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1,4-Diethynyl-2,5-dimethoxybenzene at *ca* 150 K

Michael I. Bruce,[a] Nicholas J. Head,[a] Brian W. Skelton[b]* and Allan H. White[b]

[a]Department of Chemistry, University of Adelaide, South Australia 5005, Australia, and [b]Chemistry, University of Western Australia, Crawley, WA 6009, Australia.
Correspondence e-mail: bws@crystal.uwa.edu.au

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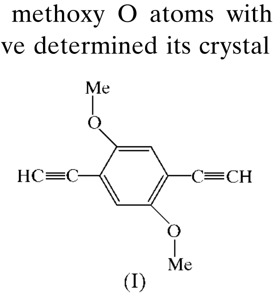
The principal determinants of packing in crystals of the title compound, $C_{12}H_{10}O_2$, which has crystallographically imposed inversion symmetry, are interactions between the alkyne H atoms and the methoxy O atoms [$H\cdots O = 2.39$ (1) Å].

Comment

Alkyne H atoms are frequently described as exhibiting acid characteristics; recent accurate studies of aromatic alkyne derivatives have demonstrated interactions between such H atoms and other electron-rich entities in crystal lattices that might come under the umbrella of 'hydrogen bonding'. Thus, low-temperature structure determinations of 1,4-diethynyl- and 1,3,5-triethynylbenzenes show that interactions between such H atoms and the triple bonds of adjacent molecules may be considerable determinants of crystal packing, while in ethynylbenzene, in addition, interactions with the aromatic π system are found (Weiss *et al.*, 1997). In systems containing aromatic nitro groups, the interactions are found to take place with the nitro substituents (Robinson *et al.*, 1999). Having on our shelves a crystalline sample of the title compound, (I), we were interested in ascertaining the nature of any such interactions that might occur therein, in view of the frequent association of the methoxy O atoms with putative positive charges, and so have determined its crystal structure.



(I)

At *ca* 150 K, the crystals diffracted well, yielding extensive good-quality data, with a concomitantly precise result, enabling definitive location of all H atoms in the X-ray sense. The asymmetric unit contains one-half of the centrosymmetric molecule, in space group $P2_1/c$. The aromatic ring is a remarkably regular hexagon; the exocyclic angles at the pendant O atom display the usual asymmetry associated with methoxy substituents, the methoxy C atom being approximately coplanar with the sequence C1–C3 [deviation = 0.054 (5) Å] and, as usual, enclosing the larger of the exocyclic angles. The C—H distances fall into three classes, *viz.* (aliphatic) methyl C—H > aromatic > ethynyl. The essentially planar molecules pack in a staggered herring-bone fashion when viewed along *a* (Figs. 1 and 2); the closest intermolecular contacts are found between the ethynyl H and the methoxy O atoms (Table 1)

In the course of submission of this paper, we were advised of a parallel contemporary study of this compound, among a

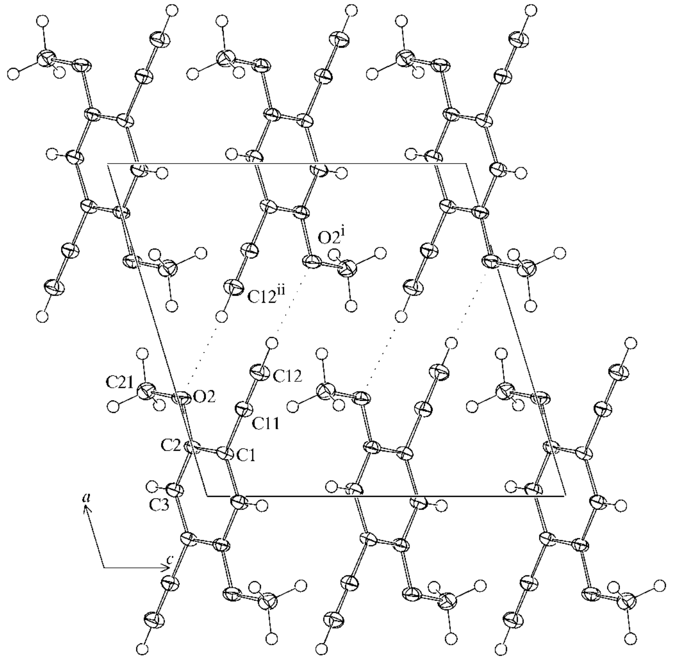


Figure 1
The unit-cell contents of the title compound, viewed along *b*. [Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.]

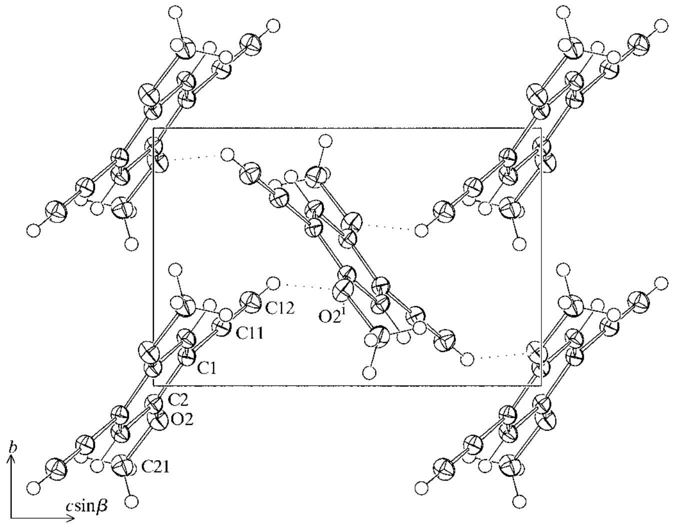


Figure 2
The unit-cell contents of the title compound, viewed along *a*. [Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

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broader array of related species, the compound in question being the subject of a room-temperature X-ray powder diffraction study using only 243 reflections, giving an R value of 0.045 (Khan *et al.*, 2003). While the results of the two studies are harmonious, the present low-temperature single-crystal study provides a degree of precision inaccessible in the powder work.

Experimental

The title compound was obtained by a conventional route, *viz.* by coupling 1,4-diiodo-2,5-dimethoxybenzene (Ramos *et al.*, 2001) with $HC{\equiv}CSiMe_3$ in the presence of $Pd(PPh_3)_4/CuI$ as catalyst (Dirk *et al.*, 2001) followed by proto-desilylation of the resulting 1,4-$(SiMe_3C{\equiv}C)_2$-2,5-$(MeO)_2C_6H_2$ (Pelter & Jones, 2000), and was identified by comparison of the IR and NMR data with literature values. Crystals suitable for X-ray diffraction were obtained from a $CDCl_3$/methanol mixture.

Crystal data

$C_{12}H_{10}O_2$
$M_r = 186.21$
Monoclinic, $P2_1/c$
$a = 9.111$ (1) Å
$b = 5.9921$ (7) Å
$c = 9.408$ (1) Å
$\beta = 106.710$ (2)°
$V = 491.93$ (9) Å^3
$Z = 2$

$D_x = 1.257$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 3004 reflections
$\theta = 2.8$–34.6°
$\mu = 0.09$ mm^{-1}
$T = 150$ (2) K
Plate, colourless
0.35 × 0.16 × 0.08 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.77$, $T_{\max} = 0.93$
10 271 measured reflections

2574 independent reflections
1957 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 37.4°$
$h = -15 \rightarrow 14$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

Refinement

Refinement on F
$R = 0.044$
$wR = 0.050$
$S = 1.11$
1957 reflections
84 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C12-H12\cdots O2^{i}$	0.94 (1)	2.39 (1)	3.227 (1)	148 (1)

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

H atoms were located from difference Fourier maps and placed at idealized positions (C—H = 0.95 Å), and their positional and $U_{\rm iso}$ values were refined.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *Xtal*3.5 *User's Manual* (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5 *User's Manual*; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5 *User's Manual*; molecular graphics: *Xtal*3.5 *User's Manual*; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5 *User's Manual*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1290). Services for accessing these data are described at the back of the journal.

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