1-Ethynyl-2-isopropoxy-3-methoxybenzene

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The crystal structure of the title compound, $C_{12}H_{14}O_2$, has been determined at 150 K. Significant intermolecular non-conventional C—H···O interactions involving the terminal acetylinic H atom are observed, which result in a zigzag hydrogen-bonded chain in the b direction.

Comment

In our quest for direct routes in the total synthesis of certain diterpene alkaloids (Atta-ur-Rahman & Choudhary, 1997, 1999; Wang & Liang, 1992), we required 1,2-dioxygenated phenylacetylenes as masked o-benzoquinones (Liao & Peddinti, 2002). In particular, we have made use of 1-ethynyl-2-isopropoxy-3-methoxybenzene, (I), which is easily synthesized on a large scale (> 20 g) in three steps from o-vanillin, (II) (Williams, Mander et al., 2003).

(I)   (II)   (III) R = H
                 (IV) R = Cl

Crystallographic data for (I) were collected at 150 K, due to the low melting point of the compound (321–323 K, uncorrected). The molecular structure of (I) is shown in Fig. 1. The methoxy group lies essentially in the plane of the aromatic ring [C4—C3—O2—C12 = 3.2 (2)°], whereas the isopropoxy group C9—O1 vector is rotated well away from this plane [C3—C2—O1—C9 = 71.5 (2)°]. The bond lengths and angles (Table 1) are as expected for a purely organic phenylacetylene, of which there are 574 structurally characterized examples in the Cambridge Structural Database (Allen, 2002); 61 bear a terminal (monosubstituted) acetylene group. The C1—C7 distance of 1.441 (2) Å (formally a single bond) reflects conjugation between the aromatic ring and the alkyne group. Nevertheless, this bond length is not significantly different from that seen in other phenylacetylenes. Interestingly, there are an additional 1407 metal-containing structures where the phenylacetylene moiety is coordinated either as an η^1 σ-donor (in its deprotonated form) or in a side-on η^2-bonding mode as a neutral ligand. The most closely related crystal structures to (I) are those of the 2,6-dioxyphenylacetylenes (III) (Evans et al., 1990) and (IV) (Evans et al., 1989). The crystal structure of (I) represents the first example of a 2,3-dioxyphenylacetylene in the literature.

There is a non-classical intermolecular hydrogen-bonding interaction involving the acetylinic H atom and the isopropoxy

Figure 1
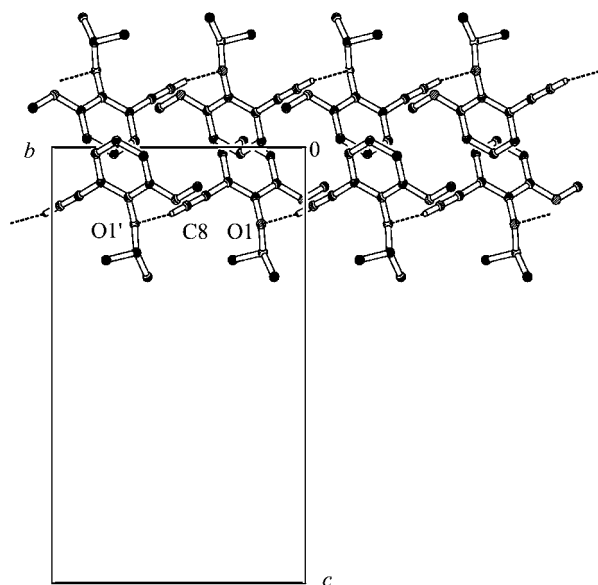ORTEP-3 plot (Farrugia, 1997) of (I) (30% probability ellipsoids).

Figure 2
PLUTON packing diagram (Spek, 1990), showing hydrogen-bonded chains with dashed hydrogen bonds. All H atoms, except for the acetylinic H, have been omitted..

group [H8···O1^i 2.31 Å, C8···O1^i 3.233 (2) Å and C8—H8···O1^i 170°; symmetry code: (i) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, z]. This results in a hydrogen-bonded chain of molecules in the b direction (Fig. 2). A weaker intramolecular C—H···O interaction occurs between the isopropoxy methine H atom and the adjacent methoxyl group [H9···O2 2.44 Å, C9···O2 3.026 (2) Å and C9—H9···O2 118°]. Avoidance of steric repulsion between the isopropoxy and methoxy methyl groups may also be significant in assisting this non-conventional hydrogen-bonding interaction. Moreover, the above-mentioned intermolecular hydrogen bond involving H8 will be important in influencing the orientation of the isopropoxy group.

We are currently employing this useful synthon (I) in the pursuit of a number of novel polycyclic organic derivatives and we shall report the results of these investigations separately (Williams, Raine & Harper, 2003).

Experimental

The synthesis of the title compound will be reported separately in a full account (Williams, Mander et al., 2003). Following distillation, (I) crystallized upon cooling to room temperature.

Crystal data

$C_{12}H_{14}O_2$	Mo $K\alpha$ radiation
$M_r = 190.23$	Cell parameters from 25
Orthorhombic, $Pbca$	reflections
$a = 9.895$ (1) Å	$\theta = 11.2–14.1°$
$b = 11.343$ (2) Å	$\mu = 0.08$ mm^{-1}
$c = 18.791$ (2) Å	$T = 150$ (2) K
$V = 2109.1$ (5) Å^3	Prism, colourless
$Z = 8$	$0.5 \times 0.5 \times 0.3$ mm
$D_x = 1.198$ Mg m^{-3}	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	$\theta_{max} = 25.0°$
Non-profiled $\omega/2\theta$ scans	$h = -1 \rightarrow 11$
Absorption correction: none	$k = -1 \rightarrow 13$
2431 measured reflections	$l = -1 \rightarrow 22$
1847 independent reflections	3 standard reflections
1368 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.037$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.4832P]$
$wR(F^2) = 0.112$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1847 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
131 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
H-atom parameters constrained	Extinction correction: SHELXL97
	Extinction coefficient: 0.0097 (15)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.395 (2)	C4—C5	1.388 (2)
C1—C6	1.404 (2)	C5—C6	1.366 (2)
C1—C7	1.441 (2)	C7—C8	1.187 (2)
C2—O1	1.376 (2)	C9—O1	1.461 (2)
C2—C3	1.400 (2)	C9—C10	1.509 (2)
C3—O2	1.367 (2)	C12—O2	1.425 (2)
C3—C4	1.387 (2)		
C2—C1—C6	119.4 (2)	C3—C4—C5	120.0 (2)
C2—C1—C7	120.4 (1)	C6—C5—C4	120.8 (2)
C6—C1—C7	120.2 (1)	C5—C6—C1	120.2 (2)
O1—C2—C1	119.2 (1)	C8—C7—C1	177.1 (2)
O1—C2—C3	120.8 (1)	O1—C9—C11	105.1 (1)
C1—C2—C3	119.8 (1)	O1—C9—C10	110.4 (1)
O2—C3—C4	124.0 (1)	C11—C9—C10	113.5 (1)
O2—C3—C2	116.3 (2)	C2—O1—C9	116.4 (1)
C4—C3—C2	119.8 (2)	C3—O2—C12	116.7 (1)

H atoms were constrained using a riding model.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994); cell refinement: CAD-4 EXPRESS; data reduction: XCAD4 (Harms, 1995); program(s) used to solve structure: SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and PLUTON (Spek, 1990); software used to prepare material for publication: WinGX (Farrugia, 1999).

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