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Synthesis, crystal, spectroscopic characterizations and electrochemical properties of 1-(2-hydroxy–4,6-dimethylphenyl)ethanone

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ABSTRACT

We obtained the compound 1-(2-hydroxy-4,6-dimethylphenyl)ethanone (L) from toluene solution. The spectroscopic properties of the compound were investigated by the infrared, electronic absorption, ^{1}H- and ^{13}C-nmr and mass spectrum techniques. Structure of the (L) was investigated by the X-ray analysis. The two molecules are very similar but crystallographically independent. The first one is linked to a neighbour via two long C-H••••O hydrogen-bonds and the second molecule is paired with a symmetry equivalent by π–π stacking. Electrochemical properties of the compound were investigated by the cyclic voltammetry at different scan rates and pH media.

KEYWORDS

X-ray;
Spectroscopy;
Electrochemical;
Reversible.

INTRODUCTION

The anhydrous mononuclear tris(β-diketonate)bismuth complexes utility for chemical vapor deposition of bismuth-containing films, for fabrication of microelectronic devices such as high-integrity ferroelectric thin-film random access memory devices and bismuth-containing high-temperature superconductors. The bismuth precursors of the present invention permit the formation of bismuth-containing films for such applications, having significantly improved stoichiometry, morphology and ferroelectric/superconducting character, relative to films produced using precursors of the prior art[1].

Bismuth(III) β-diketonates are commonly used as precursor compounds in the synthesis of bismuth oxide-based materials[2–5]. For example, Bi(dpm)$_3$ (dpmH is 2,2,6,6-tetramethyl-3,5-heptanedione) has already been adopted as a source for the preparation of Bi_2O_3 films *via* CVD because of its high volatility and monomeric structure. These compounds are also very attractive precursors in the sol-gel processing of materials. In this case, the organic fraction of the starting compounds should be kept at a minimum to avoid contamination of the final product.

Aromatic compounds are important reagents in organic synthesis[6,7]. In particular, 3,5-alkylated acetophenones and methyl benzoate derivatives are key building blocks in the synthesis of retinoic acids, which have potent anti-proliferative activity in cervical cancer cells[8], HIV-protease activity inhibitors[9], tyrosine kinase inhibitors[10], HIV–1 integrase inhibitors[11], NMDA receptor antagonists[12] and a variety of other important targets[13,14].

In this study, we prepared the 1-(2-hydroxy–4,6-dimethylphenyl)ethanone (L) compound and obtained single crystals for X-ray analysis. Analytical and spectroscopic properties of the compound (L) were investigated by the instrumental methods. Electrochemical behaviour of the compound was investigated in dmf solution.

EXPERIMENTAL

General

The organic compounds $Bi(C_6H_5)_3$, acetylacetone and solvents were purchased from commercial sources and used as received, unless noted otherwise. ($[CH_3(CH_2)_3]_4NBF_4$) was obtained from Fluka. Elemental analyses (C, H, N) were performed using a LECO CHNS 932 elemental analyzer. I.r. spectra were obtained using KBr discs (4000-400 cm^{-1}) on a Shimadzu 8300 FT-IR spectrophotometer. The electronic spectra in the 200-700 nm range were obtained on a Shimadzu 160A spectrophotometer. Molar conductance of the organic compound was determined in DMF (~10^{-3} M) at room temperature using a Jenway Model 4070 conductivity meter. Mass spectrum of the compound was recorded on a LC/MS APCI AGILENT 1100 MSD spectrophotometer. ^1H- and ^{13}C- NMR spectra were recorded on a Varian XL-200 instrument. TMS was used as internal standard and DMSO-$_{d6}$ as solvent.

Cyclic voltammograms were recorded on a Iviumstat Electrochemical workstation equipped with a low current module (BAS PA–1) recorder. The electrochemical cell was equipped with a BAS glassy carbon working electrode (area 4,6 mm^2), a platinum coil auxiliary electrode and a Ag/Ag^+ (0.03 M $AgNO_3$) reference electrode filled with tetrabutylammonium tetrafluoroborat (0.1 M) in DMF solvent and adjusted to 0.00 V vs SCE. Cyclic voltammetric measurements were made at room temperature in an undivided cell (BAS model C–3 cell stand) with a platinum counter electrode and an Ag/Ag^+ (0.03 M $AgNO_3$) reference electrode (BAS). All potentials are reported with respect to Ag/Ag^+ (0.03 M $AgNO_3$). The solutions were deoxygenated by passing dry nitrogen through the solution for 30 min prior to the experiments, and during the experiments the flow was maintained over the solution. Digital simulations were performed using DigiSim 3.0 for windows (BAS, Inc.). Experimental cyclic voltammograms used for the fitting process had the background subtracted and were corrected electronically for ohmic drop.

Preparation of the 1-(2-hydroxy-4,6-dimethylphenyl)ethanone (L)

This compound was synthesized according to the known procedure[15]. The air-stable organic compound was obtained by heating liquid acetylacetone with solid triphenylbismuth and was recrystallized from toluene. **L:** ($C_{10}H_{12}O_2$), yield: 85 %, color: colourless block, m.p.: 45 °C. Elemental analyses, found (calcd. %): C, 73.19 (73.15); H, 7.40 (7.37). ^1H NMR: (DMSO-$_{d6}$ as solvent, δ in ppm): 12.68 (s, OH, H), 6.55–7.26 (m, Ar–H, 2H), 2.28 (s, O=C-CH_3, 3H), 2.15, 2.17 (s, CH_3, 6H). ^{13}C NMR: (DMSO-$_{d6}$ as solvent, δ in ppm): δ 207.19 (C=O), 165.45-118.70 (Ar–C), 35.00–23.40 (CH_3). Mass Spectrum (LC/MS APCI): m/z 164 $[M]^+$ (54 %), 150 $[C_9H_{10}O_2]^+$ (44 %), 122 $[C_7H_6O_2]^+$ (100 %), 94 $[C_6H_6O]^+$ (64 %), 66 $[C_5H_6]^+$ (35 %). UV-Vis: (λ_{max}, nm; ε_{max}, $M^{-1}cm^{-1}$), EtOH as solvent): 355 (2500), 303 (3120), 280 (1.8 x 10^{-3}). FT-IR: (KBr, cm^{-1}): 3425 ν(OH), 2964-2903 $\nu(CH_3)$, 2750-2640 ν(O-H…O), 1705 ν(C=O). $\Lambda(1 \times 10^{-3}$ M): 1.5 $\Omega^{-1}cm^2mol^{-1}$.

X-ray structure solution and refinement for the title compound (L)

X-ray crystal diffraction analyses of the title compound (L) from crystals were grown by crystallization from toluene solution for a long time. The data were collected at 150(2)K on a Bruker APEX II diffractometer. The structure was solved using direct methods and refined on F^2 using all the reflections[16]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model. Parameters for data collection and refinement are summarised in TABLE 1.

TABLE 1 : Crystal data and structure refinement for title compound.

Empirical formula	$C_{10}H_{12}O_2$	
Formula weight	164.20	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.2942(4) Å	α= 93.516(1)°
	b = 7.5327(5) Å	β= 94.507(1)°
	c = 15.9182(10) Å	γ = 99.670(1)°
Volume	857.06(9) $Å^3$	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	352	
Crystal size	0.35 x 0.13 x 0.12 mm	
Crystal description	colourless block	
Theta range for data collection	2.57 to 27.50°.	
Index ranges	-9<=h<=9, -9<=k<=9, -20<=l<=20	
Reflections collected	8463	
Independent reflections	3933 [R(int) = 0.0204]	
Completeness to theta = 26.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9896 and 0.9700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3933 / 0 / 229	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1120	
R indices (all data)	R1 = 0.0551, wR2 = 0.1214	
CCDB number	686557	

RESULTS AND DISCUSSIONS

The organic carbonyl compound 1-(2-hydroxy–4,6-dimethylphenyl)ethanone (L) was previously synthesized and obtained the single crystals. In addition, the air-stable title compound was fully characterized by IR and X-ray diffraction[15]. We obtained the compound as colourless block. We also investigated properties of the title compound using analytical, spectroscopic, electrochemical and X-ray techniques. The compound (L) is microcrystalline, non-hygroscopic, fully soluble in most common organic solvents such as EtOH, MeOH, toluene, $CHCl_3$, DMF and DMSO. The analytical data reveal that the compound has $C_{10}H_{12}O_2$ formulae (in experimental section). The compound is a very stable solid at room temperature without decomposition for a long time. The molar conductance value is the1.5 $\Omega^{-1}mol^{-1}cm^2$, indicating the non-electrolytic nature of the compound[17]. From the toluen solution, we obtained suitable single crystals for X-ray diffraction analysis.

The ^1H- and ^{13}C-NMR spectra of the 1-(2-hydroxy–4,6-dimethylphenyl)ethanone (L) were recorded using DMSO-$_{d6}$ as a solvent, and the spectral data are given in the experimental section. The ^{13}C-NMR spectrum of the carbonyl compound is given in Figure 1. The title compound (L) has an asymmetric nature. Therefore, the hydrogen atoms in the benzene ring are shown as multiplet signal. In the ^1H-NMR spectrum, the hydrogen atom of the phenolic OH group is seen at δ 12.68 ppm as a singlet. Aromatic ring protons are shown

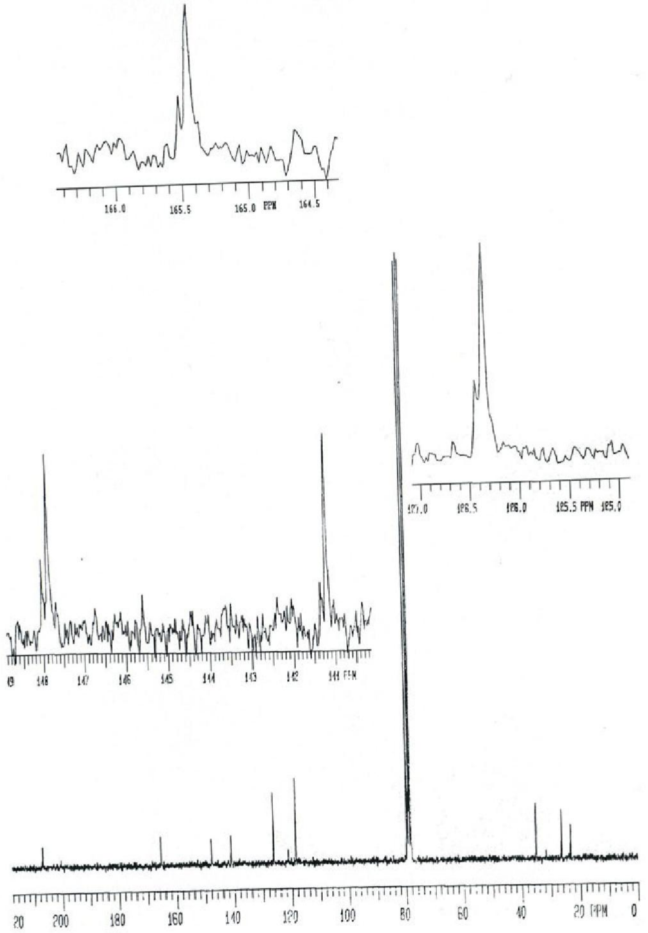


Figure 1 : ^{13}C-NMR spectrum of the title compound 1-(2-hydroxy-4,6-dimethylphenyl) ethanone (L).

in the range δ 6.55–7.26 ppm range as a multiplet. In the title compound (L), the hydrogen atoms of the acetyl group (O=C–CH_3) are observed at δ 2.28 ppm. The protons of the methyl (-CH_3) groups on the phenylene ring were seen at δ 2.15 and 2.17 ppm as a singlet.

In order to get further information about the title compound (L), the ^{13}C-NMR spectrum was investigated. In the carbonyl compound, the carbonyl carbon atom (C=O) is shown at δ 207.19 ppm. The aromatic ring C atoms were shown in the range δ 165.45–118.70 ppm. The C atoms of the aliphatic -CH_3 substitute groups were shown in the range δ 23.40–35.00 ppm.

The mass spectral studies for the title compound (L) were done using LC/MS APCI method and obtained data are given in the experimental section. The mass spectrum for the (L) compound was characterized by a peak corresponding to the carbonyl compound fragmentation. The mass spectrum of the ligand (L) shows molecular ion peak ($[M]^+$, 54 %) at *m/z* 164. Moreover, the fragmentation peaks at m/z 150 (44 %) and 122 (100 %) can be attributed to the $[C_9H_{10}O_2]^+$ and $[C_7H_6O_2]^+$ ions, respectively. The mass spectrum of the title compound (L) shows two fragmentation peaks at m/z 94 (64 %) and 66 (35 %). These peaks can be attributed to the $[C_6H_6O]^+$ and $[C_5H_6]^+$ ions, respectively.

The infrared spectral data of the title compound (L) were given in the experimental section. In the spectrum of the compound, the phenolic ν(C-OH) vibration is seen at 3425 cm^{-1}. The vibrations ν(C-H) of the methyl groups were seen in the 2964-2903 cm^{-1} range. There is both intramolecular and intermolecular H-bonding in the title compounds. This situation is confirmed by infrared spectrum of the compound. The bands in the range 2750–2640 cm^{-1} are hydrogen-bonding between the carbonyl oxygen and phenolic hydrogen atoms. The ν(C=O) vibration of the carbonyl group is shown at the 1705 cm^{-1}.

The electronic spectrum of the organic carbonyl compound 1-(2-hydroxy–4,6-dimethylphenyl)ethanone (L) was recorded in EtOH as a solvent. The spectral data are given in the experimental section. In the spectrum of the ligand, the band at the 355 nm may be assigned to the n-π* transitions. The observed bands in the 303 and 280 nm can be attributed to the π-π* and π-δ* transitions.

Experimental molecular geometry of the title compound (L)

The structure of the title compound (L) has been previously reported in 2000[15] and suitable crystals for X-ray diffraction analysis were obtained from the benzene solution. But, we obtained that suitable crystals for X-ray crystal diffraction analyses of the title compound (L) were grown by re-crystallization from toluene solution for a long time. The data were collected at 150(2)K on a Bruker APEX II diffractometer low temperature device. The structure was solved using direct methods and refined on F^2 using all the reflections[18]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon calculated positions using a riding model. Hydrogen atoms bonded to oxygen were located from difference maps and refined with a fixed thermal parameter. Parameters for data collection and refinement are summarised in TABLE 1. The title compound 1-(2-hydroxy–4,6-dimethylphenyl)ethanone (L) crystallises in triclinic *P–1* space group. The data crystal was a colorless block that had approximate dimensions; 0.35 x 0.13 x 0.12 mm. Previously reported data were collected at 293(2) K on Nicolet R3m/V diffractometer[15]. Our structural determinations on crystal data and refinement results give beter results than reported data. In the previously report, the title compound (L) has two symmetry-equivalent but essentially identical molecules in the asymmetric unit, both showing an intramolecular O••••H-O hydrogen bond. In the crystal of the title compound, $C_{10}H_{12}O_2$, the two molecules are very similar but crystallographically independent which are essentially superimposable. The first one is linked to a neighbour via two long C-H••••O-H-bonds and the second molecule is paired with a symmetry equivalent by π–π stacking. Moreover, there is a slight variation in bond lengths and angles of the two independent molecules present in the asymmetric unit. In the title compound (L), the O(1) and O(2) with O(3) and O(4) atoms are in the *trans* positions according to each other. The dihedral angle between O(1)-C(1)-C(8) (122.27(11)) is bigger than the angle O(3)-C(11)-C(18) (122.58(11)). The O(1)-H••••O(2) and O(3)-H••••O(4) interactions form a six-membered chelate rings in the crystallographically independent molecules, respectively.

A thermal ellipsoid diagram[19] of the molecule indicating atom numbering scheme with thermal ellipsoids at 50% probability is illustrated in Figure 2, intermolecular hydrogen bonding interaction between two molecules and intramolecular hydrogen bonding interactions in the crystallographically independent molecules is shown in Figures 3a-b. The crystal packing in the unit cell is in Figure 4. The packing of the molecules in a unit cell of the title compound (L) show that there is not shown the hydrogen bond the between the O(1)-H(1) ••••O(2) and O(3)-H(3) ••••O(4) atoms as superimposable. But, there is a scientific true that the weak band make the stability of the compound was strengthened. The title compound (L) has a symmetry operation #1, 1-x, 1-y, -z. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 x Ueq of the attached atom (1.5 x Ueq for methyl hydrogen atoms). There are no any solvent molecules in the crystal structure.

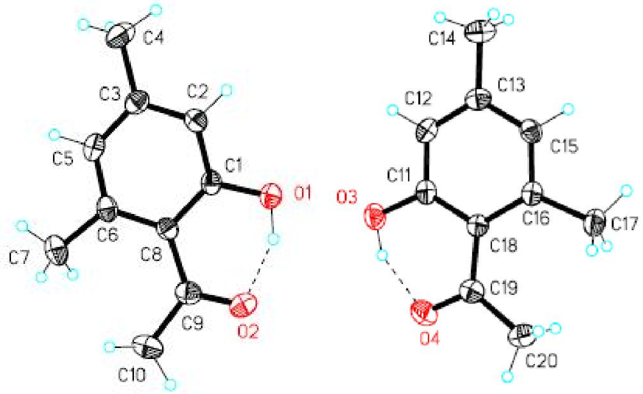
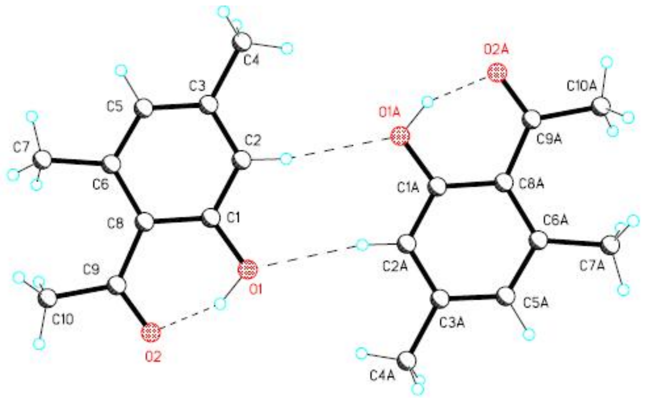
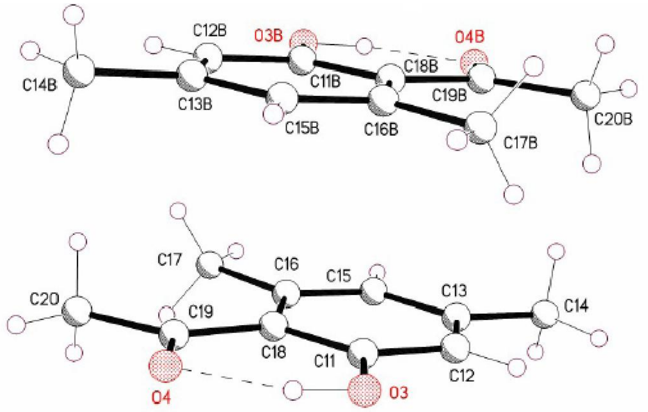


Figure 2 : ORTEP diagram of the title compound (L) with thermal ellipsoids at 50% probability.



The dashed lines depict the hydrogen bonds between the carbonyl oxygen and phenolic O-H atoms of the crystallized ligand.

Figure 3a : Intermolecular hydrogen bonds between the aromatic hydrogen and phenolic oxygen atoms of the crystallized ligand.



The dashed lines depict the hydrogen bonds between the carbonyl oxygen and phenolic O-H atoms of the crystallized ligand.

Figure 3b : Intramolecular H-bonding in superimpossible two molecules.

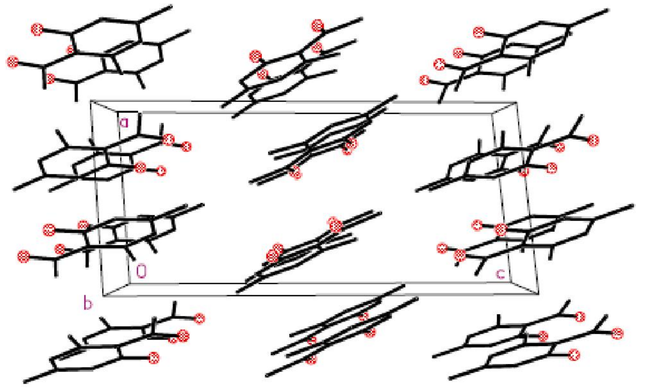


Figure 4 : Packing diagram of the ligand (L) displaying the unit cell viewed down the c axis.

Selected bond lengths and bond angles of the title compound are listed in TABLE 2. The space group is *P–1* with *a* = 7.2942(4) Å, *b* = 7.5327(5) Å, *c* = 15.9182(10) Å, α = 93.516(1)°, β = 94.507(1)°, γ = 99.670(1)° and V= 857.06(9) Å^3. According to the single crystal X-ray study, the colourless block crystallographically independent molecules have two different dihedral angles. One of them is 117.39° (11) among C(11)-C(18)-C(19) atoms, other is 125.70° (11) among C(6)-C(8)-C(9) atoms. The title compound has different bond distances. These are C(1)-O(1), C(11)-O(3), C(1)-C(2), C(11)-C(12), C(1)-C(8), C(11)-C(18), C(6)-C(7), C(16)-C(17), C(9)-O(2) and

C(19)-O(4) (1.3501(15), 1.3480(15), 1.3887(18), 1.3954(18), 1.4235(17), 1.4243(17), 1.5089(18), 1.5100(17), 1.2425(16) and 1.2358(16)), respectively. On the other hand, there are differences among the bond angles of the atoms of the same molecules. Six-membered benzene rings of the asymmetric title compound have an ideal planar conformation (apart from the methyl hydrogen atoms), and all the geometric parameters in the ring are quite normal. While the big deviations from the main plane (in the first molecule) through C2, C1, C8 and C6 are 4.75 Å, in the other molecule, the small deviations from the main plane through C11, C15, C16 and C18 are 2.11 Å. All bond lenghts and angles in the phenyl rings have normal values. The structure of the title compound does not show considerable flexibility. Exact conformation, as a balance between packing and molecular bonding forces, is complicated by charge transfer interactions which is also a balance between electronic and steric effects.

TABLE 2 : Bond lengths [Å] and angles [°] for 1-(2-hydroxy-4,6-dimethylphenyl)ethanone.

O(1)-C(1)	1.3501(15)	O(3)-C(11)	1.3480(15)
C(1)-C(2)	1.3887(18)	C(11)-C(12)	1.3954(18)
C(1)-C(8)	1.4235(17)	C(11)-C(18)	1.4243(17)
C(2)-C(3)	1.3776(18)	C(12)-C(13)	1.3766(18)
C(3)-C(5)	1.3968(19)	C(13)-C(15)	1.3972(18)
C(3)-C(4)	1.5063(18)	C(13)-C(14)	1.5064(18)
C(5)-C(6)	1.3815(19)	C(15)-C(16)	1.3823(18)
C(6)-C(8)	1.4324(17)	C(16)-C(18)	1.4280(17)
C(6)-C(7)	1.5089(18)	C(16)-C(17)	1.5100(17)
C(8)-C(9)	1.4731(18)	C(18)-C(19)	1.4788(17)
C(9)-O(2)	1.2425(16)	C(19)-O(4)	1.2358(16)
C(9)-C(10)	1.5009(19)	C(19)-C(20)	1.5013(19)

Hydrogen bonding data of the compound are given in TABLE 3. In the previously report, Armelao L. and co-workers[15] were stated each molecule exhibits an intramolecular O-H••••O hydrogen bond, with O••••O separations of 2.483(4) and 2.468(4) Å. However, we found that the molecules have both intramolecular and intermolecular hydrogen bonding interactions. These H-bond interactions are indicated in the dotted bonds in Figures 3a and b. Thus, there are four types of H-bonds. These are intramolecular hydrogen bonding interactions O(1)-H(1)••••O(2) 2.4727 (14) Å and O(3)-H(3)••••O(4) 2.4823 (15) Å. Other interactions are intermolecular hydrogen bondings C(2)-H(2)••••O(1)A 3.451 (2) Å and C(2)A-H(2)A••••O(1) 3.451 Å.

TABLE 3 : Hydrogen bonds for 1-(2-hydroxy-4,6-dimethylphenyl)ethanone [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)	0.935(17)	1.610(17)	2.4727(14)	151.6(15)
O(3)-H(3)...O(4)	0.909(17)	1.635(17)	2.4823(15)	153.8(16)
C(2)-H(2)…O(1)#1	0.950	2.53	3.451(2)	162.4

Symmetry transformations used to generate equivalent atoms: #1 1-x, 1-y, -z

These short internuclear distances are additional indications on the strength of the H-bonds involved in the lattice. Anisotropic displacement parameters (Å^2 x 10^3) for 1-(2-hydroxy-4,6-dimethylphenyl) ethanone are given in TABLE 4.

TABLE 4 : Anisotropic displacement parameters (Å^2 x 10^3) for 1-(2-hydroxy-4,6-dimethylphenyl) ethanone. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	43(1)	29(1)	25(1)	8(1)	-2(1)	0(1)
C(1)	22(1)	26(1)	25(1)	6(1)	3(1)	5(1)
C(2)	25(1)	23(1)	29(1)	1(1)	3(1)	3(1)
C(3)	26(1)	34(1)	24(1)	1(1)	4(1)	8(1)
C(4)	50(1)	50(1)	25(1)	-4(1)	3(1)	5(1)
C(5)	29(1)	35(1)	25(1)	10(1)	7(1)	9(1)
C(6)	22(1)	26(1)	32(1)	7(1)	7(1)	6(1)
C(7)	39(1)	28(1)	45(1)	12(1)	9(1)	3(1)
C(8)	19(1)	24(1)	27(1)	3(1)	2(1)	3(1)
C(9)	21(1)	31(1)	32(1)	-1(1)	0(1)	4(1)
O(2)	44(1)	43(1)	25(1)	2(1)	-5(1)	-1(1)
C(10)	36(1)	34(1)	44(1)	-7(1)	-2(1)	-1(1)
O(3)	43(1)	26(1)	34(1)	9(1)	6(1)	10(1)
C(11)	24(1)	25(1)	28(1)	6(1)	8(1)	9(1)
C(12)	26(1)	35(1)	22(1)	5(1)	4(1)	11(1)
C(13)	24(1)	32(1)	27(1)	-3(1)	4(1)	6(1)
C(14)	42(1)	40(1)	33(1)	-9(1)	-1(1)	6(1)
C(15)	28(1)	22(1)	31(1)	2(1)	6(1)	7(1)
C(16)	24(1)	26(1)	24(1)	5(1)	6(1)	9(1)
C(17)	38(1)	31(1)	28(1)	9(1)	4(1)	11(1)
C(18)	22(1)	24(1)	23(1)	2(1)	5(1)	7(1)
C(19)	25(1)	29(1)	29(1)	-1(1)	8(1)	6(1)
O(4)	51(1)	25(1)	42(1)	-1(1)	4(1)	4(1)
C(20)	34(1)	41(1)	29(1)	-4(1)	1(1)	4(1)

Cyclic voltammograms of the 1-(2-hydroxy–4,6-dimethylphenyl)ethanone (L) were run in DMF–0.1 M NBu_4BF_4 and DMSO–0.1 M NBu_4BF_4 as supporting electrolyte at 293 K. Unless otherwise stated, all potentials quoted refer to measurements run at a scan rates ('*v*') of 50, 75, 100 and 250 mV s^{-1} and against an internal ferrocene–ferrocenium standard. The results of these experiments are summarised in TABLE 5. The electrochemical curves of the title compound at 50, 75 and 100 mVs^{-1} scan rates are shown in the Figure 5. The title compound has a crystallographically independent molecule and there are two molecules in crystal nature. The cv curves of the title compound (L) at the 50, 75 and 250 mV s^{-1} scan rates in dmf solution show the reversible process ($I_{pc}: I_{pa} \cong 1.0$). The E_{pc}/E_{pa} ratios at the 50, 75 and 250 mVs^{-1} scan rates are : |-0.37| V/ 0.40 V, |-0.40| V/ |-0.40| V and |-0.22| V/ 0.25 V, respectively. The reversible process is shown in the Figure 6. At the 100 mVs^{-1} scan rate, the title ligand (L) shows the irreversible process at the all potentials. In dmso solution and at all scan rates, the ligand has the similar properties as in the dmf solutions. Oxidation-reduction peaks of the ligand in solvents changed to the lower or higher potentials by the scan rates. In the different pH media, the title compound shows an identical pattern of peaks. However, in generally, the potentials of these processes are slightly more positive in dmso than their positions in dmf.

TABLE 5 : Electrochemical data of the 1-(2-hydroxy-4,6-dimethylphenyl)ethanone.

Scan rates (mVs^{-1})	E_{pa} (V)	E_{pc} (V)	$^{i}E_{1/2}$ (mV)	$^{i}\Delta E_p$ (mV)
50	0.40, 0.33	-0.68, -0.37	15	700
75	-0.40, 0.45	-0.89, -0.40, 0.32	- 400	1290
100	0.27, -0.28	-0.43, 0.51	-	700
250	-0.36, 0.25	-0.22, 1.19	15	470

Supporting electrolyte: tetrabutylammonium tetrafluoroborat (Bu_4NBF_4) (0.1 M); concentration of the compound: 1 x 10^{-3} M. All the potentials are referenced to Ag/Ag^+ (0.03 M $AgNO_3$); where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively. $E_{1/2} = 0.5 \times (E_{pa} + E_{pc})$, $E_p = E_{pa} - E_{pc}$.

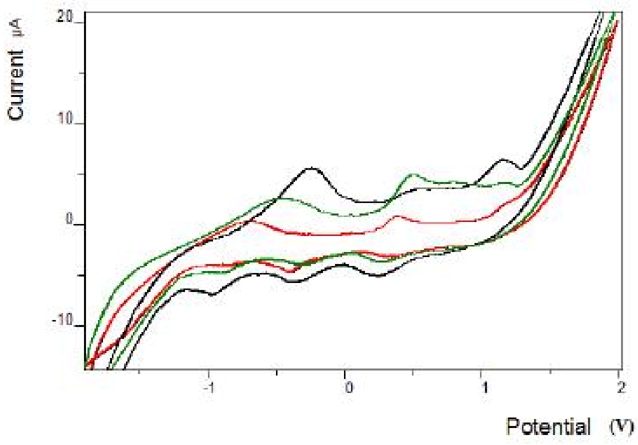


Figure 5 : Cyclic voltammograms of the title compound [L] in the presence of 0.1 M NBu_4BF_4 in dmf solutions (0.1 M) at different scan rates:—: (sr: 50 mV/s^{-1}), —: (sr: 75 mV/s^{-1}) and—: (sr: 100 mV/s^{-1}).

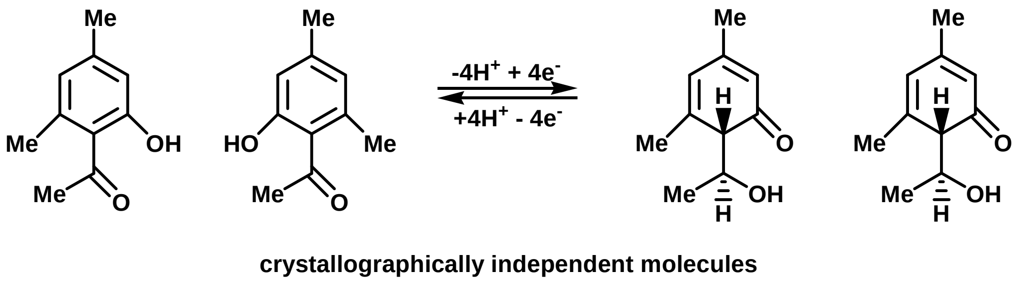


Figure 6 : Reversibl reduction-oxidation processes of the title compound (L) in dmf solution.

SUPPLEMENTARY MATERIAL

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 686557 for the reported ligand (L). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44–1223–336033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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