

2,6-Di-*tert*-butylphenol revisited at  
110 K

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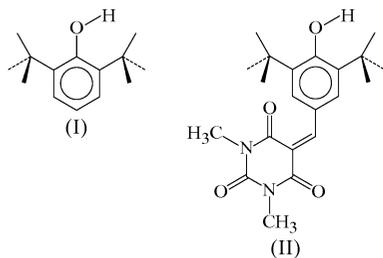
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The title compound,  $C_{14}H_{22}O$ , was studied at 110 K. The phenolic hydroxy group was found to be coplanar with the benzene ring and, due to steric hindrance from the *tert*-butyl groups, this hydroxy group does not form hydrogen bonds. The shortest intermolecular  $O \cdots O$  distance is 3.1008 (11) Å, with an  $O-H \cdots O$  angle of 117.3 (16)°. There are no significant intermolecular  $\pi-\pi$  stacking or  $C-H \cdots \pi$  interactions.

## Comment

Our interest in the structure of the title compound, (I), was aroused by the crystal structure of 5-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)-1,3-dimethylpyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione [(II); denoted (V) in Rezende *et al.*, 2005]. Compound (II) features an OH moiety that does not appear to form a hydrogen bond, with closest  $O \cdots O$  distances of 3.391 (2) and 3.010 (2) Å for the two independent molecules in (II). Cases like this are rare. The Cambridge Structural Database (CSD, Version 5.26, update of August 2005; Allen, 2002) was analysed for similar configurations. In most cases where OH groups do not donate hydrogen bonds, this is due to missing or misplaced H atoms. Only in sterically very congested situations is hydrogen bonding really impossible (see below).



Substituted phenols have a technical application as anti-oxidants. In the first step of the oxidation reaction, the phenolic H atom is released and a phenoxyl radical is formed. It is well known that the strength of the  $O-H$  bond is weaker if bulky substituents like *tert*-butyl groups are introduced in *ortho* positions, and also that the electronic influence of *para*

substituents is important (Lucarini *et al.*, 1996). Therefore, it is essential to know the conformation of the OH group in (I), which has two bulky substituents in the *ortho* positions and only an H atom in the *para* position.

The title compound, (I), is related to (II) and its structure has been published previously by Lazarev *et al.* (1992), based on a room-temperature data collection. The H-atom position of the phenolic hydroxy group could not be determined in that structure. In order to determine this H-atom position reliably, we redetermined the structure at 110 K. All H atoms could be located in the difference Fourier map and were refined freely with isotropic displacement parameters.

The hydroxy group is in the plane of the benzene ring, with a  $C6-C1-O1-H1O$  torsion angle of  $-0.4$  (14)° (Fig. 1). This finding is in accordance with high-level *ab initio* calculations (Ribeiro da Silva *et al.*, 1999) and with the crystal structures of most non-substituted phenols. The planarity is also consistent with the findings in the monoclinic form of 2,6-di-*tert*-butyl-4-methylphenol [space group  $C2/c$ , CSD refcodes MBPHOL01 (Imura *et al.*, 1983) and MBPHOL11 (Batsanov *et al.*, 2003)], where the OH torsion angle is  $-1$  or  $4$ °, respectively, but the CSD contains additional polymorphs with OH torsion angles up to 30 and 26°, respectively [orthorhombic form, space group  $P2_12_12_1$ , CSD refcodes MBPHOL02 (Bolte & Amon, 2000) and MBPHOL10 (Maze-Baudet, 1973)]. A second monoclinic polymorph [space group  $Cc$ , CSD refcode MBPHOL12 (Valentine *et al.*, 2003)] has a torsion angle of  $-3$ °. Contrary to our present results for (I), polarizability

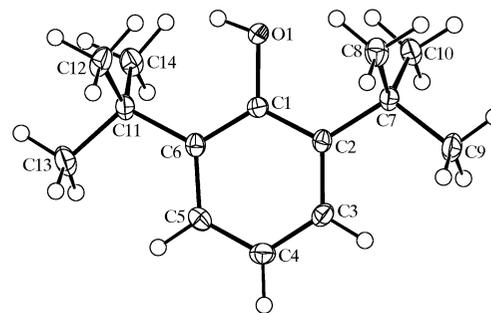


Figure 1

Displacement ellipsoid plot of (I). Ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

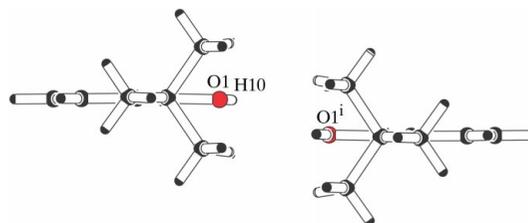


Figure 2

The packing arrangement of (I) in the crystal, which is unfavourable for hydrogen bonding. [Symmetry code: (i)  $1-x, -y, 1-z$ .]

studies (Aroney *et al.*, 1964), electron-spin resonance experiments (Nemoto *et al.*, 1981) and semi-empirical AM1 calculations (Brewster *et al.*, 1994) suggest a non-planarity of the OH group in (I).

Molecules of (I) have an approximate non-crystallographic mirror symmetry, with the benzene ring and the OH group in the mirror plane with an r.m.s. deviation (Pilati & Forni, 1998) of 0.0328 Å. When the H atoms are ignored from this calculation, the molecule has an approximate  $C_{2v}$  symmetry with an r.m.s. deviation of 0.0273 Å. A rigid-body analysis can be performed on the molecule using the program *THMAIL* (Schomaker & Trueblood, 1998). When the two *tert*-butyl groups are defined as independent rotors, low rigid-body  $R$  values of 0.062 (for all  $U$  values) and 0.046 (for diagonal  $U$  values) can be achieved. The C1—O1 distance corrected for rigid-body motion is 1.390 Å, compared with the uncorrected value of 1.3865 (12) Å.

The coplanarity of the OH group with the benzene ring leads to very short intramolecular H...H contacts with one of the *tert*-butyl groups. The shortest H...H distances are 1.90 (2) Å to H14C and 1.92 (2) Å to H12C. Accordingly, the C11—C14 and C11—C12 distances of 1.5466 (15) and 1.5480 (16) Å, respectively, are the longest C—C bonds of the *tert*-butyl groups. The congestion around the OH group can also be seen in the C—C—O bond angles of 120.59 (9)° in the direction of the H...H interactions and 116.45 (8)° in the opposite direction, showing that the O atom is slightly bent away. These H...H interactions are certainly a reason for the weakness of the O—H bond.

Due to the steric shielding of the two *tert*-butyl groups, there is no intermolecular hydrogen bonding involving the OH group. Thus, the shortest intermolecular O...O distance is 3.1008 (11) Å, with an O—H...O angle of 117.3 (16)° (Fig. 2). As there are no hydrogen-bond acceptors in the molecule (apart from the phenolic OH group itself), no intramolecular hydrogen bonding is present. Significant intermolecular  $\pi$ — $\pi$  stacking and C—H... $\pi$  interactions are not observed. Consequently, the density of the crystal is rather low and the packing index (Kitajgorodskij, 1973) is only 67.5%, which is at the lower end of the 65–75% range expected for organic solids (Dunitz, 1995).

A study of the CSD (update of August 2005) gives 90 entries with one or more 2,6-di-*tert*-butyl-substituted phenol moieties. In 34 of these entries, the coordinates of the OH H atoms are not deposited on the CSD, and three additional entries were not considered because of disorder. Of the remaining 53 entries, 29 do not form any hydrogen bonds with the shielded OH group as donor. In 24 entries, the shielded OH group is a hydrogen-bond donor with various acceptor atoms in the crystal structure. In none of the 90 entries is there a hydrogen bond between shielded OH groups.

## Experimental

Single crystals for the diffraction experiment were obtained by slow evaporation of a solution of 2,6-di-*tert*-butylphenol (ACROS Organics) in ethanol.

## Crystal data

$C_{14}H_{22}O$	$D_x = 1.080 \text{ Mg m}^{-3}$
$M_r = 206.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 13875 reflections
$a = 7.1369 (2) \text{ \AA}$	$\theta = 2.2\text{--}27.5^\circ$
$b = 18.6755 (6) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 9.8009 (4) \text{ \AA}$	$T = 110 (2) \text{ K}$
$\beta = 103.694 (3)^\circ$	Plate, yellow
$V = 1269.19 (8) \text{ \AA}^3$	$0.48 \times 0.48 \times 0.06 \text{ mm}$
$Z = 4$	

## Data collection

Nonius KappaCCD area-detector diffractometer	2912 independent reflections
$\varphi$ and $\omega$ scans	2409 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.78$ , $T_{\text{max}} = 1.0$	$\theta_{\text{max}} = 27.5^\circ$
27689 measured reflections	$h = -9 \rightarrow 9$
	$k = -23 \rightarrow 24$
	$l = -12 \rightarrow 12$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.4344P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
2912 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
224 parameters	
All H-atom parameters refined	

**Table 1**

Selected geometric parameters (Å, °).

O1—C1	1.3865 (12)	C3—C4	1.3913 (15)
C1—C6	1.4144 (13)	C4—C5	1.3863 (15)
C1—C2	1.4152 (14)	C5—C6	1.4003 (14)
C2—C3	1.3954 (14)		
O1—C1—C6	120.59 (9)	C6—C1—C2	122.95 (9)
O1—C1—C2	116.45 (8)		

The X-ray intensities were obtained with two different exposure times and rotation angles of 1°. 364  $\varphi$  and 414  $\omega$  scans were measured with an exposure time of 40 s per frame, and 156  $\varphi$  scans with an exposure time of 8 s per frame. All C-bound H atoms were refined freely with isotropic displacement parameters in order to demonstrate that the outcome of the free refinement of H1O is reliable.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *PEAKREF* (Schreurs, 2005); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: coordinates adapted from literature (Lazarev *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1284). Services for accessing these data are described at the back of the journal.

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