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Three 2,5-dialkoxy-1,4-diethynylbenzene derivatives

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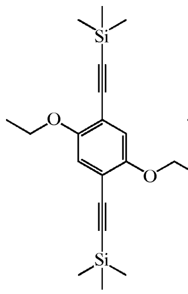
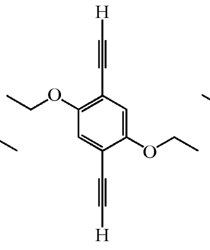
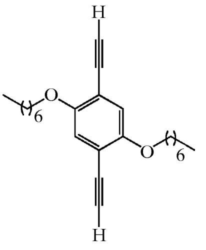
2,5-Diethoxy-1,4-bis[(trimethylsilyl)ethynyl]benzene, $C_{20}H_{30}O_2Si_2$, (I), constitutes one of the first structurally characterized examples of a family of compounds, *viz*. the 2,5-dialkoxy-1,4-bis[(trimethylsilyl)ethynyl]benzene derivatives, used in the preparation of oligo(phenyleneethynylene)s *via* Pd/Cu-catalysed cross-coupling. 2,5-Diethoxy-1,4-diethynylbenzene, $C_{14}H_{14}O_2$, (II), results from protodesilylation of (I). 1,4-Diethynyl-2,5-bis(heptyloxy)benzene, $C_{24}H_{34}O_2$, (III), is a long alkyloxy chain analogue of (II). The molecules of compounds (I)–(III) are located on sites with crystallographic inversion symmetry. The large substituents either in the alkynyl group or in the benzene ring have a marked effect on the packing and intermolecular interactions of adjacent molecules. All the compounds exhibit weak intermolecular interactions that are only slightly shorter than the sum of the van der Waals radii of the interacting atoms. Compound (I) displays C—H$\cdots\pi$ interactions between the methylene H atoms and the acetylenic C atom. Compound (II) shows π–π interactions between the acetylenic C atoms, complemented by C—H$\cdots\pi$ interactions between the methyl H atoms and the acetylenic C atoms. Unlike (I) or (II), compound (III) has weak nonclassical hydrogen-bond-type interactions between the acetylenic H atoms and the ether O atoms.

Comment

Among highly conjugated polymers, those composed of alternating aryl and ethynyl units, such as the oligo(phenyleneethynylene)s (OPEs), a type of monodisperse and shaped-persistent oligomer, have been the object of increasing interest in academic and industrial research laboratories owing to their potential applications as molecular wires (Kushmerick *et al.*, 2002; Tour, 2000; Reinerth *et al.*, 1998; Cygan *et al.*, 1998; Bumm *et al.*, 1996), rectifiers (Dhirani *et al.*, 1997), data storage systems (Reed *et al.*, 2001; Feringa *et al.*, 1993), photoluminescent and electroluminescent devices (Yamaguchi *et al.*, 2005), and nonlinear optical materials (Koynov *et al.*, 2005; Meier *et al.*, 2001). Modification of OPEs is needed in order to improve both processability and long-term stability. One of the methods for improving their stability and solubility is the attachment of long linear alkoxy side chains to the main backbone. Additionally, alkoxy side chains can lead to highly ordered supramolecular architectures and reduce the HOMO–LUMO gap and the band gap in the solid state (Wackerly & Moore, 2006; Jiang *et al.*, 2004; Zhou *et al.*, 2004; Zhou, Liu *et al.*, 2003; Zhou, Zhao *et al.*, 2003; Meier *et al.*, 2001; Perahia *et al.*, 2001; Müllen & Rabe, 1998). A possible way to synthesize OPEs with alkoxy side chains is by using a two-step Sonogashira–Hagihara reaction: a palladium-catalysed cross-coupling condensation between 2,5-bis(alkoxy)benzene halides and terminal trimethylsilylacetylenes or 2-methylbut-3-yn-2-ol as the protecting group precursors in the presence of CuI, followed by a base-promoted deprotection of the capped acetylides (Tykwinski, 2003; Sonogashira, 2002; Takahashi *et al.*, 1980; Zhao *et al.*, 2007). The structures of trimethylsilylated 1,4-diethynylbenzene (Weiss *et al.*, 1997; Ahmed *et al.*, 1972) and the 2,5-bis(alkoxy) ring-substituted derivatives 1,4-diethynyl-2,5-dimethoxybenzene and 1,4-diethynyl-2,5-bis(octyloxy)benzene (Khan *et al.*, 2003) are known. The X-ray structures of 1,4-bis(trimethylsilylethynyl)naphthalene and 9,10-bis(trimethylsilylethynyl)anthracene were reported by Khan *et al.* (2004). We report here the


(I)


(II)


(III)

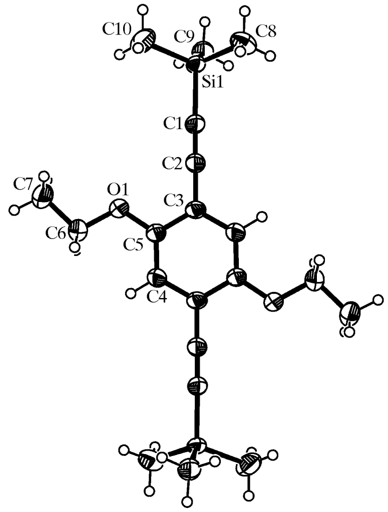


Figure 1
An *ORTEP-3* plot (Farrugia, 1997) of (I) (50% probability displacement ellipsoids).

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structures of the three 2,5-dialkoxy-1,4-diethynylbenzene derivatives (I)–(III).

Compound (I) is symmetrical and has the expected planar overall structure (Fig. 1). The bond distances and angles do not show any abnormal values. The prevailing intermolecular interaction (defined to be shorter than the sum of the van der Waals radii of the interacting atoms) in (I) is the C—H$\cdots\pi$ interaction between the methylene H atoms of the ethoxy group and the terminal acetylenic C atom (C6—H6*B*$\cdots$C1), with an interaction distance of 2.86 Å and an angle of 153°, the C$\cdots$C distance being 3.772 (4) Å (Fig. 2; only the stronger interactions are shown). One molecule of (I) has these interactions to four separate molecules [with symmetry codes $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$, $(1 - x, \frac{1}{2} + y, -\frac{1}{2} - z)$ and $(x, \frac{1}{2} - y, \frac{1}{2} + z)$]. Another, weaker, intermolecular interaction is also present, between the H atoms of adjacent trimethylsilyl groups [H8*A*$\cdots$H9*B*$(1 - x, \frac{1}{2} - y, \frac{1}{2} + z)$], with a contact distance of 2.39 Å.

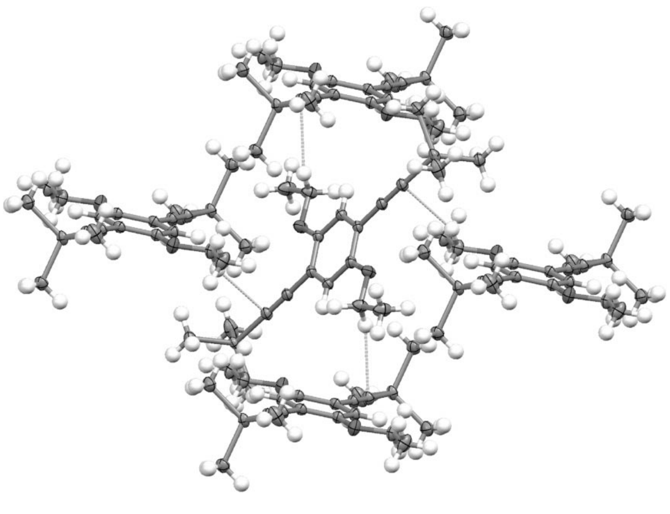

Figure 2
The packing (Macrae *et al.*, 2006) of (I). For clarity, only the C—H$\cdots\pi$ interactions are shown.

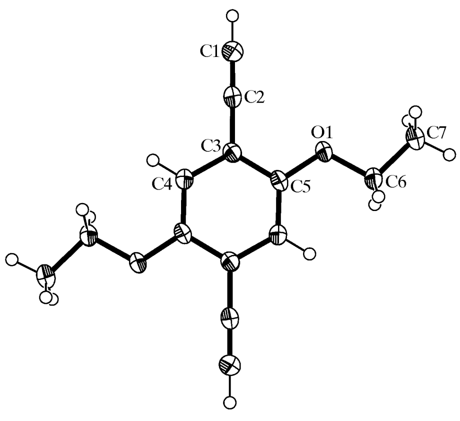

Figure 3
An *ORTEP-3* (Farrugia, 1997) plot of (II) (50% probability displacement ellipsoids).

Compound (II) does not have the bulky trimethylsilyl groups and thus shows a different packing behaviour. Like (I), compound (II) is symmetrical and planar with no abnormal bond distances or angles (Fig. 3). The absence of the bulky trimethylsilyl group allows the molecules a closer approach, and completely different packing results, with interactions to eight separate molecules [with symmetry codes $(-x, 1 - y, -z)$, $(-x, -1 - y, -z)$, $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$, $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$, $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(-1 + x, y, -1 + z)$]. The molecules of (II) are arranged in planes with π–π interactions between the acetylenic C1 atoms of adjacent molecules, the C1$\cdots$C1 distance being 3.224 (2) Å. In addition to the π–π interactions, in-plane C—H$\cdots\pi$ interaction between the acetylenic atom C1 and the methyl atom H7*B* exist, the contact distance C1$\cdots$H7*B*$(x, -1 + y, z)$ being 2.88 Å (Fig. 4). These planes stack on top of each other with a twist angle of 36.7° between the planes. The C—H$\cdots\pi$ interactions between the planes are mediated through methylene H atoms (H6*A*) and the benzene π systems (C4) of adjacent molecules, the contact distance H6*A*$\cdots$C4$(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$ being 2.85 Å.

The long heptyloxy chain has an opposite effect on the packing when compared with compound (II). Compound (III) is symmetrical and planar, like the other two compounds, and the bond distances and angles within the molecule are normal (Fig. 5). Unlike (I) and (II), compound (III) exhibits, as the only sufficiently short intermolecular interaction, a nonclassical hydrogen bond between the molecules (Fig. 6). The contact distance between atoms H1 and O1$(-\frac{1}{2} + x, \frac{3}{2} - y, z)$ is 2.54 Å, with an angle of 161° and a C$\cdots$O distance of 3.449 (2) Å. Similar contact distances are frequently found in nonclassical hydrogen bonds. As in (I), each molecule of (III) interacts with four other molecules [with symmetry codes $(-\frac{1}{2} - x, -\frac{1}{2} + y, -z)$, $(-\frac{1}{2} + x, \frac{3}{2} - y, -z)$, $(-\frac{1}{2} - x, -\frac{1}{2} + y, -z)$ and $(\frac{1}{2} + x, \frac{3}{2} - y, z)$]. Even though the bond lengths in all three compounds do not show abnormal values, there is a significant variation in the bond lengths of the central benzene ring,

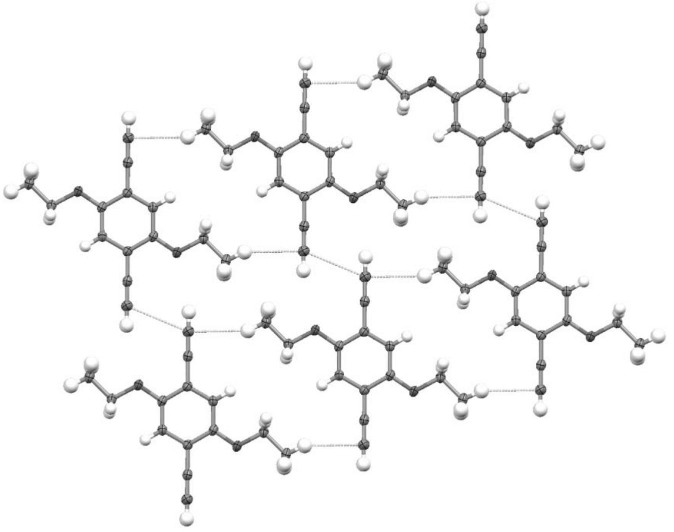

Figure 4
The packing (Macrae *et al.*, 2006) of (II), showing the in-plane interactions.

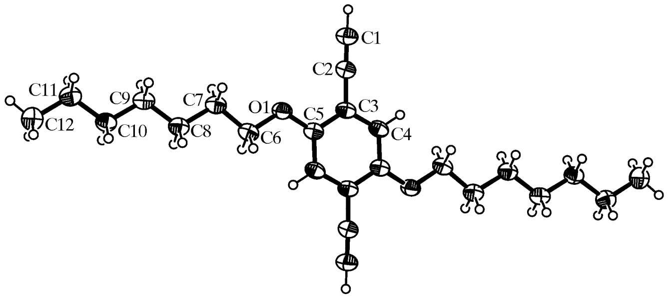

Figure 5
An *ORTEP-3* (Farrugia, 1997) plot of (III) (50% probability displacement ellipsoids).

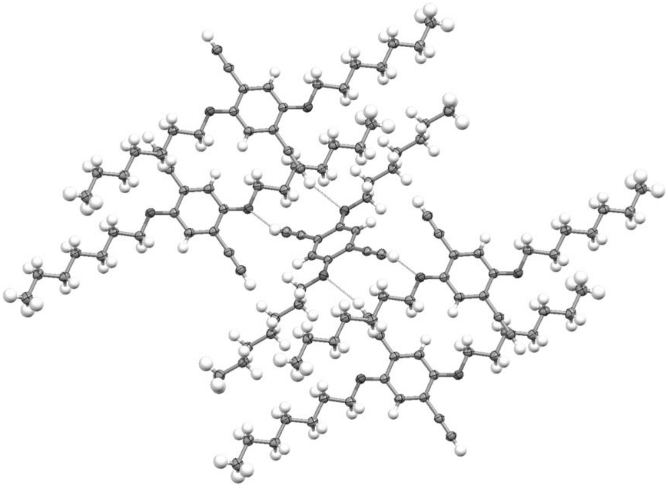

Figure 6
The packing (Macrae *et al.*, 2006) of (III), showing the C—H···O interactions.

which is typical for this type of symmetrical tetrasubstituted benzenes. The bond length between the unsubstituted C4 atom and the alkoxy-substituted C5 atom is on average 0.034 [for (I)], 0.015 [for (II)] and 0.010 Å [for (III)] shorter than the other bond lengths in the benzene ring.

Experimental

Compound (I) was obtained by Sonogashira cross-coupling (Weder & Wrighton, 1996) of 1,4-diethoxy-2,5-diiodobenzene (1.50 g, 3.59 mmol) with trimethylsilylacetylene (TMSA; 1.5 ml, 10.54 mmol) in dried tetrahydrofuran (20 ml) and *N*-ethyldiisopropylamine (25 ml). The reaction was catalysed by $PdCl_2(PPh_3)_2$ (0.293 g, 0.42 mmol) and CuI (0.06 g, 0.32 mmol). After 16 h of stirring at 318 K under a nitrogen atmosphere, the dark-brown mixture was filtered and evaporated under vacuum. Purification by column chromatography (silica gel S60, CH_2Cl_2/cyclohexane 1:3) gave a dark-yellow solid that was further purified by sublimation. The resulting solid was dissolved in CH_2Cl_2, forming a light-yellow solution which was evaporated slowly in air at room temperature, affording colorless crystals in 35% yield (m.p. 305–309 K). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (2H, *s*, Ar), 4.02 (4H, *q*, CH_2, J_{HH} = 14 Hz), 1.40 (4H, *t*, Me, J_{HH} = 14 Hz), 0.29 (18H, *s*, Me); ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.97, 117.75, 101.06, 100.24, 65.30, 14.79, 0.058; IR (KBr): 2969 (*s*), 2151 (*s*), 1499 (*s*), 1394 (*s*), 1213 (*sh*), 1043 (*s*), 840 (*br*), 760 (*s*).

Compound (II) was obtained by adding K_2CO_3 (1.61 g, 11.6 mmol) to (I) (1.91 g, 5.3 mmol) in a purged Schlenk tube. Degassed CH_2Cl_2 (7 ml) and MeOH (3 ml) were then added to the solids, forming a yellow solution, and stirring was begun. After 4 h at room temperature, the now cloudy yellow mixture was filtered and evaporated under vacuum, yielding a light-yellow solid. Colorless crystals suitable for X-ray diffraction were obtained as previously described for compound (I) (yield 73.8%, m.p 347–348 K). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (2H, *s*, Ar), 4.07 (4H, *q*, CH_2, J_{HH} = 14 Hz), 3.40 (2H, *s*, H—CC), 1.43 (6H, *t*, CH_3, J_{HH} = 14 Hz); ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.83, 117.92, 113.36, 82.42, 79.79, 65.20, 14.75; IR (KBr): 3288 (*s*), 2984 (*s*), 2932 (*s*), 2883 (*s*), 2107 (*s*), 1932 (*s*), 1496 (*m*), 1218 (*m*), 1040 (*s*), 674 (*m*). MS (ESI): 158 [$M^+ - (C_2H_5)_2 + H_2$], 214 (M^+) *m*/*z*.

Compound (III) was prepared by refluxing 4,4′-[2,5-bis(heptyloxy)-1,4-phenylene]bis(2-methylbut-3-yn-2-ol) in toluene with an excess of NaOH for 4 h. After this, the still hot solution was filtered and concentrated under vacuum. Good quality single crystals were obtained by allowing the yellow solution to cool to room temperature (yield 99%, m.p. 346–347 K). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.95 (2H, *s*, Ar), 3.97 (4H, *t*, CH_2, J_{HH} = 27 Hz), 3.32 (2H, *s*, H—CC), 1.76 (4H, *Q*, CH_2, J_{HH} = 27 Hz), 1.469–1.257 [16H, $(CH_2)_4$], 0.89 (3H, *d*, CH_3, J_{HH} = 9); ^{13}C NMR (65 MHz, $CDCl_3$): δ 153.86, 117.64, 113.15, 82.23, 79.65, 69.54, 31.62, 28.99, 28.85, 25.72, 22.44, 13.93; IR (KBr): 3265 (*s*), 2927 (*s*), 2932 (*s*), 2866 (*s*), 2105 (*w*), 1497 (*s*), 1275 (*m*). MS (ESI): 158 [$M^+ - (C_2H_5)_2 + H_2$], 354 (M^+) *m*/*z*.

Compound (I)

Crystal data

$C_{20}H_{30}O_2Si_2$
M_r = 358.62
Monoclinic, $P2_1/c$
a = 10.132 (1) Å
b = 9.887 (2) Å
c = 12.169 (4) Å
β = 107.46 (2)°
V = 1162.9 (5) Å^3
Z = 2
Mo *K*α radiation
μ = 0.16 mm^{-1}
T = 173 (2) K
0.25 × 0.2 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
9367 measured reflections
2032 independent reflections
1568 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.175
S = 0.76
2032 reflections
113 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Compound (II)

Crystal data

$C_{14}H_{14}O_2$
M_r = 214.25
Monoclinic, $P2_1/c$
a = 9.748 (2) Å
b = 8.890 (2) Å
c = 7.566 (2) Å
β = 112.74 (3)°
V = 604.7 (3) Å^3
Z = 2
Mo *K*α radiation
μ = 0.08 mm^{-1}
T = 173 (2) K
0.3 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
4943 measured reflections
1045 independent reflections
910 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.095$
$S = 1.07$
1045 reflections
74 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Compound (III)

Crystal data

$C_{24}H_{34}O_2$
$M_r = 354.51$
Monoclinic, $P2_1/a$
$a = 6.7246$ (2) Å
$b = 16.7456$ (5) Å
$c = 9.8026$ (3) Å
$\beta = 97.320$ (2)°
$V = 1094.85$ (6) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.07$ mm^{-1}
$T = 173$ (2) K
0.6 × 0.5 × 0.4 mm

Data collection

Nonius KappaCCD diffractometer
3729 measured reflections
1920 independent reflections
1458 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.107$
$S = 0.99$
1920 reflections
119 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.10$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

H atoms were visible in electron-density maps, but were placed in idealized positions and allowed to ride on their parent atoms at distances of 0.95 (aromatic and acetylinic), 0.98 (methyl) and 0.99 Å (methylene), with $U_{\rm iso}$(H) values of 1.2 or 1.5 times $U_{\rm eq}$(C).

For all compounds, data collection: *COLLECT* (Hooft, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3181). Services for accessing these data are described at the back of the journal.

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