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Crystallographic identification of an unexpected by-product in an Ullmann's reaction toward bi-phenyls: 1-(4-hexyloxy-3-hydroxyphenyl)ethanone

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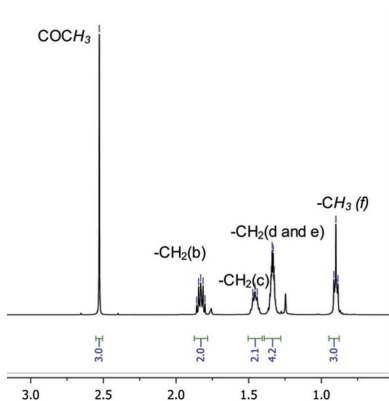
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The synthesis of 3,3'-diacetoxy-4,4'-bis(hexyloxy)biphenyl following the nickel-modified Ullmann reaction yielded a by-product which was identified successfully by crystallographic analysis as 1-(4-hexyloxy-3-hydroxyphenyl)ethanone, C₁₄H₂₀O₃. This unexpected nonbiphenyl by-product exhibited IR, ¹H NMR, ¹³C NMR and COSY (correlation spectroscopy) spectra fully consistent with the proposed structure. The compound crystallized in the orthorhombic *Pbca* space group, with two independent formula units in the asymmetric unit (one of which was slightly disordered), and showed a supramolecular architecture in which molecules linked by hydroxy-ethanone O—H···O interactions are organized in columns separated by the aliphatic tails.

1. Introduction

Substituted triphenylenes are the most extensively studied class of compounds that give rise to columnar liquid crystalline (LC) phases (Pal *et al.*, 2013; Bushby & Kawata, 2011). In this context, we recently proposed a synthetic pathway to triphenylenes exhibiting terminal functionalizations at the 2- and 7-positions (Zelcer *et al.*, 2013), which allows their incorporation into extended systems like oligomers and polymers (Zelcer *et al.*, 2007, 2013), with the bridging chains attached to the furthest separated positions (2 and 7) of the triphenylene units. This synthetic pathway involved substituted 4,4'-diacetoxy-3,3'-bis(hexyloxy)biphenyl (Zelcer *et al.*, 2013) as a key intermediate compound. We then decided to explore the influence of the point of attachment of substituents on the LC properties of such polymers, looking first for materials derived from 3,6-difunctionalized triphenylenes. In order to synthesize these compounds, our synthetic strategy also involved a key intermediate biphenyl, in the present case, bearing acetoxy protecting groups at the 3- and 3'-positions, as shown in the Scheme. The key reaction for the synthesis of biphenyl (V) involved a nickel-catalyzed Ullmann reaction (Zembayashi *et al.*, 1977; Hong *et al.*, 2001). The products were fully characterized by ¹H NMR, ¹³C NMR, FT-IR, elemental analysis and HRMS.

During the course of the Ullmann reaction, we also isolated a second product and attempted to identify it using the same set of techniques. We envisaged different possible substituted biphenyls, but none of the proposed structures could explain the experimental spectra of the product obtained. We then succeeded in crystallizing it and solved its molecular structure. Unexpectedly, the compound was not a substituted biphenyl,

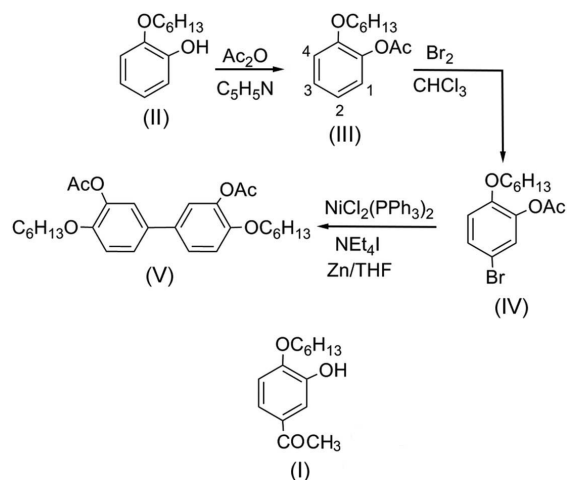


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but a rearranged phenyl product, namely 1-(4-hexyloxy-3-hydroxyphenyl)ethanone, (I) (see Scheme). We report herein the crystal and molecular structure of (I), along with its completely assigned ^1H NMR, ^{13}C NMR, COSY (correlation spectroscopy) and FT-IR spectra, and suggest a possible mechanism for its formation.

2. Experimental

All chemical precursors were purchased from Sigma–Aldrich and used without further purification. Operations under an inert atmosphere were carried out using standard Schlenk techniques. ^1H NMR spectra were measured on a Bruker AM500 spectrometer, using CDCl_3 as solvent and its residual peaks as internal references (7.26 p.p.m. for ^1H). Differential scanning calorimetry (DSC) was performed with a Shimadzu DSC-50 apparatus. Elemental analysis was carried out at UMYMFOR, Conicet, and Department of Organic Chemistry, FCEN, UBA, Argentina.



2.1. Synthesis and crystallization

2.1.1. Synthesis of 2-(hexyloxy)phenyl acetate, (III). 2-(Hexyloxy)phenol, (II) (10 g, 0.05 mol), was acetylated with acetic anhydride (20 ml) and pyridine (20 ml) at room temperature for 16 h. Examination by thin-layer chromatography (TLC; cyclohexane/ CH_2Cl_2 , 1:1 *v/v*, stain I_2) showed the complete conversion of (II) ($R_F = 0.46$) into a slower-moving product ($R_F = 0.35$). The mixture was concentrated and (III) was obtained as an oily syrup (yield 11.4 g, 97%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.18 (*ddd*, 1H, *ArH*), 7.06 (*dd*, 1H, $J = 7.75, 1.75$ Hz, *ArH*), 6.97 (*dd*, 1H, $J = 8.25, 1.25$ Hz, *ArH*), 6.93 (*td*, 1H, $J = 7.5, 1.5$ Hz, *ArH*), 3.98 (*t*, 2H, $J = 6.5$ Hz, CH_2O –), 2.31 (*s*, 3H, CH_3COO –), 1.78 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{O}$ –), 1.48 [*m*, 2H, $\text{CH}_2(\text{CH}_2)_2\text{O}$ –], 1.39–1.36 [*m*, 4H, $(\text{CH}_2)_2(\text{CH}_2)_2\text{O}$ –], 0.96 [*t*, 3H, $J = 7.0$ Hz, $-\text{O}(\text{CH}_2)_5\text{CH}_3$].

2.1.2. Synthesis of 5-bromo-2-(hexyloxy)phenyl acetate, (IV). Compound (III) (3.0 g, 0.013 mol) was placed in a round-bottomed two-necked flask equipped with a pressure-compensated funnel and CH_2Cl_2 (7.5 ml) was added. The flask was cooled to 273 K in an ice bath and a vessel bubbler with an Na_2CO_3 solution was placed in the remaining neck. Then a solution of Br_2 (0.75 ml, 0.015 mol) in CH_2Cl_2 (2.8 ml) was

introduced into the funnel and added dropwise under continuous stirring over a period of 90 min, resulting in a red solution. The ice bath was removed and the solution stirred until it remained colourless. When TLC (cyclohexane–dichloromethane, 1:1 *v/v*, UV and FeCl_3 stain) showed the complete conversion of the starting material ($R_F = 0.48$) into a faster-moving spot ($R_F = 0.55$), dichloromethane (50 ml) was added to the mixture and the organic phase was washed with $\text{NaHCO}_3(\text{ss})$ and water, then dried over Na_2SO_4 , filtered and evaporated under reduced pressure. The product was purified by chromatographic column [cyclohexane \rightarrow cyclohexane– CH_2Cl_2 (95:5 *v/v*)]. Compound (II) was a colourless oil (yield 2.9 g, 71%); ^1H NMR (500 MHz, CDCl_3): δ 7.28 (*dd*, 1H, $J = 8.7, 2.4$ Hz, *ArH*), 7.17 (*d*, 1H, $J = 2.4$ Hz, *ArH*), 6.81 (*d*, 1H, $J = 8.8$ Hz, *ArH*), 3.94 (*t*, 2H, $J = 6.5$ Hz, CH_2O –), 2.29 (*s*, 3H, CH_3COO –), 1.75 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{O}$ –), 1.45–1.30 [*m*, 6H, $\text{O}(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$], 0.90 [*t*, 3H, $J = 7.0$ Hz, $\text{O}(\text{CH}_2)_5\text{CH}_3$]; ^{13}C NMR (CDCl_3 , 125.7 MHz): δ 168.7 ($-\text{OCOCH}_3$), 150.2, 140.8, 129.7, 126.1, 114.7, 111.9 (*Ar*), 69.1 (OCH_2), 31.6, 29.2, 25.7, 22.7 [$\text{OCH}_2(\text{CH}_2)_4\text{CH}_3$], 20.6 ($-\text{OCOCH}_3$), 14.1 [$\text{OCH}_2(\text{CH}_2)_4\text{CH}_3$]. FT-IR diagnostic bands: 3074 ($\nu_{\text{C}_{\text{aromatic}}-\text{H}}$), 2958 ($\nu_{\text{CH}_3^{\text{assym}}}$), 2931 ($\nu_{\text{CH}_2^{\text{assym}}}$), 2872 ($\nu_{\text{CH}_3^{\text{sym}}}$), 2859 ($\nu_{\text{CH}_2^{\text{sym}}}$), 1776 cm^{-1} ($\nu_{\text{C}=\text{O}}$). Microanalysis found (calculated) for $\text{C}_{14}\text{H}_{19}\text{BrO}_3$ (%): C 54.2 (53.3), H 6.0 (6.0).

2.1.3. Synthesis of 3,3'-diacetoxy-4,4'-bis(hexyloxy)biphenyl, (V), and 1-(4-hexyloxy-3-hydroxyphenyl)ethanone, (I). In a Schlenk round-bottomed flask, $\text{NiCl}_2(\text{PPh}_3)_2$ (0.55 g, 0.84 mmol) and $\text{N}(\text{CH}_2\text{CH}_3)_4\text{I}$ (0.23 g, 0.89 mmol) were added, dried and degassed, applying three cycles of vacuum/argon. Then, under an argon atmosphere, a suspension of Zn dust (1.1 g, 17 mmol) in dried and deoxygenated tetrahydrofuran (THF, 2 ml) was added. The mixture was stirred for 30 min. In another Schlenk flask, a solution of deoxygenated (IV) (2.5 g, 7.8 mmol) in THF (11 ml) was added to the first flask and the reaction mixture was stirred at 329 K for 20 h under an argon atmosphere. When TLC (cyclohexane– AcOEt , 10:1 *v/v*, FeCl_3 stain) showed complete consumption of (IV) ($R_F = 0.43$) and the formation of a new spot that corresponds to (V) ($R_F = 0.23$), the reaction was stopped. Finally, the suspension was filtered through compacted silica, washed with ethyl ether and the filtrate concentrated *in vacuo*. The resulting solid was purified by column chromatography (silica, cyclohexane/ethyl acetate up to 20:1 *v/v*), to give a white solid (yield 550 mg, 30%). Analysis found (calculated) for $\text{C}_{28}\text{H}_{38}\text{O}_6$ (%): C 70.6 (71.4), H 7.7 (8.1). ^1H NMR (500 MHz, CDCl_3): δ 7.35 (*dd*, 2H, $J = 7.7, 2.3$ Hz, *ArH*), 7.23 (*d*, 2H, $J = 2.3$ Hz, *ArH*), 7.00 (*d*, 2H, $J = 8.0$ Hz, *ArH*), 4.05 (*t*, $J = 6.5$ Hz, 4H, CH_2O –), 2.34 (*s*, 6H, $-\text{OCOCH}_3$), 1.80 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{O}$ –), 1.50–1.30 [*m*, 12H, $\text{O}(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$], 0.94 [*t*, 6H, $J = 7.1$ Hz, $\text{O}(\text{CH}_2)_5\text{CH}_3$]; ^{13}C NMR (125.7 MHz, CDCl_3): δ 169.1 ($-\text{OCOCH}_3$), 149.9, 140.4, 133.1, 125.0, 121.2, 113.7 (*Ar*), 69.0 (OCH_2), 31.6, 29.3, 25.7, 22.7 [$\text{OCH}_2(\text{CH}_2)_4\text{CH}_3$], 20.7 ($-\text{OCOCH}_3$), 14.1 [$\text{OCH}_2(\text{CH}_2)_4\text{CH}_3$]; FT-IR diagnostic bands: 3045 ($\nu_{\text{C}_{\text{aromatic}}-\text{H}}$), 2958 ($\nu_{\text{CH}_3^{\text{assym}}}$), 2934 ($\nu_{\text{CH}_2^{\text{assym}}}$), 2867 ($\nu_{\text{CH}_3^{\text{sym}}}$), 2859 ($\nu_{\text{CH}_2^{\text{sym}}}$), 1771 cm^{-1} ($\nu_{\text{C}=\text{O}}$). A second set of fractions was collected and evaporated to dryness, yielding (I) as a white solid. Single crystals of (I) were grown by slow

Table 1
 Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₂₀ O ₃
<i>M_r</i>	236.30
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	170
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.3847 (10), 9.0716 (4), 30.3953 (12)
<i>V</i> (Å ³)	5345.0 (4)
<i>Z</i>	16
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	0.08
Crystal size (mm)	0.32 × 0.26 × 0.18
Data collection	
Diffractometer	Oxford Diffraction Xcalibur (Eos, Gemini) CCD diffractometer
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)
<i>T_{min}</i> , <i>T_{max}</i>	0.95, 0.98
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	18445, 6210, 3357
<i>R_{int}</i>	0.058
(sin θ/λ) _{max} (Å ⁻¹)	0.683
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.067, 0.189, 1.02
No. of reflections	6210
No. of parameters	365
No. of restraints	23
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.29, -0.31

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

evaporation from CHCl₃ solutions. Crystallographic analysis allowed us to establish the nature of (I) as 1-(4-hexyloxy-3-hydroxyphenyl)ethanone (see below) [yield 100 mg, 10%; m.p. 368 K (Fisher–Jones)]. Thermal data from DSC runs: Cr 340 K (6, 8 kJ mol⁻¹), Cr' 366 K (28 kJ mol⁻¹). FT-IR diagnostic bands: 3308 (*br*, νO–H), 3099 (*sh*, νC_{aromatic}–H), 2953 (νCH₃^{assym}), 2927 (νCH₂^{assym}), 2873 (νCH₃^{sym}), 2859 (νCH₂^{sym}), 1666 cm⁻¹ (νC=O). Analysis found (calculated) for C₁₄H₂₀O₃ (%): C 70.7 (71.1), H 8.4 (8.5). ¹H NMR (500 MHz, CDCl₃): δ 7.53 (*d*, 1H, *J* = 2.0 Hz, *ArH*-2), 7.51 (*dd*, 1H, *J* = 8.3, 2.1 Hz, *ArH*-6), 6.86 (*d*, 1H, *J* = 8.3 Hz, *ArH*-5), 5.79 (*s*, 1H, *OH*), 4.10 (*t*, *J* = 6.6 Hz, 2H, CH₂O–), 2.53 (*s*, 1H, CH₃CO–), 1.84 (*m*, 2H, CH₂CH₂O–), 1.46–1.32 [*m*, 6H,

O(CH₂)₂(CH₂)₃CH₃], 0.90 [*t*, 3H, *J* = 7.0 Hz, O(CH₂)₅CH₃]; ¹³C NMR (CDCl₃, 125.7 MHz): δ 197.1 (–COCH₃), 150.2, 145.6, 130.9, 121.9, 114.5, 110.7 (Ar), 69.2 (OCH₂), 31.6, 29.1, 26.5, 25.7 [OCH₂(CH₂)₄CH₃], 22.7 (–COCH₃), 14.1 [OCH₂(CH₂)₄CH₃]. For a complete assignment of the ¹H NMR and ¹³C NMR spectra, see *Results and discussion* (§3).

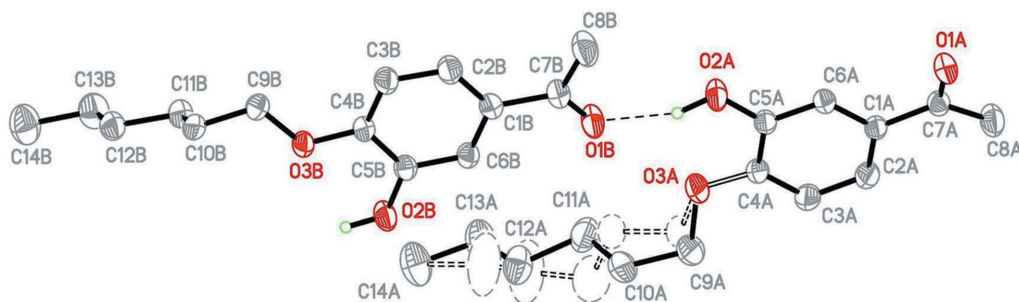
2.2. Refinement

Crystal data, data collection and structure refinement details for (I) are summarized in Table 1. All H atoms were originally found in difference maps, but were treated differently in the refinement. The O–H groups were refined freely with free *U*_{iso} values, while the C–H groups were repositioned in their expected positions and allowed to ride, with C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for aromatic H atoms, C–H = 0.97 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for methylene H atoms, and C–H = 0.96 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl H atoms. The hexyl tail in one of the independent molecules appeared disordered over two positions. A split model was refined with restrained geometry and displacement parameters, and the refined occupancies were 0.691 (4) and 0.309 (4).

3. Results and discussion

The title compound, (I), crystallizes in the orthorhombic space group *Pbca* and the asymmetric unit consists of two independent molecules (Fig. 1), one of which is disordered (see *Refinement*, §2.2). Unexpectedly, these molecules do not correspond to any kind of substituted biphenyl, but to 1-(4-hexyloxy-3-hydroxyphenyl)ethanone.

Once the chemical nature of (I) had been established crystallographically, further evidence was obtained from spectral data. Indeed, the IR spectrum of (I) shows the expected νCH₂ and νCH₃ bands in the 2850–2950 cm⁻¹ region, a νC_{aromatic}–H band at *ca* 3100 cm⁻¹ and a νC–C_{aromatic} band at *ca* 1600 cm⁻¹, all of which are already present in the starting material 5-bromo-2-(hexyloxy)phenyl acetate, (IV). In agreement with the lack of an acetoxy group and the presence of a ketone moiety, the νC=O band shifted from 1776 cm⁻¹ in (IV) to 1666 cm⁻¹ in (I), an identical value to that found in benzophenone. Compound (I) also exhibits an additional broad band at 3308 cm⁻¹, assigned to the new phenolic O–H group. ¹H NMR, ¹³C NMR and COSY spectra are shown on


Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 40% probability level. Single broken lines represent hydrogen bonds and double broken lines (and empty ellipsoids) correspond to the (unlabelled) minor fraction of the disordered hexyl group.

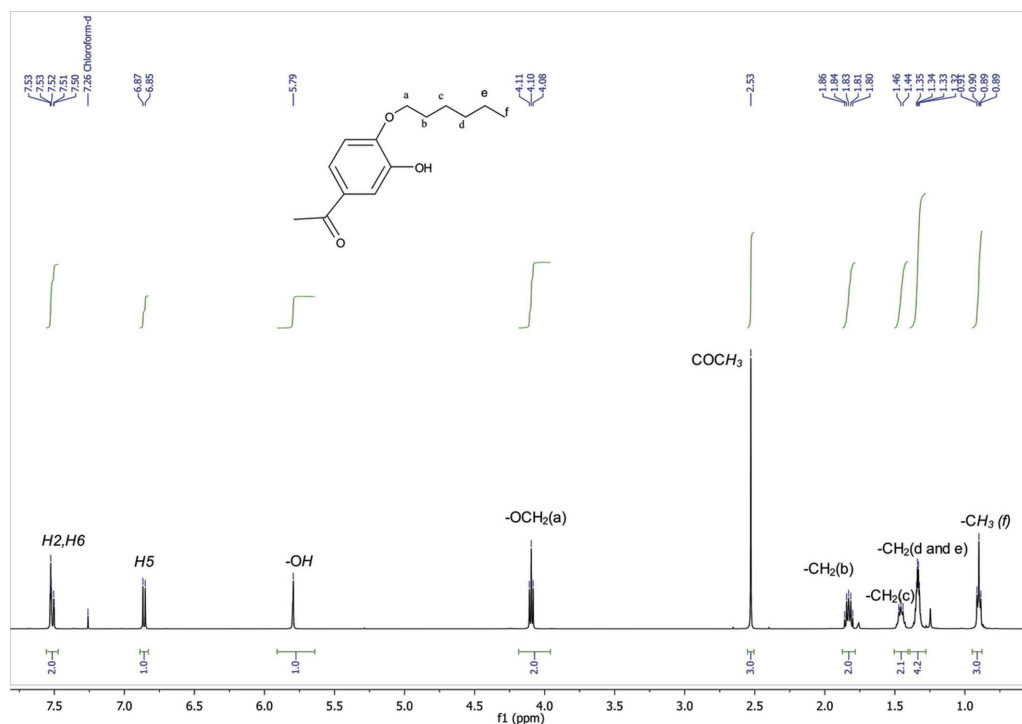


Figure 2
The assigned ^1H NMR spectrum of (I).

Figs. 2, 3 and 4, respectively, which also contain the assignment of each detected signal. The ^1H NMR spectrum of (I) shows the characteristic signals of the aromatic ring at about 7.0 p.p.m. The multiplicities of the different signals are in agreement with the substitution pattern observed and, as

expected, the aromatic H-2 atom was the more unprotected (at low fields) due to the neighbouring effect of the OH and ketone groups. This assignment was confirmed by the coupling constant observed, *i.e.* $J = 2.0$ Hz, a value typical for *meta*-coupling. The aromatic H-6 atom was found at 7.50 p.p.m. as a

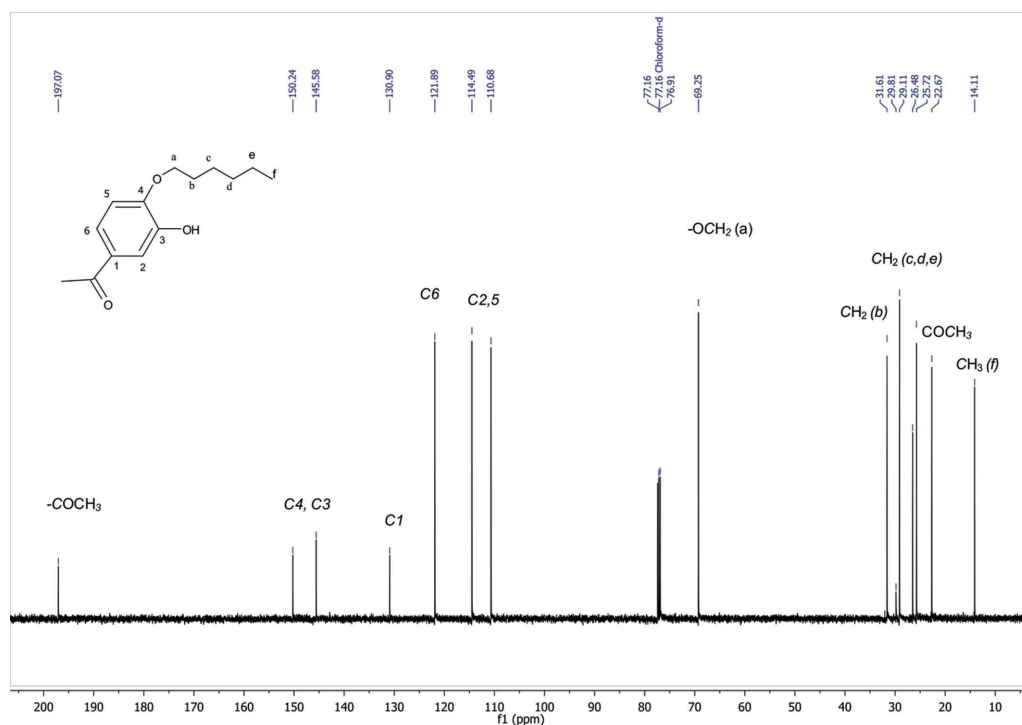


Figure 3
The assigned ^{13}C NMR spectrum of (I).

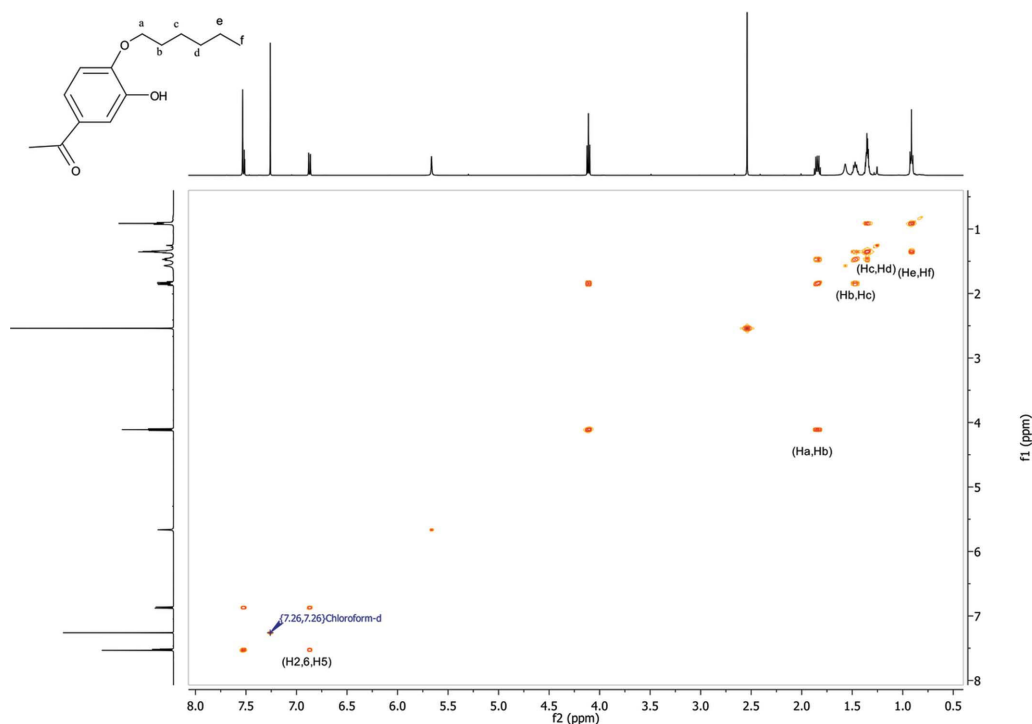


Figure 4
The COSY (correlation spectroscopy) analysis for (I).

Table 2
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2A-H2OA \cdots O1B$	0.96 (3)	1.83 (3)	2.735 (2)	156 (3)
$O2B-H2OB \cdots O1A^i$	0.92 (3)	1.89 (3)	2.779 (2)	161 (3)

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

doublet of doublets with $J = 8.3$ Hz, typical of *ortho*-coupling, and $J = 2.0$ Hz due to *meta*-coupling with H-2. Aromatic H-5 was found at 6.86 p.p.m. as a doublet with the same *ortho*-coupling. Other diagnostic signals were that of the phenolic H atom, detected as a singlet at 5.79 p.p.m., that of the α -methylene group of the hexyloxy tail, detected at 4.10 p.p.m. (the other signals corresponding to this hydrocarbon chain appeared in the range 1.86–0.89 p.p.m.) and the singlet of the

methyl group of the ketone group at 2.53 p.p.m. The COSY spectrum showed both the correlation between the aromatic H atoms and the lack of interactions for the signal at 5.79 p.p.m., as expected for the phenol H atom. The most distinctive signal in the ^{13}C NMR spectrum of (I) is that at 197.1 p.p.m., which corresponds to the ketone C atom; all other observed signals are in agreement with the proposed structure.

Since the molecular structure of (I) does not depart from expected values, the discussion of the structure will be restricted to the supramolecular architecture.

Intermolecular interactions are dominated by hydroxy-ethanone $O-H \cdots O$ hydrogen bonds (Table 2) which link molecules into columnar arrays built up by the *c*-glide plane in an $\cdots A-B-A-B \cdots$ sequence along [001] (Fig. 5, left). The interactive part in the columns (O atoms and π rings) are in turn 'shielded' from external interactions by the hexyl tails

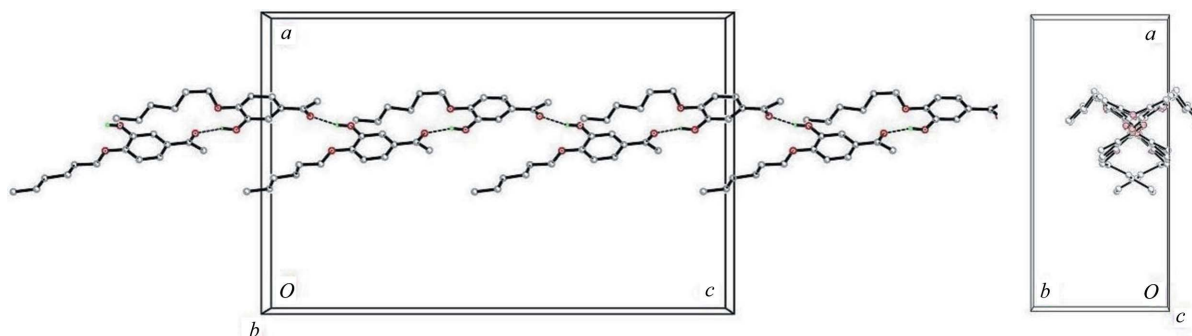


Figure 5
The columnar arrays in the structure of (I), showing (left) the $\cdots A-B-A-B \cdots$ sequence along [001] and (right) a single column seen in projection, showing the 'shielding' of the potentially interactive core.

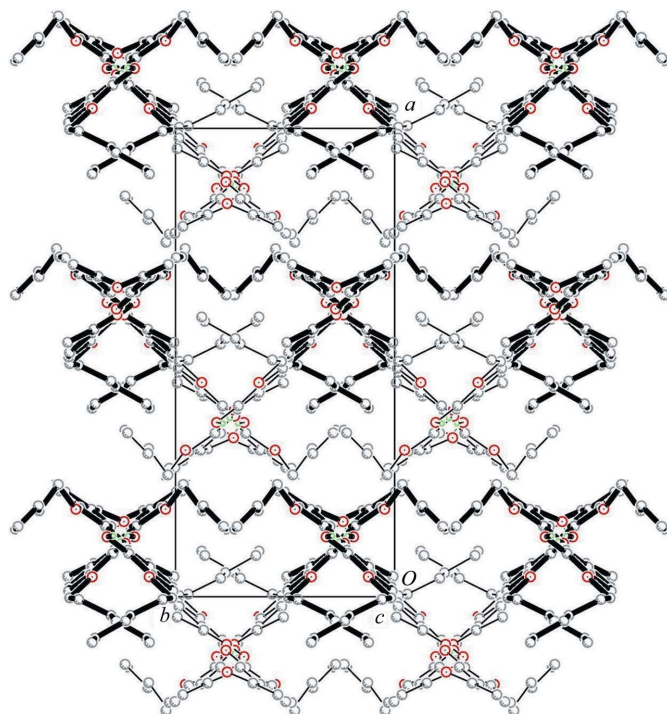


Figure 6
A packing view drawn along the column direction. Neighbouring columns are shown arbitrarily in light and dark for clarity.

wrapping the around the columns (Fig. 5, right). Thus, inter-column interactions are attained solely through weaker van der Waals forces (Fig. 6). Irrespective of this fact, the structure appears well packed, with no room for solvent molecules and a Kitajgorodskij packing index of 0.67% (PLATON; Spek, 2009).

As is common practice when dealing with compounds containing alkyl C_nH_{2n+1} tails, we looked in the Cambridge Structural Database (CSD, Version 5.3, update of May 2015; Groom & Allen, 2014) for other members of the series, *viz.* of the 1-[4-(*n*-yloxy)-3-hydroxyphenyl]ethanone type ($n \neq 6$), for comparison purposes. To our surprise, we found that no further members of the family have been reported. In fact, even the parent (3-hydroxyphenyl)ethanone skeleton is rare, with only two structures including this moiety reported in the CSD (refcodes JIVREL and HALYOI; Byrn *et al.*, 1991, 1993). However, in these cases, the (3-hydroxyphenyl)ethanone skeleton does not appear as an isolated molecule or as the core of a higher homologue, but as part of complex structures. Consequently, it is not possible to compare the *C*(7) synthon responsible of the chain array in (I) with related structures. More frequently observed is the (2-hydroxyphenyl)ethanone skeleton, with both substituents in neighbouring sites. This disposition, however, largely promotes an intramolecular O—H...O synthon defining an internal *R*(6) loop, and compar-

isons are again precluded. Thus, against this background, the present structure of (I) could be considered as ‘novel’.

From a chemical point of view, it is well known (Matsumoto *et al.*, 1983; Sperotto *et al.*, 2010) that the Ni-modified Ullmann reaction involves in a first step a reduction of Ni^{2+} to Ni^0 , and it is Ni^0 that reacts, in our case, *via* an oxidative addition of a molecule of (IV). This complex then reacts with another molecule of (IV) to give an intermediate in which nickel is oxidized to Ni^{4+} . The last step in the formation of the biaryl product involves a reductive elimination which reconstitutes the nickel catalyst. We think that a plausible explanation for the formation of (I) could involve a cleavage of the O—C linkage of the acetoxy group which suffers an intramolecular rearrangement to give product (I), in which the acyl group replaces the Br atom.

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supporting information

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Crystallographic identification of an unexpected by-product in an Ullman's reaction toward biphenyls: 1-(4-hexyloxy-3-hydroxyphenyl)ethanone

Veronica E. Manzano, Ricardo Baggio and Fabio D. Cukiernik

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

1-(4-Hexyloxy-3-hydroxyphenyl)ethanone

Crystal data

$C_{14}H_{20}O_3$	$D_x = 1.175 \text{ Mg m}^{-3}$
$M_r = 236.30$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Pbca</i>	Cell parameters from 2185 reflections
$a = 19.3847 (10) \text{ \AA}$	$\theta = 3.9\text{--}26.4^\circ$
$b = 9.0716 (4) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 30.3953 (12) \text{ \AA}$	$T = 170 \text{ K}$
$V = 5345.0 (4) \text{ \AA}^3$	Blocks, colourless
$Z = 16$	$0.32 \times 0.26 \times 0.18 \text{ mm}$
$F(000) = 2048$	

Data collection

CCD Oxford Diffraction Xcalibur (Eos, Gemini) diffractometer	18445 measured reflections
Radiation source: Enhance (Mo) X-ray Source	6210 independent reflections
Detector resolution: $16.1158 \text{ pixels mm}^{-1}$	3357 reflections with $I > 2\sigma(I)$
thick slices scans	$R_{\text{int}} = 0.058$
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	$\theta_{\text{max}} = 29.0^\circ$, $\theta_{\text{min}} = 3.7^\circ$
$T_{\text{min}} = 0.95$, $T_{\text{max}} = 0.98$	$h = -18 \rightarrow 25$
	$k = -12 \rightarrow 11$
	$l = -39 \rightarrow 27$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 0.6907P]$
$wR(F^2) = 0.189$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} < 0.001$
6210 reflections	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
365 parameters	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
23 restraints	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1A	0.66050 (9)	0.23557 (17)	0.59045 (5)	0.0446 (4)	
C1A	0.68678 (11)	0.3851 (2)	0.52954 (6)	0.0346 (5)	
C2A	0.72377 (12)	0.5033 (3)	0.51287 (7)	0.0459 (6)	
H2A	0.7473	0.5660	0.5319	0.055*	
C3A	0.72574 (13)	0.5281 (3)	0.46765 (7)	0.0523 (7)	
H3A	0.7518	0.6056	0.4565	0.063*	
C4A	0.68947 (11)	0.4392 (3)	0.43964 (7)	0.0398 (5)	
C5A	0.65089 (11)	0.3203 (2)	0.45608 (7)	0.0348 (5)	
C6A	0.65032 (11)	0.2950 (2)	0.50085 (7)	0.0338 (5)	
H6A	0.6251	0.2162	0.5120	0.041*	
C7A	0.68423 (11)	0.3532 (3)	0.57753 (7)	0.0370 (5)	
C8A	0.70922 (14)	0.4665 (3)	0.60948 (7)	0.0559 (7)	
H8AA	0.7034	0.4304	0.6389	0.084*	
H8AB	0.6832	0.5556	0.6058	0.084*	
H8AC	0.7572	0.4861	0.6042	0.084*	
O2A	0.61431 (9)	0.23021 (17)	0.42929 (5)	0.0474 (4)	
H2OA	0.6184 (15)	0.253 (3)	0.3985 (10)	0.078 (9)*	
O3A	0.68699 (9)	0.45456 (19)	0.39488 (5)	0.0529 (5)	0.691 (4)
C9A	0.7402 (3)	0.5463 (7)	0.37586 (14)	0.082 (3)	0.691 (4)
H9AA	0.7850	0.5150	0.3866	0.099*	0.691 (4)
H9AB	0.7331	0.6479	0.3847	0.099*	0.691 (4)
C10A	0.7384 (3)	0.5354 (7)	0.32708 (13)	0.0944 (19)	0.691 (4)
H10A	0.7827	0.5671	0.3156	0.113*	0.691 (4)
H10B	0.7322	0.4328	0.3190	0.113*	0.691 (4)
C11A	0.6841 (3)	0.6226 (8)	0.30612 (15)	0.0990 (19)	0.691 (4)
H11A	0.6846	0.7217	0.3182	0.119*	0.691 (4)
H11B	0.6396	0.5791	0.3128	0.119*	0.691 (4)
C12A	0.6936 (3)	0.6308 (5)	0.25457 (14)	0.0882 (15)	0.691 (4)
H12A	0.7399	0.6651	0.2480	0.106*	0.691 (4)
H12B	0.6886	0.5327	0.2423	0.106*	0.691 (4)
C13A	0.6455 (3)	0.7257 (6)	0.23440 (13)	0.0829 (16)	0.691 (4)
H13A	0.6538	0.8260	0.2441	0.099*	0.691 (4)
H13B	0.5993	0.6981	0.2435	0.099*	0.691 (4)
C14A	0.6503 (2)	0.7191 (4)	0.18381 (9)	0.0906 (11)	0.691 (4)
H14A	0.6161	0.7830	0.1712	0.136*	0.691 (4)
H14B	0.6423	0.6198	0.1741	0.136*	0.691 (4)
H14C	0.6954	0.7503	0.1746	0.136*	0.691 (4)
O3'	0.68699 (9)	0.45456 (19)	0.39488 (5)	0.0529 (5)	0.309 (4)
C9'	0.7129 (7)	0.5850 (12)	0.3735 (2)	0.065 (4)	0.309 (4)

H9C	0.7629	0.5854	0.3747	0.078*	0.309 (4)
H9D	0.6962	0.6717	0.3888	0.078*	0.309 (4)
C10'	0.6901 (5)	0.5904 (14)	0.3267 (2)	0.065 (3)	0.309 (4)
H10C	0.6411	0.6126	0.3256	0.078*	0.309 (4)
H10D	0.6971	0.4946	0.3133	0.078*	0.309 (4)
C11'	0.7281 (6)	0.7021 (13)	0.3016 (2)	0.099 (2)	0.309 (4)
H11C	0.7372	0.7855	0.3207	0.119*	0.309 (4)
H11D	0.7723	0.6610	0.2930	0.119*	0.309 (4)
C12'	0.6905 (6)	0.7593 (9)	0.2593 (2)	0.0888 (16)	0.309 (4)
H12C	0.6449	0.7937	0.2675	0.107*	0.309 (4)
H12D	0.7158	0.8431	0.2478	0.107*	0.309 (4)
C13'	0.6837 (8)	0.6543 (13)	0.2259 (2)	0.128 (7)	0.309 (4)
H13C	0.6557	0.5732	0.2366	0.153*	0.309 (4)
H13D	0.7289	0.6154	0.2187	0.153*	0.309 (4)
C14'	0.6503 (2)	0.7191 (4)	0.18381 (9)	0.0906 (11)	0.309 (4)
H14D	0.6466	0.6434	0.1619	0.136*	0.309 (4)
H14E	0.6051	0.7559	0.1907	0.136*	0.309 (4)
H14F	0.6784	0.7980	0.1728	0.136*	0.309 (4)
O1B	0.60177 (9)	0.23252 (19)	0.33965 (5)	0.0522 (5)	
C1B	0.56349 (11)	0.1185 (2)	0.27495 (7)	0.0378 (5)	
C2B	0.52063 (13)	0.0158 (3)	0.25549 (8)	0.0479 (6)	
H2B	0.4972	-0.0517	0.2730	0.057*	
C3B	0.51213 (13)	0.0121 (3)	0.21008 (7)	0.0457 (6)	
H3B	0.4829	-0.0571	0.1974	0.055*	
C4B	0.54704 (11)	0.1109 (2)	0.18399 (7)	0.0361 (5)	
C5B	0.59232 (11)	0.2134 (2)	0.20315 (7)	0.0353 (5)	
C6B	0.59926 (11)	0.2174 (2)	0.24814 (7)	0.0358 (5)	
H6B	0.6282	0.2870	0.2609	0.043*	
C7B	0.57128 (12)	0.1276 (3)	0.32316 (7)	0.0416 (6)	
C8B	0.54339 (15)	0.0076 (3)	0.35173 (8)	0.0631 (8)	
H8BA	0.5577	0.0238	0.3816	0.095*	
H8BB	0.5606	-0.0858	0.3418	0.095*	
H8BC	0.4939	0.0076	0.3502	0.095*	
O2B	0.62791 (9)	0.31252 (18)	0.17830 (5)	0.0486 (5)	
H2OB	0.6302 (15)	0.282 (3)	0.1493 (10)	0.074 (9)*	
O3B	0.54257 (8)	0.11987 (17)	0.13942 (4)	0.0410 (4)	
C9B	0.49771 (12)	0.0171 (3)	0.11721 (7)	0.0442 (6)	
H9BA	0.4519	0.0206	0.1301	0.053*	
H9BB	0.5154	-0.0824	0.1204	0.053*	
C10B	0.49432 (12)	0.0580 (3)	0.06956 (7)	0.0430 (6)	
H10E	0.4692	-0.0182	0.0539	0.052*	
H10F	0.5409	0.0601	0.0578	0.052*	
C11B	0.46042 (13)	0.2049 (3)	0.06046 (7)	0.0482 (6)	
H11E	0.4895	0.2835	0.0717	0.058*	
H11F	0.4165	0.2095	0.0757	0.058*	
C12B	0.44862 (13)	0.2275 (3)	0.01119 (7)	0.0488 (6)	
H12E	0.4930	0.2265	-0.0035	0.059*	
H12F	0.4222	0.1446	0.0001	0.059*	

C13B	0.41190 (15)	0.3665 (3)	-0.00099 (9)	0.0654 (8)
H13E	0.4380	0.4504	0.0098	0.078*
H13F	0.3670	0.3681	0.0131	0.078*
C14B	0.40268 (18)	0.3804 (4)	-0.05076 (9)	0.0767 (9)
H14G	0.3800	0.4717	-0.0574	0.115*
H14H	0.3752	0.2997	-0.0613	0.115*
H14I	0.4470	0.3784	-0.0648	0.115*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0620 (11)	0.0419 (9)	0.0300 (7)	0.0026 (8)	-0.0001 (8)	0.0012 (7)
C1A	0.0330 (11)	0.0417 (12)	0.0289 (10)	0.0050 (10)	-0.0012 (10)	-0.0020 (10)
C2A	0.0444 (13)	0.0527 (14)	0.0406 (12)	-0.0118 (11)	-0.0068 (11)	-0.0009 (12)
C3A	0.0468 (14)	0.0654 (16)	0.0447 (13)	-0.0223 (13)	-0.0028 (12)	0.0127 (13)
C4A	0.0370 (12)	0.0521 (14)	0.0304 (11)	-0.0013 (10)	-0.0028 (10)	0.0051 (11)
C5A	0.0343 (12)	0.0382 (12)	0.0319 (10)	0.0024 (9)	-0.0034 (10)	-0.0019 (10)
C6A	0.0366 (12)	0.0335 (11)	0.0313 (10)	0.0025 (9)	0.0008 (10)	0.0014 (10)
C7A	0.0345 (12)	0.0428 (13)	0.0336 (11)	0.0068 (10)	-0.0021 (10)	-0.0014 (11)
C8A	0.0708 (18)	0.0616 (17)	0.0354 (12)	-0.0131 (14)	-0.0033 (13)	-0.0061 (13)
O2A	0.0681 (12)	0.0454 (9)	0.0286 (8)	-0.0104 (8)	-0.0061 (8)	-0.0008 (8)
O3A	0.0593 (11)	0.0687 (12)	0.0307 (8)	-0.0116 (9)	0.0007 (8)	0.0101 (8)
C9A	0.086 (5)	0.115 (6)	0.045 (3)	-0.033 (4)	0.003 (3)	0.028 (3)
C10A	0.081 (4)	0.154 (6)	0.048 (2)	-0.019 (4)	0.004 (3)	0.033 (3)
C11A	0.115 (5)	0.120 (5)	0.062 (3)	-0.045 (3)	-0.029 (3)	0.017 (3)
C12A	0.129 (4)	0.063 (2)	0.073 (3)	-0.019 (3)	-0.030 (3)	0.013 (3)
C13A	0.104 (4)	0.092 (4)	0.052 (3)	0.001 (3)	-0.002 (3)	-0.001 (3)
C14A	0.123 (3)	0.094 (3)	0.0552 (18)	0.009 (2)	0.0003 (19)	0.0209 (19)
O3'	0.0593 (11)	0.0687 (12)	0.0307 (8)	-0.0116 (9)	0.0007 (8)	0.0101 (8)
C9'	0.075 (10)	0.064 (7)	0.056 (7)	-0.018 (7)	0.014 (6)	0.022 (6)
C10'	0.039 (5)	0.121 (10)	0.035 (5)	-0.008 (6)	-0.015 (5)	0.020 (6)
C11'	0.114 (5)	0.120 (5)	0.062 (3)	-0.046 (4)	-0.028 (3)	0.018 (3)
C12'	0.129 (4)	0.063 (3)	0.074 (3)	-0.019 (3)	-0.030 (3)	0.013 (3)
C13'	0.147 (15)	0.188 (19)	0.048 (6)	0.047 (13)	0.017 (9)	-0.008 (9)
C14'	0.123 (3)	0.094 (3)	0.0552 (18)	0.009 (2)	0.0003 (19)	0.0209 (19)
O1B	0.0753 (12)	0.0512 (10)	0.0300 (8)	-0.0076 (9)	-0.0045 (8)	-0.0008 (8)
C1B	0.0417 (13)	0.0400 (12)	0.0316 (11)	0.0018 (10)	0.0017 (10)	-0.0007 (10)
C2B	0.0550 (15)	0.0503 (14)	0.0383 (12)	-0.0120 (12)	0.0020 (12)	0.0017 (12)
C3B	0.0505 (14)	0.0506 (14)	0.0362 (12)	-0.0122 (11)	-0.0018 (12)	-0.0043 (12)
C4B	0.0390 (12)	0.0403 (12)	0.0290 (10)	0.0003 (10)	0.0002 (10)	-0.0027 (10)
C5B	0.0399 (12)	0.0324 (11)	0.0337 (11)	0.0012 (9)	0.0002 (10)	-0.0029 (10)
C6B	0.0381 (12)	0.0364 (11)	0.0330 (11)	-0.0010 (9)	-0.0028 (10)	-0.0063 (10)
C7B	0.0494 (14)	0.0414 (13)	0.0339 (11)	0.0045 (11)	0.0003 (11)	0.0016 (11)
C8B	0.088 (2)	0.0647 (18)	0.0368 (12)	-0.0158 (15)	0.0003 (14)	0.0072 (13)
O2B	0.0676 (12)	0.0491 (10)	0.0291 (8)	-0.0192 (8)	0.0032 (8)	-0.0042 (8)
O3B	0.0461 (9)	0.0476 (9)	0.0292 (7)	-0.0124 (7)	-0.0015 (7)	-0.0046 (7)
C9B	0.0422 (13)	0.0512 (14)	0.0393 (12)	-0.0109 (11)	-0.0023 (11)	-0.0082 (12)
C10B	0.0402 (13)	0.0542 (14)	0.0346 (11)	-0.0050 (11)	-0.0027 (11)	-0.0107 (11)

C11B	0.0485 (15)	0.0583 (16)	0.0378 (12)	-0.0018 (12)	-0.0008 (12)	-0.0098 (12)
C12B	0.0482 (15)	0.0570 (15)	0.0413 (13)	0.0029 (12)	0.0001 (12)	-0.0064 (12)
C13B	0.072 (2)	0.0632 (19)	0.0611 (17)	0.0143 (15)	-0.0031 (16)	-0.0058 (15)
C14B	0.094 (2)	0.079 (2)	0.0569 (17)	0.0228 (18)	-0.0088 (17)	0.0122 (17)

Geometric parameters (Å, °)

O1A—C7A	1.227 (3)	C11'—H11D	0.9700
C1A—C2A	1.386 (3)	C12'—C13'	1.398 (7)
C1A—C6A	1.389 (3)	C12'—H12C	0.9700
C1A—C7A	1.488 (3)	C12'—H12D	0.9700
C2A—C3A	1.393 (3)	C13'—C14'	1.551 (6)
C2A—H2A	0.9300	C13'—H13C	0.9700
C3A—C4A	1.368 (3)	C13'—H13D	0.9700
C3A—H3A	0.9300	C14'—H14D	0.9600
C4A—O3'	1.368 (2)	C14'—H14E	0.9600
C4A—O3A	1.368 (2)	C14'—H14F	0.9600
C4A—C5A	1.405 (3)	O1B—C7B	1.228 (3)
C5A—O2A	1.354 (2)	C1B—C2B	1.381 (3)
C5A—C6A	1.380 (3)	C1B—C6B	1.396 (3)
C6A—H6A	0.9300	C1B—C7B	1.475 (3)
C7A—C8A	1.494 (3)	C2B—C3B	1.390 (3)
C8A—H8AA	0.9600	C2B—H2B	0.9300
C8A—H8AB	0.9600	C3B—C4B	1.375 (3)
C8A—H8AC	0.9600	C3B—H3B	0.9300
O2A—H2OA	0.96 (3)	C4B—O3B	1.360 (2)
O3A—C9A	1.445 (4)	C4B—C5B	1.406 (3)
C9A—C10A	1.486 (5)	C5B—O2B	1.362 (3)
C9A—H9AA	0.9700	C5B—C6B	1.374 (3)
C9A—H9AB	0.9700	C6B—H6B	0.9300
C10A—C11A	1.463 (7)	C7B—C8B	1.494 (3)
C10A—H10A	0.9700	C8B—H8BA	0.9600
C10A—H10B	0.9700	C8B—H8BB	0.9600
C11A—C12A	1.580 (6)	C8B—H8BC	0.9600
C11A—H11A	0.9700	O2B—H2OB	0.92 (3)
C11A—H11B	0.9700	O3B—C9B	1.443 (2)
C12A—C13A	1.409 (6)	C9B—C10B	1.496 (3)
C12A—H12A	0.9700	C9B—H9BA	0.9700
C12A—H12B	0.9700	C9B—H9BB	0.9700
C13A—C14A	1.542 (4)	C10B—C11B	1.511 (3)
C13A—H13A	0.9700	C10B—H10E	0.9700
C13A—H13B	0.9700	C10B—H10F	0.9700
C14A—H14A	0.9600	C11B—C12B	1.529 (3)
C14A—H14B	0.9600	C11B—H11E	0.9700
C14A—H14C	0.9600	C11B—H11F	0.9700
O3'—C9'	1.440 (5)	C12B—C13B	1.495 (3)
C9'—C10'	1.490 (6)	C12B—H12E	0.9700
C9'—H9C	0.9700	C12B—H12F	0.9700

C9'—H9D	0.9700	C13B—C14B	1.529 (3)
C10'—C11'	1.467 (7)	C13B—H13E	0.9700
C10'—H10C	0.9700	C13B—H13F	0.9700
C10'—H10D	0.9700	C14B—H14G	0.9600
C11'—C12'	1.566 (7)	C14B—H14H	0.9600
C11'—H11C	0.9700	C14B—H14I	0.9600
C2A—C1A—C6A	119.29 (19)	H11C—C11'—H11D	107.5
C2A—C1A—C7A	121.7 (2)	C13'—C12'—C11'	114.4 (6)
C6A—C1A—C7A	118.96 (19)	C13'—C12'—H12C	108.6
C1A—C2A—C3A	120.0 (2)	C11'—C12'—H12C	108.6
C1A—C2A—H2A	120.0	C13'—C12'—H12D	108.6
C3A—C2A—H2A	120.0	C11'—C12'—H12D	108.6
C4A—C3A—C2A	120.3 (2)	H12C—C12'—H12D	107.6
C4A—C3A—H3A	119.8	C12'—C13'—C14'	112.4 (6)
C2A—C3A—H3A	119.8	C12'—C13'—H13C	109.1
C3A—C4A—O3'	125.2 (2)	C14'—C13'—H13C	109.1
C3A—C4A—O3A	125.2 (2)	C12'—C13'—H13D	109.1
C3A—C4A—C5A	120.36 (19)	C14'—C13'—H13D	109.1
O3'—C4A—C5A	114.4 (2)	H13C—C13'—H13D	107.9
O3A—C4A—C5A	114.4 (2)	C13'—C14'—H14D	109.5
O2A—C5A—C6A	119.2 (2)	C13'—C14'—H14E	109.5
O2A—C5A—C4A	121.90 (19)	H14D—C14'—H14E	109.5
C6A—C5A—C4A	118.9 (2)	C13'—C14'—H14F	109.5
C5A—C6A—C1A	121.1 (2)	H14D—C14'—H14F	109.5
C5A—C6A—H6A	119.4	H14E—C14'—H14F	109.5
C1A—C6A—H6A	119.4	C2B—C1B—C6B	118.83 (19)
O1A—C7A—C1A	119.7 (2)	C2B—C1B—C7B	121.6 (2)
O1A—C7A—C8A	120.8 (2)	C6B—C1B—C7B	119.5 (2)
C1A—C7A—C8A	119.5 (2)	C1B—C2B—C3B	120.8 (2)
C7A—C8A—H8AA	109.5	C1B—C2B—H2B	119.6
C7A—C8A—H8AB	109.5	C3B—C2B—H2B	119.6
H8AA—C8A—H8AB	109.5	C4B—C3B—C2B	119.9 (2)
C7A—C8A—H8AC	109.5	C4B—C3B—H3B	120.1
H8AA—C8A—H8AC	109.5	C2B—C3B—H3B	120.1
H8AB—C8A—H8AC	109.5	O3B—C4B—C3B	125.6 (2)
C5A—O2A—H2OA	114.2 (17)	O3B—C4B—C5B	114.38 (19)
C4A—O3A—C9A	115.5 (2)	C3B—C4B—C5B	120.00 (19)
O3A—C9A—C10A	110.2 (4)	O2B—C5B—C6B	119.00 (19)
O3A—C9A—H9AA	109.6	O2B—C5B—C4B	121.58 (18)
C10A—C9A—H9AA	109.6	C6B—C5B—C4B	119.4 (2)
O3A—C9A—H9AB	109.6	C5B—C6B—C1B	121.0 (2)
C10A—C9A—H9AB	109.6	C5B—C6B—H6B	119.5
H9AA—C9A—H9AB	108.1	C1B—C6B—H6B	119.5
C11A—C10A—C9A	114.5 (5)	O1B—C7B—C1B	119.9 (2)
C11A—C10A—H10A	108.6	O1B—C7B—C8B	120.1 (2)
C9A—C10A—H10A	108.6	C1B—C7B—C8B	120.0 (2)
C11A—C10A—H10B	108.6	C7B—C8B—H8BA	109.5

C9A—C10A—H10B	108.6	C7B—C8B—H8BB	109.5
H10A—C10A—H10B	107.6	H8BA—C8B—H8BB	109.5
C10A—C11A—C12A	111.9 (5)	C7B—C8B—H8BC	109.5
C10A—C11A—H11A	109.2	H8BA—C8B—H8BC	109.5
C12A—C11A—H11A	109.2	H8BB—C8B—H8BC	109.5
C10A—C11A—H11B	109.2	C5B—O2B—H2OB	111.0 (18)
C12A—C11A—H11B	109.2	C4B—O3B—C9B	117.76 (17)
H11A—C11A—H11B	107.9	O3B—C9B—C10B	108.61 (18)
C13A—C12A—C11A	112.5 (5)	O3B—C9B—H9BA	110.0
C13A—C12A—H12A	109.1	C10B—C9B—H9BA	110.0
C11A—C12A—H12A	109.1	O3B—C9B—H9BB	110.0
C13A—C12A—H12B	109.1	C10B—C9B—H9BB	110.0
C11A—C12A—H12B	109.1	H9BA—C9B—H9BB	108.3
H12A—C12A—H12B	107.8	C9B—C10B—C11B	114.51 (19)
C12A—C13A—C14A	111.7 (4)	C9B—C10B—H10E	108.6
C12A—C13A—H13A	109.3	C11B—C10B—H10E	108.6
C14A—C13A—H13A	109.3	C9B—C10B—H10F	108.6
C12A—C13A—H13B	109.3	C11B—C10B—H10F	108.6
C14A—C13A—H13B	109.3	H10E—C10B—H10F	107.6
H13A—C13A—H13B	107.9	C10B—C11B—C12B	111.25 (19)
C13A—C14A—H14A	109.5	C10B—C11B—H11E	109.4
C13A—C14A—H14B	109.5	C12B—C11B—H11E	109.4
H14A—C14A—H14B	109.5	C10B—C11B—H11F	109.4
C13A—C14A—H14C	109.5	C12B—C11B—H11F	109.4
H14A—C14A—H14C	109.5	H11E—C11B—H11F	108.0
H14B—C14A—H14C	109.5	C13B—C12B—C11B	115.3 (2)
C4A—O3'—C9'	121.4 (4)	C13B—C12B—H12E	108.5
O3'—C9'—C10'	110.8 (5)	C11B—C12B—H12E	108.5
O3'—C9'—H9C	109.5	C13B—C12B—H12F	108.5
C10'—C9'—H9C	109.5	C11B—C12B—H12F	108.5
O3'—C9'—H9D	109.5	H12E—C12B—H12F	107.5
C10'—C9'—H9D	109.5	C12B—C13B—C14B	111.7 (2)
H9C—C9'—H9D	108.1	C12B—C13B—H13E	109.3
C9'—C10'—C11'	111.7 (6)	C14B—C13B—H13E	109.3
C9'—C10'—H10C	109.3	C12B—C13B—H13F	109.3
C11'—C10'—H10C	109.3	C14B—C13B—H13F	109.3
C9'—C10'—H10D	109.3	H13E—C13B—H13F	107.9
C11'—C10'—H10D	109.3	C13B—C14B—H14G	109.5
H10C—C10'—H10D	107.9	C13B—C14B—H14H	109.5
C12'—C11'—C10'	114.9 (6)	H14G—C14B—H14H	109.5
C12'—C11'—H11C	108.5	C13B—C14B—H14I	109.5
C10'—C11'—H11C	108.5	H14G—C14B—H14I	109.5
C12'—C11'—H11D	108.5	H14H—C14B—H14I	109.5
C10'—C11'—H11D	108.5		

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>
O2 <i>A</i> —H2O <i>A</i> ···O1 <i>B</i>	0.96 (3)	1.83 (3)	2.735 (2)	156 (3)
O2 <i>B</i> —H2O <i>B</i> ···O1 <i>A</i> ⁱ	0.92 (3)	1.89 (3)	2.779 (2)	161 (3)

Symmetry code: (i) *x*, $-y+1/2$, $z-1/2$.