.

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