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ORIGINAL PAPER

Synthesis, Crystal Structure and DFT Study of 5-*tert*-Butyl-2-hydroxy-1,3-phenylene-bis(phenylmethanone)

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Abstract The title compound $C_{24}H_{22}O_3$, [common name: 4-*tert*-butyl-2,6-dibenzoylphenol (**bdbpH**)] (**I**), crystallizes in the orthorhombic space group *P*2(1)2(1)2(1) with unit cell parameters $a = 7.7633(3)$, $b = 11.4457(6)$ and $c = 21.5319(8)$ Å, $\alpha = \beta = \gamma = 90°$, Z = 4. In the crystal structure of **I**, the dihedral angles between the mean planes of the central phenyl ring and the two benzene rings are 71.3(1)° and 44.9(7)°. The two benzene rings are not coplanar with dihedral angles of 42.6(7)° between them. An intramolecular O–H···O hydrogen bond is observed in the asymmetric unit. The crystal packing is stabilized by weak intermolecular C–H···O interactions. Comparison of the optimized geometries by means of a density functional theory molecular orbital theoretical calculation at the B3LYP/6-31g(d) level with the corresponding crystal structures gives support to these observations. The electronic spectra of **I** and 4-methyl-2,6-dibenzoylphenol (**mdbpH**) also predicted by the B3LYP/6-31g(d) method show some blue shifts compared with their experimental data.

Keywords 4-*tert*-Butyl-2,6-dibenzoylphenol · Crystal structure · Hydrogen bonds · DFT MO calculations · Electronic absorption spectra

Introduction

Phenol-based Schiff bases are capable of forming metal complexes that have important applications in several areas of chemical research [1–3]. The title compound, 5-(*tert*-butyl)-2-hydroxy-1,3-phenylene-bis(phenylmethanone) is an important precursor, which can be used for the synthesis of Schiff bases containing NNO donors [4, 5]. The kinetically inert Co(III) compounds can be converted in reducing biological environments into the kinetically labile Co(II) derivatives and provide the means for the delivery of NNO-donor ligands, e.g. some cytotoxins, to specific locations [6, 7]. We have reported earlier the synthesis and crystal structure of biologically important diketones, 4-methyl-2,6-dibenzoylphenol (**mdbpH**) [8]. A closely related compound 2,6-dibenzoylhydroquinone has been structurally characterized by Desiraju and co workers [9]. As part of our on-going work on phenol-based Schiff base chemistry, we herein report the synthesis, spectra and crystal structure of 5-*tert*-butyl-2-hydroxy-1,3-phenylene-bis(phenylmethanone) (**bdbpH**) and density functional theory (DFT) studies of **mdbpH** and **bdbpH**. A comparison of theoretical (based on DFT MO calculations) and experimental electronic spectra are also presented.

Experimental

All the chemicals were of reagent grade and were used as received. Solvents were purified by standard methods [10] and freshly distilled prior to use.

Physical Measurements

Elemental analyses were carried out on a CARLO ERBA modal DP 200 instrument. Melting points of the compounds in capillaries are uncorrected. The electrospray ion mass spectra were recorded on a MICROMASS QUATTRO II triple quadruple mass spectrometer. Infrared spectra were

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recorded on a Shimadzu IR prestige-21 FT spectrophotometer with KBr pellets (4,000–400 cm^{-1}). Electronic spectra in 10^{-3} mol L^{-1} CH_3CN solution were obtained on a Perkin-Elmer Lambda 35 UV–Visible spectrophotometer. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) measurements were carried out on a Burker DRX-300 spectrometer in $CDCl_3$ with chemical shifts relative to $SiMe_4$.

Synthesis of 5-Methyl-2-hydroxy-1,3-phenylene-bis(phenylmethanone)(**mdbpH**)(**I**)

The synthesis and crystal structure of the precursor **mdbpH** have been published previously [8].

Synthesis of 5-*tert*-butyl-2-hydroxy-1,3-phenylene-bis(phenylmethanone)(**bdbpH**)(**I**)

4-*tert*-Butylphenol (3.75 g, 0.025 mol) was added to anhydrous $AlCl_3$ (20.0 g, 0.150 mol) dissolved in dry nitrobenzene (30.0 ml) with stirring for 10 min. In an ice bath and benzoyl chloride (10.5 g, 0.075 mol) was added over a period of 1.5 h. The stirred reaction mixture was brought to ambient temperature, stirred for 1 h and then heated to 80 °C and stirred for 8 h. The hot bath was replaced by an ice bath and an ice cooled solution of 6 M HCl (40.0 ml) was slowly added. The resulting mixture was allowed to stand overnight. The organic layer was separated and was steam distilled to remove nitrobenzene. The solid mass left in the flask was extracted with chloroform and dried over anhydrous $NaHCO_3$. The chloroform solution was treated with activated charcoal and filtered. The filtrate was allowed to crystallize. Needle shaped crystals of the title compound were collected by filtration and recrystallized from petroleum spirits with a yield of 40 %. Crystals suitable for X-ray crystallography were grown as yellow needles by slow evaporation from the chloroform solution (mp 419–421 K). Composition for $C_{24}H_{22}O_3$: found (calculated): C 80.20 (80.42); H, 6.07 (6.18).

Positive ES-MS: *m/z* 359(100, MH])$^+$. FTIR (selected, KBr, cm^{-1}): 3311 [ν(O–H)], 1,664 [ν(C=O)], 1,618 [ν(C=O/H-bonded)], 1,609 [ν(C–C)/ring]. UV–Vis (λ_{max}/nm) (ε/M^{-1} cm^{-1}) (CH_3CN): 248(4,324), 355(1,637), ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 9H, t-butyl); δ 7.48–7.65 (m, 12H, C_6H_5 and C_6H_2); δ 12.16 (s,1H, OH). ^{13}C NMR ($CDCl_3$): δ 30.8 (CH_3), 33.9 (*tert*-C), 122.0, 123.9, 125.9, 126.4, 126.7, 128.4, 128.8, 129.3, 130.6, 131.7, 133.1, 135.6, 137.7 (aromatic), 160.2 (C–O/phenolate), 197.3 (C=O).

Structure Determination and Refinement

X-ray data for (**I**) was collected with an Oxford Diffraction Gemini Eos CCD area detector using *CrysAlisPro* software [11] and graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) at 173(2) K. The structure was solved by direct methods using SHELXS97 [12] and all of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97 [12]. H1 was located by a Fourier difference map and refined isotropically with O1···H1 fixed at 0.85(2) Å. All of the remaining H atoms were placed in their calculated positions and then refined using the riding model with Atom—H lengths of 0.95 Å (CH) or 0.98 Å (CH_3). Isotropic displacement parameters for these atoms were set to 1.18–1.20 (CH) or 1.50 (CH_3) times U_{eq} of the parent atom. A multi-scan absorption correction was performed using *CrysAlis* RED and all calculations including molecular graphics were performed using SHELXTL [13]. The structure was refined using the twin law (10−1)(10−1) with a BASF value of 0.14. Crystal and experimental data for (**I**) are listed in Table 1. A diagram for the molecular structure of (**I**) is shown in Fig. 1. Bond lengths and bond angles are all within expected ranges (Table 2) [14].

Computational Details

A density functional theory (DFT) geometry optimized molecular orbital calculation (WebMo Pro [15]) with the GAUSSIAN-03 program package [16] employing the B3LYP (Becke three parameter Lee–Yang–Parr exchange correlation functional, which combines the hybrid exchange functional of Becke [17] with the gradient-correlation functional of Lee, Yang and Parr [18] and the 6-31g(d) basis set [19] was performed on the title molecules. No solvent corrections were made in these calculations. Starting geometries were taken from X-ray refinement data. The geometry results in the free molecule state are, therefore, compared to those in the crystalline state. A comparison of selected bond distances and angles in the crystal to that from the DFT calculation is given in Table 2. Based on the optimized geometries and by DFT MO calculations, electronic spectra were predicted (Table 4). All calculations were performed on a Workstation PC using the default convergence criteria.

Results and Discussion

Compound (**I**) was prepared by reacting 4-*tert*-butylphenol and benzoyl chloride in the presence of anhydrous $AlCl_3$ in a 1:3:6 ratios as a yellow crystalline solid in 40 % yield (Scheme 1).

The mass spectrum of **I** exhibits the molecular ion corresponding to $[(2,6\text{-}PhCO)_2C_6H_2(4\text{-}C(CH_3)_3)(OH)]$. The IR spectrum shows absorption at 1,664 and 1,618 cm^{-1} due to the ν(C=O) and hydrogen bonded ν(C=O), respectively. Further, a broad band appearing around 3,311 cm^{-1} due to

Table 1 Crystal and experimental data for **I**

Formula	$C_{24}H_{22}O_3$
Formula weight	358.42
Crystal color, habit	Pale yellow, block
Crystal size (mm)	0.50 × 0.22 × 0.18
Crystal system	Orthorhombic
Space group, *Z*	$P2_12_12_1$, 4
Temperature/K	173(2)
a (Å)	7.7633(3)
b (Å)	11.4457(6)
c (Å)	21.5319(8)
α (°)	90
β (°)	90
γ (°)	90
Volume $Å^3$	1913.25(14)
F(000)	760
D_{calc} (g cm^{-3})	1.244
μ (mm^{-1})	0.081
Independent reflections/ Parameters	2,711/251
No. of reflections [$I > 2\sigma(I)$]/*R* int	17,587/0.0173
$2\theta_{max}$ (°) with MoKα	56.56
Index ranges	$-10 \le h \le 10$, $-15 \le k \le 14$, $-28 \le l \le 28$
R, R_w [$I > 2\sigma$ (I)]	0.0390, 0.1131
Goodness-of-fit on F^2	1.133
$(\Delta\rho)_{max/min}$/e $Å^{-3}$	0.237/−0.170
Measurement	Oxford Diffraction Gemini Eos CCD area detector
Program system	*CrysAlis Pro*
Structure determination	SHELXS97
Refinement	Full-matrix least-squares on F^2 (SHELXL97)

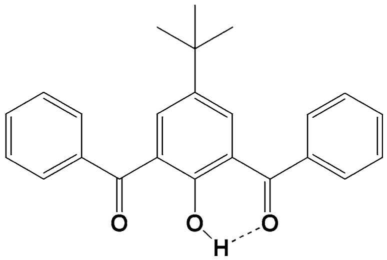


Fig. 1 $C_{24}H_{22}O_3$ (**I**)

ν(O–H) strongly suggests the presence of intra-molecular hydrogen bonding between the phenolic hydrogen and benzoyl oxygen. This is confirmed by the X-ray structure determination.

The ^{1}H NMR spectrum of **I** shows a significant downfield shift of the phenolic OH (δ 12.16 ppm) due to intramolecular hydrogen bonding between the benzoyl oxygen and the phenolic OH. The aromatic protons and the aliphatic –$C(CH_3)_3$ protons are observed as multiplets in the 7.48–7.65 ppm region and as singlet at 1.27 ppm, respectively.

In the ^{13}C NMR spectrum of compound **I**, signals at δ 197.3 (C7, C14) and 160.2 (C1) are due to the >C=O (benzoyl) and >C–O (phenolic) carbons, respectively. The aromatic carbons appear in the 122.0–137.7 ppm region. The tertiary carbon and methyl carbon in the butyl group is observed at 33.9 and 30.8 ppm, respectively. Thus, the ^{13}C NMR data corroborate well with ^{1}H NMR findings.

X-ray Crystal Structure of I

In the title compound, $C_{24}H_{22}O_3$, (**I**), the molecule consists of two benzoyl groups bonded to the carbon atom at the 2,6-position of the central phenyl ring (Fig. 2). The mean plane of the central phenyl ring (C1–C6) forms dihedral angles of 44.9(7)° and 71.3(1)° with the mean planes of the benzene rings (C8–C13 and C15–C20) of the benzoyl groups, respectively. The two benzene rings are not coplanar with dihedral angles of 42.6(7)° between them. The phenolic hydrogen atom forms a hydrogen bond of length 2.557(2) Å with atom O2 of the carbonyl group, similar to that, observed in $[(PhCO)_2(4\text{-}Me)C_6H_2(OH)]$ [8] (2.585(19) Å) and in $[(PhCO)_2C_6H_2(OH)_2]$ [9] (2.566(3) Å). In **mdbpH**, the 4-methyl substituent does not participate in intermolecular hydrogen bonding, whereas in (**I**) the 4-*tert*-butyl substituent, displays weak C–H···O intermolecular interactions (Fig. 3, Table 3) similar to that seen in $[(PhCO)_2C_6H_2(OH)_2]$. The O2···C7 bond (1.239(2) Å) is slightly longer than the O3···C14 bond (1.212(2) Å) supporting the observation that the O2 atom is involved as a weak intermolecular hydrogen-bond acceptor whereas the O3 atom is not involved in intermolecular interactions, as described in this molecule (Table 3). Thus crystal packing in (**I**) is stabilized by strong O–H···O intramolecular hydrogen bonds (O(1)–H(1)···O(2)) and weak C–H···O intermolecular interactions (Fig. 3).

Optimized Geometry

DFT calculations were performed on **mdbpH** and **bdbpH** (**I**) at the B3LYP/6-31g(d) level of theory. Starting geometries were taken from X-ray refinement data. After the DFT geometry optimization calculation on **bdbpH** and **mdbpH**, the bond lengths and bond angles remained relatively the same throughout the structure (Table 2). The dihedral angles between the mean plane of the central phenyl ring and peripheral benzene rings were calculated as 47.7(1)° and

Table 2 Selected structural parameters by X-ray diffraction and theoretical calculations for **mdbpH** and **I**

Bond lengths (Å)	Exp.	Calc.	Bond angle (°)	Exp.	Calc.
$C_{21}H_{16}O_3$ (**mdbpH**)					
O(1)–C(1)	1.352(2)	1.339	O(1)–C(1)–C(6)	118.04(15)	118.59
O(2)–C(8)	1.240(2)	1.246	O(1)–C(1)–C(2)	122.32(16)	121.98
O(3)–C(15)	1.218(2)	1.246	C(6)–C(1)–C(2)	119.60(16)	119.40
C(1)–C(6)	1.393(3)	1.413	C(3)–C(2)–C(1)	118.51(16)	118.71
C(1)–C(2)	1.411(2)	1.427	C(3)–C(2)–C(8)	121.50(16)	122.37
C(2)–C(3)	1.404(2)	1.411	C(1)–C(2)–C(8)	119.97(16)	118.90
C(2)–C(8)	1.470(2)	1.475	C(4)–C(3)–C(2)	122.41(16)	122.39
C(3)–C(4)	1.382(2)	1.390	C(3)–C(4)–C(5)	117.46(17)	117.45
C(4)–C(5)	1.392(3)	1.403	C(3)–C(4)–C(7)	121.53(17)	121.76
C(4)–C(7)	1.507(3)	1.511	C(4)–C(5)–C(7)	120.98(18)	120.82
C(5)–C(6)	1.388(3)	1.394	C(6)–C(5)–C(4)	122.21(17)	122.78
C(6)–C(15)	1.505(2)	1.509	C(5)–C(6)–C(1)	119.62(16)	119.12
C(8)–C(9)	1.493(2)	1.497	C(5)–C(6)–C(15)	118.45(16)	116.94
C(9)–C(14)	1.385(3)	1.404	C(1)–C(6)–C(15)	121.83(17)	123.81
C(9)–C(10)	1.391(3)	1.404	O(2)–C(8)–C(2)	120.78(16)	120.61
C(10)–C(11)	1.380(3)	1.395	O(2)–C(8)–C(9)	118.65(16)	117.42
C(11)–C(12)	1.377(4)	1.398	C(2)–C(8)–C(9)	120.57(16)	121.98
C(12)–C(13)	1.377(4)	1.398	C(14)–C(9)–C(10)	119.62(16)	119.27
C(13)–C(14)	1.385(3)	1.392	C(14)–C(9)–C(8)	118.73(17)	117.76
C(15)–C(16)	1.479(3)	1.495	C(10)–C(9)–C(8)	121.86(17)	122.88
C(16)–C(21)	1.385(3)	1.402	C(11)–C(10)–C(9)	120.1(2)	120.25
C(16)–C(17)	1.392(3)	1.404	C(12)–C(11)–C(10)	119.9(2)	120.14
C(17)–C(18)	1.374(3)	1.392	C(11)–C(12)–C(13)	120.7(2)	119.93
C(18)–C(19)	1.387(3)	1.398	C(12)–C(13)–C(14)	119.6(2)	120.05
C(19)–C(20)	1.379(3)	1.396	C(13)–C(14)–C(9)	120.3(2)	120.43
C(20)–C(21)	1.380(3)	1.394	O(3)–C(15)–C(16)	121.19(17)	120.35
			O(3)–C(15)–C(6)	118.49(18)	120.43
			C(16)–C(15)–C(6)	120.26(16)	121.29
			C(21)–C(16)–C(17)	118.71(18)	119.27
			C(21)–C(16)–C(15)	122.52(17)	122.68
			C(17)–C(16)–C(15)	118.72(18)	117.92
			C(18)–C(17)–C(16)	120.3(2)	120.41
			C(17)–C(18)–C(19)	120.4(2)	120.01
			C(18)–C(19)–C(20)	119.9(2)	119.96
			C(19)–C(20)–C(21)	119.8(2)	120.06
			C(20)–C(21)–C(16)	120.81(19)	120.26
$C_{24}H_{22}O_3$ (**I**)					
O(1)–C(1)	1.343(2)	1.339	O(1)–C(1)–C(2)	118.28(16)	118.78
O(2)–C(7)	1.239(2)	1.246	O(1)–C(1)–C(6)	122.61(16)	122.11
O(3)–C(14)	1.212(2)	1.226	C(2)–C(1)–C(6)	119.07(16)	119.08
C(1)–C(2)	1.398(2)	1.412	C(3)–C(2)–C(1)	119.67(16)	119.13
C(1)–C(6)	1.412(2)	1.425	C(3)–C(2)–C(14)	119.36(16)	116.88
C(2)–C(3)	1.387(3)	1.394	C(1)–C(2)–C(14)	120.93(16)	123.86
C(2)–C(14)	1.511(2)	1.509	C(2)–C(3)–C(4)	122.56(16)	123.26
C(3)–C(4)	1.404(2)	1.406	C(5)–C(4)–C(3)	116.68(16)	116.53
C(4)–C(5)	1.387(2)	1.392	C(5)–C(4)–C(21)	122.67(17)	123.39
C(4)–C(21)	1.528(3)	1.539	C(3)–C(4)–C(21)	120.65(16)	120.08

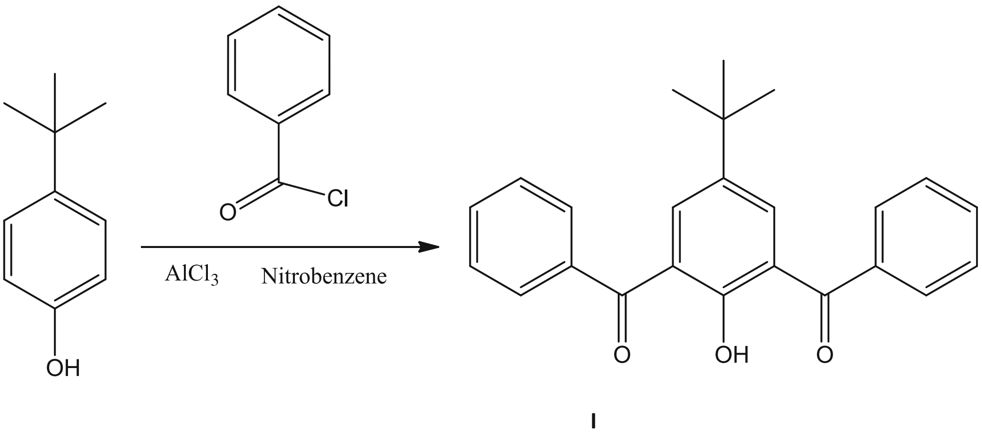
Table 2 continued

Bond lengths (Å)	Exp.	Calc.	Bond angle (°)	Exp.	Calc.
C(5)–C(6)	1.404(3)	1.412	C(4)–C(5)–C(6)	122.47(16)	122.72
C(6)–C(7)	1.476(2)	1.475	C(5)–C(6)–C(1)	119.02(16)	118.96
C(7)–C(8)	1.493(2)	1.498	C(5)–C(6)–C(7)	122.65(16)	122.16
C(8)–C(13)	1.392(2)	1.404	C(1)–C(6)–C(7)	118.32(17)	118.86
C(8)–C(9)	1.393(2)	1.404	O(2)–C(7)–C(6)	120.17(16)	120.66
C(9)–C(10)	1.382(3)	1.395	O(2)–C(7)–C(8)	118.38(16)	117.40
C(10)–C(11)	1.383(3)	1.396	C(6)–C(7)–C(8)	121.44(16)	121.93
C(11)–C(12)	1.380(3)	1.398	C(13)–C(8)–C(9)	119.46(16)	119.17
C(12)–C(13)	1.384(3)	1.392	C(13)–C(8)–C(7)	118.07(16)	117.96
C(14)–C(15)	1.490(2)	1.495	C(9)–C(8)–C(7)	122.31(15)	122.17
C(15)–C(20)	1.386(3)	1.402	C(10)–C(9)–C(8)	120.04(17)	120.76
C(15)–C(16)	1.384(3)	1.404	C(9)–C(10)–C(11)	120.05(19)	120.13
C(16)–C(17)	1.384(3)	1.392	C(12)–C(11)–C(10)	120.35(18)	119.92
C(17)–C(18)	1.383(4)	1.398	C(11)–C(12)–C(13)	119.96(17)	120.06
C(18)–C(19)	1.372(3)	1.396	C(12)–C(13)–C(8)	120.10(18)	120.42
C(19)–C(20)	1.391(3)	1.394	O(3)–C(14)–C(15)	121.11(16)	120.30
C(21)–C(24)	1.512(3)	1.510	O(3)–C(14)–C(2)	119.11(16)	118.34
C(21)–C(23)	1.539(3)	1.547	C(15)–C(14)–C(2)	119.68(15)	121.25
C(21)–C(22)	1.535(3)	1.547	C(20)–C(15)–C(16)	119.62(17)	119.27
			C(20)–C(15)–C(14)	121.62(16)	122.65
			C(16)–C(15)–C(14)	118.69(17)	117.95
			C(17)–C(16)–C(15)	119.69(19)	120.41
			C(18)–C(17)–C(16)	120.1(2)	119.96
			C(19)–C(18)–C(17)	120.54(19)	120.00
			C(18)–C(19)–C(20)	119.7(2)	120.06
			C(15)–C(20)–C(19)	120.26(18)	120.29
			C(24)–C(21)–C(4)	111.97(19)	112.15
			C(24)–C(21)–C(23)	110.1(3)	108.19
			C(4)–C(21)–C(23)	108.73(19)	109.48
			C(24)–C(21)–C(22)	107.9(2)	108.26
			C(4)–C(21)–C(22)	110.03(16)	109.42
			C(23)–C(21)–C(22)	108.1(2)	109.29

61.4(2)°, slightly twisted from that observed in the crystals at 44.97(7)° and 71.29(6)° for **bdbpH**. Similarly, the DFT values for the dihedral angles between the central phenyl ring and peripheral benzene rings for **mdbpH** were calculated as 47.0(6)° and 61.5(2)°, respectively, as compared to 54.11(6)°, 74.32(5)° in the crystal. The dihedral angle between the mean planes of the two benzene rings of the benzoyl groups were calculated as 28.13° (**bdbpH**) and 28.24° (**mdbpH**) compared with those of the single crystal values, 42.67(6)° (**bdbpH**) and 27.04(10)° (**mdbpH**), clearly suggesting that these are not coplanar and that the presence of a t-propyl group in the para position of the central phenyl ring **bdbpH** plays a significant role in C–H···O hydrogen bonding, intermolecular interactions and crystal packing when compared to that of the methyl group similarly placed in **mdbpH**.

Electronic Absorption Spectra

The theoretical DFT calculations using the B3LYP/6-31g(d) basis set for **mdbpH** and **bdbpH** show that each has two absorptions, which are consistent with the experimental data (Table 4). The first predicted band at 284 nm in **mdbpH** and 293 nm in **bdbpH** exhibit some blue shifts compared to the experimental data. However, the second predicted band at 257 nm in **mdbpH** and 259 nm in **bdbpH** display some red shift in comparison with the experimental values. For **mdbpH** and **bdbpH**, the bands in



Scheme 1 Synthesis of 5-tert-butyl-2-hydroxy-1,3-phenylenebis(phenylmethanone)

Fig. 2 Molecular structure of $C_{24}H_{22}O_3$ (**I**), with the atom labelling scheme of the asymmetric unit and 50 % probability displacement ellipsoids of non-H atoms

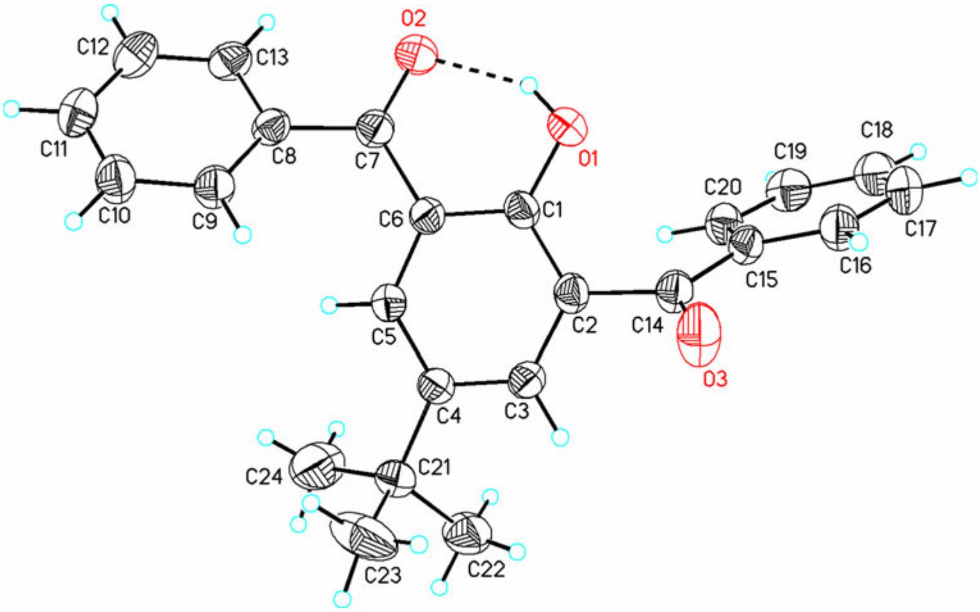
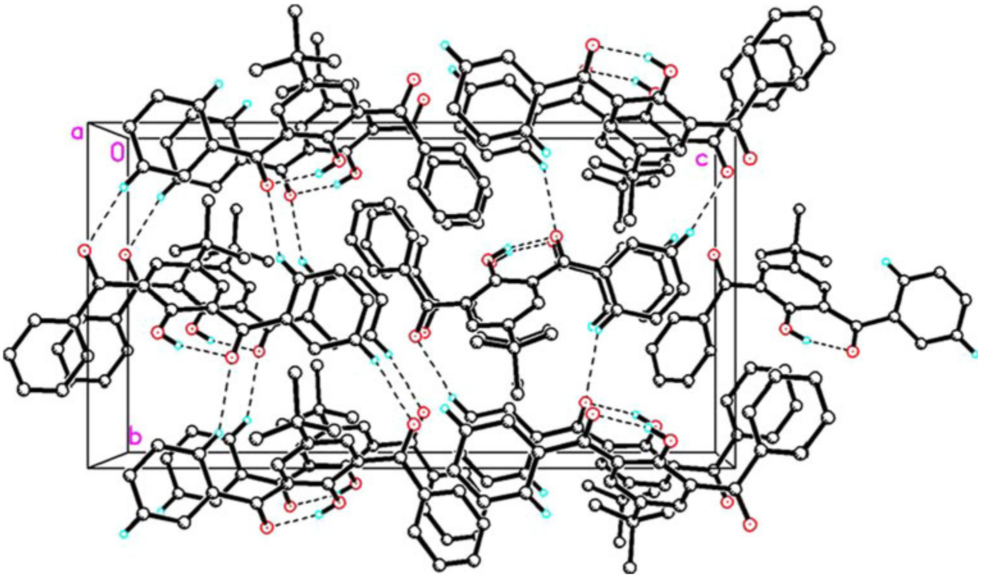
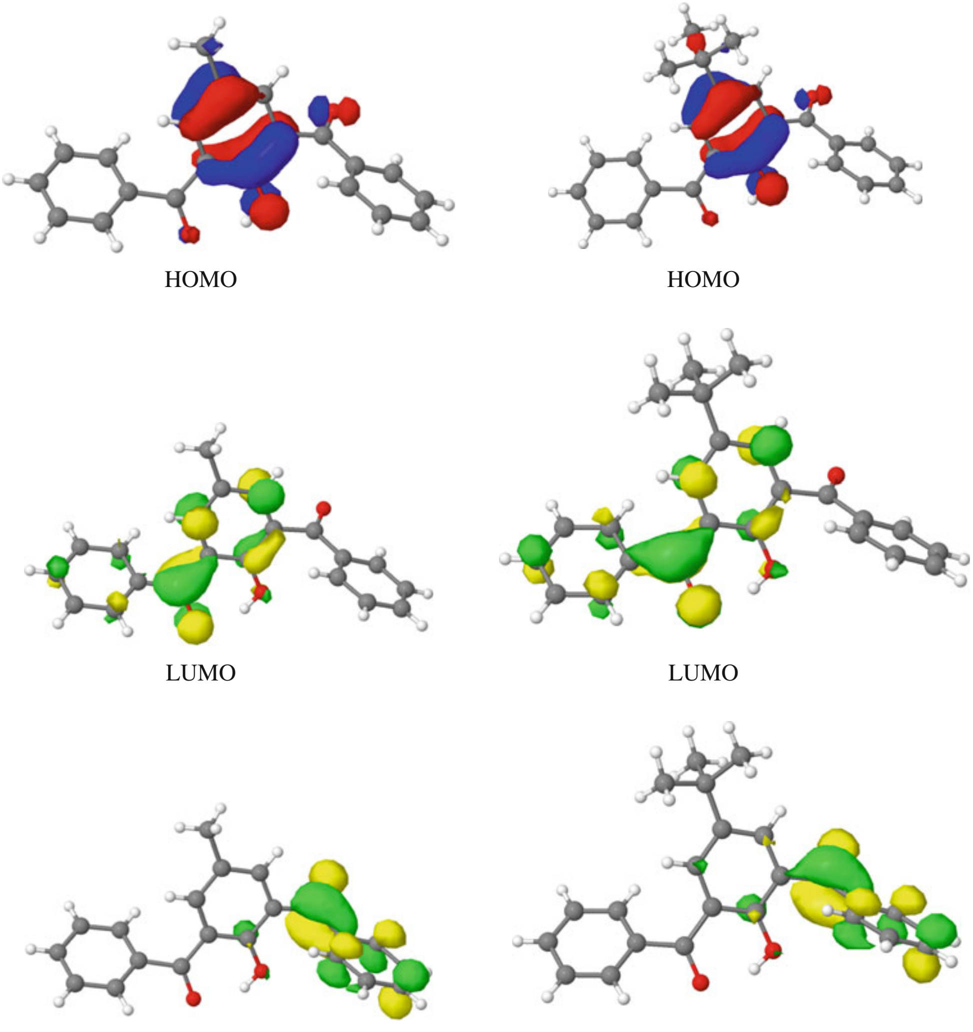


Fig. 3 Crystal packing of $C_{24}H_{22}O_3$ (**I**) viewed along the *a* axis. *Dashed lines* indicate the strong O–H···O intramolecular hydrogen bond and weak C–H···O intermolecular interactions




HOMO HOMO

LUMO LUMO

LUMO +1 LUMO +1

Fig. 4 Surfaces of the frontier molecular orbitals for **mdbpH** and **I**

Table 3 Hydrogen bond and intermolecular interactions for compound (**I**) (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1)–H(1)···O(2)	0.835(17)	1.80(2)	2.557(2)	150(3)
C(9)–H(9A)···O(2)#1	0.95	2.51	3.350(2)	147.1
C(12)–H(12A)···O(3)#2	0.95	2.48	3.407(2)	166.4

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, $y + 1/2$, $-z + 3/2$; #2 $-x + 1$, $y - 1/2$, $-z + 3/2$

the visible region (352–355 nm) are assigned to phenolato O^- to phenyl charge transfer transition while the other bands (248–257 nm) are assigned to carbonyl $\pi \rightarrow \pi^*$ transitions. The calculated oscillator strengths for the absorptions qualitatively agree with the measured molar absorptivities for these transitions. Predicted surfaces of the frontier molecular orbitals of **mdbpH** and **bdbpH** are shown in Fig. 4. For **mdbpH** and **bdbpH**, as seen from Fig. 4, in the HOMO, electronic density is distributed on the central phenyl ring containing oxygen, in the LUMO, electronic density is distributed on the carbonyl group and central phenyl ring and in the LUMO + 1, electronic density is mainly delocalized on one benzoyl group. The lowest energy transition observed in the experimental spectrum correlates with the HOMO–LUMO gap and the higher energy absorption correlates with the HOMO–LUMO + 1 transition. The calculated oscillator strengths for the absorptions qualitatively agree with the measured molar absorptivities for these transitions. It is evident, therefore, that electron transitions among the frontier

Table 4 Electronic absorption spectra by experiment and calculation at B3LYP/6-31g(d) basis set for **mdbpH** and **bdbpH**

λ (nm)	log ε (M^{-1} cm^{-1})	λ (nm)	Oscillator strength
Experimental		Calculated	
mdbpH, $C_{21}H_{16}O_3$			
352	3.24	284	0.16036
257	3.57	258	0.17688
bdbpH, $C_{24}H_{22}O_3$			
355	3.21	293	0.15547
248	3.63	259	0.17619

molecular orbitals are corrsponding to the transitions of phenolato O^- to phenyl charge transfer and $\pi \rightarrow \pi^*$ transitions.

Supplementary Material

CCDC 857168 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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