

A hydrogen-bonded dimer of 13-hydroxy-13-[(triisopropylsilyl)- ethynyl]pentacene-6(13*H*)-one

Amar Boudebous, Edwin C. Constable, Catherine E. Housecroft,* M. Neuburger and S. Schaffner

Department of Chemistry, University of Basel, Spitalstrasse 51, CH4056 Basel, Switzerland

Correspondence e-mail: catherine.housecroft@unibas.ch

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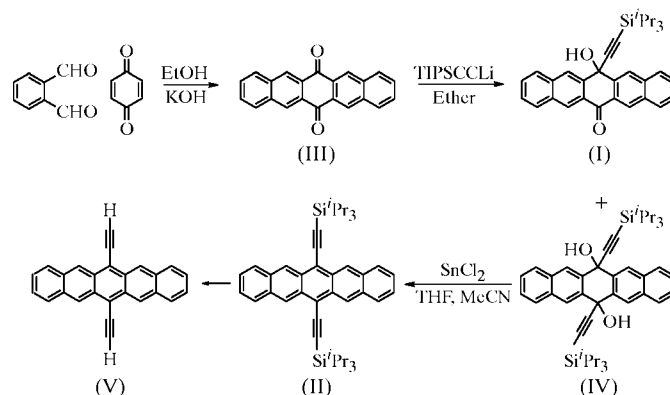
The title compound, $C_{33}H_{34}O_2Si$, has been obtained as a product in the synthesis of 6,13-bis[(triisopropylsilyl)ethynyl]-6,13-dihydropentacene-6,13-diol. The solid-state structure reveals a dimer, with strong hydrogen bonds holding the two molecules in a face-to-face arrangement [$O \cdots O = 2.746$ (2) Å and $O-H \cdots O = 173$ (2)°]. Within each dimer, the pentacene units are π -stacked (the distance between the mean least-squares planes of 22 C atoms is 3.60 Å).

Comment

The design of photo- and redox-active systems with potential application as photocatalysts for solar energy conversion is a research imperative for the 21st century (Eisenberg & Nocera, 2005). With the aim of designing photocatalytic systems involving redox- and photoactive transition metal complexes, we have focused on a modular approach using $\{M(\text{tpy})_2\}$ metallotectons (tpy is 2,2':6',2''-terpyridine). We have shown that pendant or bridging aromatic units may be used to control energy- and electron-transfer processes (Constable *et al.*, 2005; Figgemeier *et al.*, 2003; Hjelm *et al.*, 2005, and references therein). In the course of our synthetic programme to tune the highest occupied molecular orbital–lowest unoccupied molecular orbital properties and band gap of bridging aromatic moieties, our attention has turned to pentacene units, which have attractive energetic properties (Meng *et al.*, 2005; Sakamoto *et al.*, 2004; Swartz *et al.*, 2005). In this paper, we report the structure of the title compound, (I), a product obtained in the synthesis of 6,13-diethynylpentacene.

We required 6,13-diethynylpentacene, (V), to introduce it as a spacer between two $\{M(\text{tpy})_2\}$ units, and used minor variations on the literature procedure to prepare 6,13-bis[(triisopropylsilyl)ethynyl]pentacene, (II) (Anthony *et al.*, 2001, 2002; Payne, Delcamp *et al.*, 2004; Swartz *et al.*, 2005). Pentacene-6,13-dione, (III), was prepared as a yellow solid from the reaction of cyclohexa-2,5-diene-1,4-dione with 1,2-benzenedicarbaldehyde in ethanolic KOH in 95% yield (Ried

& Anthöfer, 1953). Reaction of (III) with (triisopropylsilyl)ethynyllithium (TIPSCCLi) in tetrahydrofuran gave a green solid comprising the desired diol, 6,13-bis[(triisopro-



pylsilyl)ethynyl]-6,13-dihydropentacene-6,13-diol, (IV), and a highly fluorescent (λ_{em} 434 nm) product, characterized as 13-hydroxy-13-[(triisopropylsilyl)ethynyl]pentacene-6(13*H*)-one, (I). We have subsequently optimized the yield of orange (I) by reaction of (III) with one equivalent of TIPSCCLi.

We have determined the solid-state crystal structure of (I). Fig. 1 shows the structure of a molecule of (I), together with the numbering scheme adopted. The bond distances and angles in (I) are unexceptional; the Si1—C1/C4/C7 distances lie in the range 1.880 (3)–1.883 (3) Å, with Si1—C10 being shorter at 1.837 (2) Å. Five of the C—Si—C bond angles fall in the range 105.9 (1)–110.7 (1)°, while C4—Si1—C7 is larger [115.4 (1)°].

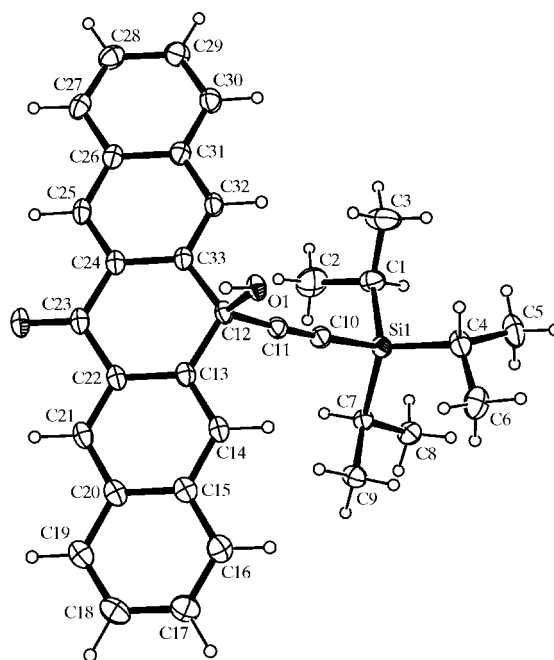


Figure 1

A view of a single molecule of (I), showing the numbering scheme adopted. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Relatively few pentacene derivatives have been structurally characterized to date (Anthony *et al.*, 2001; Borgen, 1966; Campbell *et al.*, 1962; Chan *et al.*, 2005; Dzyabchenko *et al.*, 1979; Holmes *et al.*, 1999; Klarner *et al.*, 2001; Mattheus *et al.*, 2001, 2002; Meng *et al.*, 2005; Miller *et al.*, 2003; Ohkita *et al.*, 2000; Payne, Odom *et al.*, 2004; Sakamoto *et al.*, 2004; Siegrist *et al.*, 2001; Swartz *et al.*, 2005; Uno *et al.*, 2005). As expected on the basis of hydrogen bonding (see below) and the non-aromatic ring structure, the carbonyl C—O bond in (I) is slightly longer [C23—O2 = 1.238 (3) Å] than that in the quinone pentacene-6,13-dione (1.215 Å; Dzyabchenko *et al.*, 1979). Within the pentacene system, the aromatic rings exhibit typical delocalized C—C bond distances in the range 1.358 (4)–1.424 (3) Å, similar to those of the aromatic rings in other pentacenes and 6,13-dihydropentacenes. In the central ring, the C—C bonds to the carbonyl group are a little longer

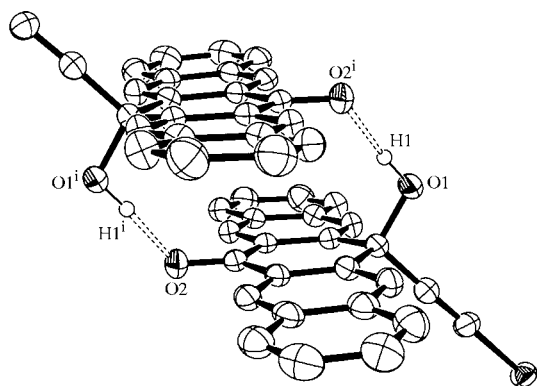


Figure 2
The dimeric assembly of two molecules of (I) in the crystal structure. H atoms other than those involved in hydrogen bonding have been omitted, as have the triisopropylsilyl groups. [Symmetry code: (i) $2-x, 1-y, -z$].

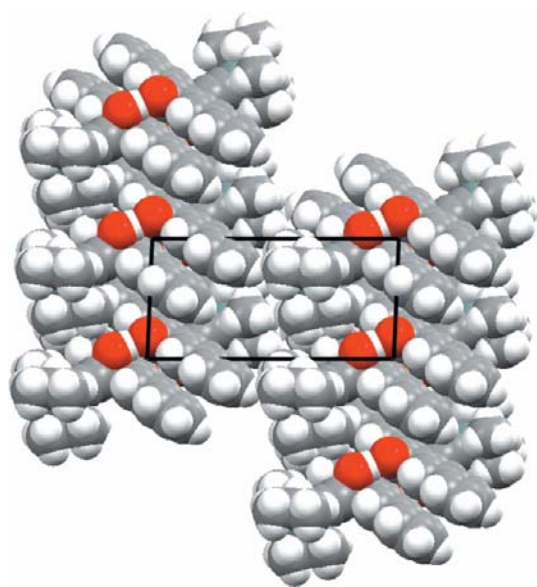


Figure 3
A space-filling diagram of (I), viewed down the *b* axis, showing the packing of the dimers into columns, between which lie the triisopropylsilyl groups.

[1.476 (3) and 1.474 (3) Å] and similar in length to those in pentacene-6,13-dione (1.483 Å; Dzyabchenko *et al.*, 1979). The formally single C—C bonds to C12 in the central ring show distances of 1.528 (3) and 1.535 (3) Å, which are similar to, if slightly longer than, those in 6,13-dihydropentacene (1.475 and 1.524 Å; Mattheus *et al.*, 2002). In contrast with 6,13-dihydropentacene, where the least-squares planes through the ‘naphthalene’ units intersect at the Csp^3 atoms at an angle of 28° (Mattheus *et al.*, 2002), the pentacene ring system in (I) is nearly planar, with the deviation of the sp^3 atom C12 from the least-squares plane of the aromatic rings being only 0.16 Å.

The molecules of (I) form a hydrogen-bonded dimer in the solid state (Fig. 2), in which the hydroxy group of one molecule is strongly hydrogen bonded to the carbonyl O atom of a second [O1 \cdots O2ⁱ = 2.746 (2) Å and O1—H1 \cdots O2ⁱ = $173(2)^\circ$; symmetry code: (i) $2-x, 1-y, -z$]. The consequence of this tight hydrogen bonding is efficient offset face-to-face π -stacking of the two pentacene rings; the distance between least-squares planes, each of 22 C atoms, is 3.60 Å. The dimers are linked along the *b* axis by hydrogen-bonded interactions [C16—H16ⁱ \cdots O2ⁱⁱ, with C16 \cdots O2ⁱⁱ = 3.447 (3) Å, and C27—H27ⁱ \cdots O1ⁱⁱⁱ, with C27 \cdots O1ⁱⁱⁱ = 3.318 (3) Å; symmetry codes: (ii) $x, 1+y, z$; (iii) $x, 1-y, z$]. When viewed along the *b* axis (Fig. 3), the solid-state structure reveals packing of the dimers into columns. The dimers are π -stacked with offset face-to-face π -stacking of pentacene rings (the distance between least-squares planes, each of 22 C atoms, is 3.52 Å). The triisopropylsilyl (TIPS) substituents are directed outwards from these columns and form an intermeshed assembly between them.

Of the 26 4-hydroxycyclohexa-2,5-dienones present in the Cambridge Structural Database (Version 5.27; Allen, 2002; Bruno *et al.*, 2002), the majority exhibit extended or linear hydrogen-bond connectivity, and in only two cases is a dimeric structure related to (I) observed. In the case of 4-ethynyl-4-hydroxy-2,3,5,6-tetramethylcyclohexa-2,5-dienone (Bilton *et al.*, 2000), the monomer unit is related to (I) and the dimer has similar metrical parameters, although the hydrogen bond is significantly weaker [O—H \cdots O = 1.94 (3) and 1.96 (3) Å; O \cdots O = 2.826 (2) and 2.786 (2) Å; O—H \cdots O = $172(2)$ and $178(3)^\circ$]. Once again, the hydrogen-bonding facilitates offset face-to-face π -stacking, and the distance between the least-squares planes of the aromatic rings in the dimer is 3.54 Å. The second example is found in 4,5,7-trichloro-3a-hydroxy-1-(4-methylphenyl)-2-(4-methylphenylimino)-2,3,3a,6-tetrahydro-1*H*-indol-6-one (Doepp *et al.*, 1995), in which strong hydrogen bonds (O \cdots O = 2.722 Å) also support the coplanar arrangement of aromatic rings (the distance between the least-squares planes of the aromatic rings is 3.38 Å), although these are slipped such that there is no direct ring overlap.

Experimental

Pentacene-6,13-dione (5.00 g, 16.2 mmol) was dissolved in freshly distilled diethyl ether (50 ml) and the solution was added to a mixture of (triisopropylsilyl)ethyne (6.00 ml, 4.88 g, 26.7 mmol) and *n*-BuLi (5 ml, 1.6 *M* in tetrahydrofuran, 8 mmol) in tetrahydrofuran (10 ml). The mixture was stirred at room temperature under nitrogen for 24 h, and then the solvent was removed *in vacuo* and the residue purified

by chromatography over silica gel (hexanes–CHCl₃, 1:1) to give 13-hydroxy-13-[(triisopropylsilyl)ethynyl]pentacene-6(13*H*)-one, (I), as a green solid (5.50 g, 69.2%; m.p. > 673 K), together with some 6,13-bis[(triisopropylsilyl)ethynyl]-6,13-dihydropentacene-6,13-diol (1.26 g, 11.7%). ¹H NMR (250 MHz, CDCl₃, 297 K): δ 8.811 (H^{P5,7}, *s*, 2H), 8.722 (H^{P12,14}, *s*, 2H), 8.03 (H^{P4,8}, *d*, 2H, *J* = 8.2 Hz), 7.92 (H^{P1,11}, *d*, 2H, *J* = 8.2 Hz), 7.62 (H^{P2,10}, *d*, 2H, *J* = 8.2, 6.8 and 1.3 Hz), 7.60 (H^{P3,9}, *d*, 2H, *J* = 8.2, 6.8 and 1.3 Hz), 1.78 (H^{TIPS}, *m*, 3H), 1.15 (H^{TIPS}, *m*, 18H); ¹³C NMR (CDCl₃, 62.5 MHz, 297 K): δ 206.9, 138.8, 135.6, 132.8, 129.7, 129.6, 128.9, 128.6, 128.2, 127.3, 127.2, 108.2, 90.0, 68.6, 18.6, 11.2; EIMS: *m/z* 474.1 [M + H]⁺; UV–VIS (nm): 266, 276, 320, 356; emission (nm): 434 (λ_{ex} 356 nm).

Crystal data

C ₃₃ H ₃₄ O ₂ Si	<i>D</i> _x = 1.201 Mg m ⁻³
<i>M</i> _r = 490.72	Mo <i>K</i> α radiation
Triclinic, <i>P</i> 1̄	Cell parameters from 5830 reflections
<i>a</i> = 8.8875 (3) Å	<i>θ</i> = 1–27°
<i>b</i> = 8.9910 (3) Å	<i>μ</i> = 0.11 mm ⁻¹
<i>c</i> = 17.6023 (7) Å	<i>T</i> = 173 K
α = 90.406 (2)°	Plate, colourless
β = 92.2227 (19)°	0.40 × 0.34 × 0.02 mm
γ = 105.032 (2)°	
<i>V</i> = 1357.19 (9) Å ³	
<i>Z</i> = 2	

Data collection

Nonius KappaCCD area-detector diffractometer	6138 independent reflections
φ and ω scans	3673 reflections with <i>I</i> > 3σ(<i>I</i>)
Absorption correction: multi-scan (DENZO and SCALEPACK; Otwinowski & Minor, 1997)	<i>R</i> _{int} = 0.015
<i>T</i> _{min} = 0.96, <i>T</i> _{max} = 1.00	<i>θ</i> _{max} = 27.5°
11207 measured reflections	<i>h</i> = –11 → 11
	<i>k</i> = –11 → 11
	<i>l</i> = –22 → 22

Refinement

Refinement on <i>F</i> ²	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.047	<i>w</i> = 1/[σ(<i>F</i>) + 0.04 <i>P</i>]
<i>wR</i> (<i>F</i> ²) = 0.064	where <i>P</i> = [max(<i>F</i> _o , 0) + 2 <i>F</i> _c]/3
<i>S</i> = 1.07	(Δ/ <i>σ</i>) _{max} < 0.001
3673 reflections	Δρ _{max} = 0.30 e Å ⁻³
329 parameters	Δρ _{min} = –0.22 e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1–H1...O2 ⁱ	0.94 (2)	1.81 (2)	2.746 (2)	173 (2)

Symmetry code: (i) –*x* + 2, –*y* + 1, –*z*.

Hydroxy atom H1 was located in a difference map and refined freely. All other H atoms were treated as riding, with C–H distances of 1.00 Å and with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: COLLECT (Nonius, 2001); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Betteridge *et al.*, 2003); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: CRYSTALS.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3004). Services for accessing these data are described at the back of the journal.

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