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# Synthesis, spectroscopy, X-ray structure and redox behaviors of 4-(*N*-*R*-salicylideneimine)-2,6-diphenylphenols

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#### Abstract

A series of sterically hindered 4-(*N*-*R*-salicylaldimine)-2,6-diphenylphenols (**X**), where R = H (**1**), 3-CH<sub>3</sub> (**2**), 5-CH<sub>3</sub> (**3**), 3-OCH<sub>3</sub> (**4**), 4-OCH<sub>3</sub> (**5**), 5-OCH<sub>3</sub> (**6**), 3-'Bu (**7**), 5-'Bu (**8**), 3,5-'Bu<sub>2</sub>(**9**) and 5,6-benzo(**10**), were synthesized and their structure as well as redox behavior studied by analytical, spectroscopic [<sup>1</sup>H, (<sup>13</sup>C) NMR, IR, UV–vis and mass spectrometry] and cyclic voltammetric (CV) techniques. Single crystal X-ray diffraction studies of **7** evidenced its existence as non-planar enol–imine tautomer structure, in which the phenol ring of the molecule is twisted around C–N single bond by 21.5(2)°. The packing structure of **7** is stabilized by C–H··· $\pi$ (Ph) and O···O and C···O intermolecular short contact interactions. The CV of **X** display rate is dependent on irreversible and quasi-reversible redox waves in the anodic and cathodic regions due to oxidation and reduction of phenolic and iminic groups, respectively. As evidenced by ESR and UV–vis study, chemical oxidation of **X** by PbO<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> in MeCN and CHCl<sub>3</sub> generates stable phenoxyl radicals [( $g \sim 2.005$  and  $\lambda \sim 450$  nm (1600–8200 M<sup>-1</sup> cm<sup>-1</sup>)]. © 2007 Elsevier B.V. All rights reserved.

Keywords: 2,6-Diphenylphenol-salicylaldimines; Redox behavior; X-ray crystal structure

# 1. Introduction

Salicylaldimines (SAs) continues to be a subject of current interest, because they are widely used as a precursor for a design of various metal complexes, in organic synthesis and flexible multifunctional ligands as building blocks for constructing novel supramolecular frameworks with interesting electronic, magnetic, optical and catalytic properties [1]. Their fundamental properties such as photo- and thermo-induced proton transfer effects suggest the possibility of using these compounds as elements for constructing the optical switches or optical memory devices [2]. Furthermore, the subtle factors such as  $\pi \cdots \pi$  and CH $\cdots \pi$  interactions appearing in SA, have also been important in a variety of molecular phenomena at physical, chemical and biological levels [1c,3,4]. The realization of the widespread occurrence of phenoxyl type tyrosyl radicals in the chemistry of living system enzymes such as ribonucleotide reductase,

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galactose oxidase and photosystem II (PSII) [5] has simulated considerable interest and research activity in the molecular systems involving readily oxidizable bulky phenolic fragments [6].

The coordination chemistry of SA ligands bearing readily oxidizable terminal bulky 2,6-<sup>t</sup>Bu<sub>2</sub>-1-hydroxyphenyl group on the imine nitrogen, 4-(N-salicylaldimine)-2,6-<sup>t</sup>Bu<sub>2</sub>phenol and their transition metal complexes, which are oxidized with PbO2 producing stable phenoxyl radical complexes are reported by one of us in 1981 [7a-c]. Although, the chemistry of bidentate SA and other ligands having peripherally bonded sterically hindered 2,6-<sup>t</sup>Bu<sub>2</sub>-1-hydroxyphenyl arms and their transition metal complexes are well studied, their 2,6-di-phenylphenol bearing SA analogous are not reported in the literature. In continuation to our systematic study of the chemistry of sterically demanded redox active SA ligands and their transition metal complexes [7,8], we present studies on synthesis, spectroscopy, structural characterization and redox behavior of a new series of a bulky SA (X) prepared on the basis of salicylaldehyde derivatives and sterically hindered 2,6-di-phenyl-p-aminophenol in which electron-donating tert-butyl groups on 2,6-di-tert-butylphenolic



R = H(1), 3-CH<sub>3</sub> (2), 5-CH<sub>3</sub>(3), 3-CH<sub>3</sub>O(4), 4-CH<sub>3</sub>O(5), 5-CH<sub>3</sub>O(6),

### Scheme 1.

residue was replaced by electron-withdrawing phenyl arms as shown in Scheme 1.

# 2. Experimental

### 2.1. Physical property measurements

The experimental procedures and instruments used for analytical, spectroscopic [<sup>1</sup>H, (<sup>13</sup>C) NMR, IR, UV–vis and ESR] and X-ray crystallographic measurements as well as chemical and electrochemical oxidations were carried out as described recently [7c,d]. The electrospray mass spectra were carried out on a Micromass Quattro LC–MS/MS in methanol solution.

### 2.2. Preparation of compounds

All the solvents were reagent grade and used without further purification. The reagent grade chemicals, 2,6-di-phenylphenol, 2,4-di-t-butylphenol, salicylaldehyde, CH<sub>3</sub>O-, CH<sub>3</sub>-, C(CH<sub>3</sub>)<sub>3</sub>substituted salicylaldehydes, 2-hydroxynaphthaldehyde and tetraethylammonium tetrafloroborat (TEATFB) were purchased from Aldrich Chemical Co. The reagents 3.5-<sup>t</sup>Bu<sub>2</sub>-salicylaldeyde [9] and 2,6-di-phenyl-*p*-aminophenol [10] were synthesized according to published procedures. 2,6-Di-phenylphenol-salicylaldimines (X) were prepared using standard procedures involving the condensation of equimolecular amounts of appropriate salicylaldehyde derivatives with *p*-amino-2,6-di-phenylphenol as described earlier [11]. The analytical and physical data for X compounds are presented in Table 1. The oxidation of X were carried out by mixing of degassed solutions of N-2,6-di-phenylphenol-

Table 1	
Physical and analytical	data for X compounds

*R*-salicylaldimines and PbO<sub>2</sub> under high vacuum  $(10^{-3} \text{ to})$  $10^{-4}$  mm of Hg) in a 25 ml vessel equipped with a 3–4 mm quartz tubes at one end for taking ESR spectra. Cyclic voltammetry was performed using a standard three-electrode configuration with a platinum working and counter electrodes and an Ag/AgCl reference electrode. Crystals of 7 ( $R=3^{-t}Bu$ ) suitable for X-ray analysis were obtained by crystallization from methanol. The m/z (%) data main peaks extracted from ESI MS spectra for some X was as follows. LC-MS/MS m/z (%) peaks for 2: 380(80)  $[M+H]^+$ , 291(15), 242(20), 154(42), 149(100), 108(35); for **3**: 380(100)  $[M]^+$ , 363(8), 272(4), 221(4), 118(20); for 4: 395(100)  $[M]^+$ , 380(7), 366(7), 352(7), 254(17), 248(17), 222(3), 137(3), 107(3); for 5: 396(100)  $[M + H]^+$ , 380(20), 248(15), 152(57), 130(20); for **6**: 396(100) [*M*+H]<sup>+</sup>, 380(6), 302(12), 262(12), 138(4); for 7: LC–MS/MS m/z (%);  $m/z = 422(100) [M]^+$ , 380(4), 221(3), 148(8), 120(8), 116(22); for 8: 422(100), 395(2), 302(2), 221(2).

XRD data are collected on a STOE IPDSII image plate detector using Mo K $\alpha$  radiation ( $\lambda = 0.71019$  Å) from a suitable single crystal mounted on a glass fiber. Crystallographic data for compound **7**, 4-(*N*-3-<sup>*I*</sup>Bu-salicylideneimine)-2,6-di-phenylphenol, are given in Table 2. Data collection: Stoe X-AREA [12]. Cell refinement: Stoe X-AREA [12]. Data reduction: Stoe X-RED [12]. The structure was solved by direct methods using SIR97 [13] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on  $F^2$  using SHELXL-97 [14]. All the hydrogen atoms of methyl and methylene were positioned geometrically and refined by a riding model with  $U_{iso}$  1.2 times that of attached atoms. Molecular drawings were obtained using ORTEP-III [15].

# 3. Results and discussion

# 3.1. UV–vis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopic characterization of X

The X SA was obtained as yellow solids in good yields and it is not air sensitive. Their structure were identified by satisfactory microanalyses, UV–vis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI MS techniques, as well as X-ray structural descriptions of 7 [R = 3-C(CH<sub>3</sub>)<sub>3</sub>] indicates its existence as the non-planar enol–imine

Compound	Yield (%)	mp (°C)	Formula	Elemental analysis, found/calcd. (%)		
				С	Н	Ν
1	92	124	C <sub>25</sub> H <sub>19</sub> NO <sub>2</sub>	83.18/3.83	5.53/5.24	3.65/3.83
2	91	110	C <sub>26</sub> H <sub>21</sub> NO <sub>2</sub>	81.68/82.25	5.48/5.57	3.56/3.68
3	89	113	C <sub>26</sub> H <sub>21</sub> NO <sub>2</sub>	81.68/82.25	5.80/5.57	3.42/3.68
4	93	164	C <sub>26</sub> H <sub>21</sub> NO <sub>3</sub>	79.91/78.92	5.56/5.35	3.13/3.54
5	91	160	C <sub>26</sub> H <sub>21</sub> NO <sub>3</sub>	77.57/78.92	5.48/5.35	3.33/3.54
6	93	177	C <sub>26</sub> H <sub>21</sub> NO <sub>3</sub>	77.50/78.92	5.58/5.35	3.21/3.54
7	89	204	C <sub>29</sub> H <sub>27</sub> NO <sub>2</sub>	81.96/82.63	6.57/6.46	2.78/3.32
8	88	135	C <sub>29</sub> H <sub>27</sub> NO <sub>2</sub>	81.06/82.63	6.59/6.46	2.88/3.32
9	78	169	C33H35NO2	81.84/82.98	7.63/7.38	2.72/2.93
0	95	210	C <sub>29</sub> H <sub>21</sub> NO <sub>2</sub>	82.58/83.29	5.31/5.09	3.44/3.37

Table 2	
Crystal data and structure refinement for compoun	d 7

Formula	C <sub>29</sub> H <sub>27</sub> NO <sub>2</sub>
Formula weight	421.52
Temperature (K)	297(2)
Wavelength (Mo Ka)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a, b, c (Å)	9.1780(8), 10.6136(9), 12.5465(11)
$\alpha, \beta, \gamma$ (°)	89.154(7), 71.657(6), 80.076(7)
Volume (Å <sup>3</sup> )	1141.70(17)
Ζ	2
Calculated density $(g cm^{-3})$	1.2262(2)
$\mu (\mathrm{mm}^{-1})$	0.076
F (0 0 0)	448.0
Crystal size (mm)	$0.18 \times 0.28 \times 0.34$
$\theta$ range (°)	1.95, 27.98
Index ranges	$-12 \le h \le 12, -13 \le k \le 13, -16 \le l \le 16$
Reflections collected	13539
Independent reflections	$5420 (R_{\text{int}} = 0.047)$
Reflections observed (> $2\sigma$ )	3474
Absorption correction	Integration
Refinement method	Full-matrix least-squares on $F^2$
Data/restrains/parameters	5420/0/305
Goodness-of-fit on $F^2$	1.030
Final <i>R</i> indices $[I > 2\sigma(I)]$	0.043
Largest difference in peak and hole $(Å^{-3})$	0.150, -0.140

tautomeric form in solid state and in non-polar and low polar solvents. The assignments of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **X** are presented in Tables 3 and 4. The m/z data extracted from electrospray mass spectroscopic (ESI MS) spectra of some **X** compounds are presented in Experimental section. ESI MS spectra of **X** scanned m/z from 500 to 100 exhibit well-resolved peaks corresponding to the parent molecular ions ( $[M]^+$  and  $[M + H]^+$ ) and cationic fragment ions due to losses of Ph, OCH<sub>3</sub>, biphenyl and other groups (see Section 2). The representative ESI MS spectrum of **5** and assignment of main cationic fragment ions peaks is presented in Fig. 1. The m/z values of the parent molecular ions are in accord agreement with the proposed formula in Scheme 1. Our preliminary examination indicates that the complexation reactivity's of **X** with Cu(II), Co(II), Ni(II), Pd(II) and Zn(II) metal ions are different from those for 2,6-<sup>t</sup>Bu<sub>2</sub>-

Table 3			
<sup>1</sup> H NMR :	spectral data c	of X compour	ld (δ ppm)

1-hydroxyphenyl bearing SA analogs. In particularly, in the complexations of **X** with Cu(II) unlike their 2,6-ditertbutylated analogs [7b,c], no any oxidative C–C coupling of uncoordinated **X** ligands were observed.

Characteristic IR absorption frequencies of **X** are given in Table 5. The strong bands observed in the region of  $1613-1618 \text{ cm}^{-1}$  and a broad absorption at ca.  $2600-2700 \text{ cm}^{-1}$ in the IR spectra of **X** are attributed to C=N and intramolecular hydrogen bonded vOH (O-H. . .N), respectively (Table 5). It is interesting that the characteristic vOH stretching of phenolic hydroxyl group except CH<sub>3</sub>O substituted **4–6** which exhibit absorptions at 3377, 3430 and 3386 cm<sup>-1</sup>, respectively, were appeared in the range of 3505–3535 cm<sup>-1</sup>. The observed lowering of vOH in **4–6** suggests the existence of the intermolecular CH<sub>3</sub>O···H–O interactions in these compounds.

The electronic spectra of **X** recorded in ethanol (Table 5) and MeCN (Table 6) are significantly different. As can be seen from Table 6 in MeCN, except **10** no absorption features at longer wavelength ( $\lambda > 380$  nm) for all SA compounds were observed. Except **10** the similar spectral patterns also were observed even in the case of higher concentrated THF solutions of SA (**X**) in the range of 260–267, 315–335 and 351–375 nm regions. The absorptions <380 nm are assigned to intraligand  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions in the enol–iminic tautomers. The low intense bands ( $\varepsilon = 102-558$  M<sup>-1</sup> cm<sup>-1</sup>) in the range of 420–467 nm region (Table 5) detected in EtOH solutions is attributed to  $n \rightarrow \pi^*$  transitions in the dipolar zwitterionic or ketoamine tautomeric structures of **X** [16].

### 3.2. Crystal structure description of 7

The molecular structures of **7**, with the atom-labeling scheme, are shown in Fig. 2, selected bond lengths and angles are given in Table 7. The molecular structure of **7** can be described as consisting of three structural fragments; *tert*-butyl- and phenyl-substituted phenol cores divided by central part, which contains C=N double bond. The central part of the molecule is characterized by pseudoaromatic six-membered chelate ring, which contains OH–C=C–C=N (phenol–imine tautomer) heterodienic moiety. In **7**, the phenol–imine tautomer is favored over the keto-amine form in the solid state. This is evident from the observed O2–C21 bond distance of 1.352(2) Å, which is consistent with an O–C single bond character in

Compound	OH/NH	CH=N	OH	OCH <sub>3</sub>	Sal.PhH	PhH (m)	CH <sub>3</sub>	$^{t}\mathrm{Bu}H(\mathrm{s})$
1	13.40	8.66	5.49	_	6.87–7.03 m	7.26-7.61	_	_
2	13.68	8.67	5.47	_	7.19-7.23, 6.83	7.42-7.61	2.31	-
3	13.13	8.65	5.48	_	7.16–7.26, 6.93 d	7.42-7.63	2.32	-
4	13.73	8.72	5.48	3.92	6.87-7.02, 7.26	7.42-7.63	_	-
5	13.83	8.59	5.45	3.84	6.48 d, 4.24 m	7.42-7.63	_	_
6	12.90	8.66	5.50	3.80	6.88, 6.97, 7.76	7.42-7.63	_	-
7	14.06	8.69	5.44	_	6.86 t, 7.20–7.21	7.35-7.62	_	1.47
8	13.15	8.70	5.41	_	7.28–7.39, 6.60 d	7.42-7.62	_	1.32
9	13.72	8.71	5.45	_	7.20, 7.21 d	7.28-7.58	_	1.32, 1.49
10	15.65	9.39, 8.11	5.56	-	8.1d, 7.22 d, 7.28 d	7.35–7.82	-	-

Table 4  $^{13}\text{C}$  NMR chemical shifts  $\delta$  (ppm) for  $\boldsymbol{X}$  in CDCl\_3

Compound	CH=N	Ar–C	$CH_3$	О <i>С</i> Н <sub>3</sub>	$C(CH_3)_3$	$C(CH_3)_3$
1	160.9	160.7, 148.5, 141.1, 136.9, 132.1, 131.9, 129.6, 129.2,	_	-	_	_
		128.9, 127.9, 122.5, 119.2, 118.9, 117.1				
2	161.0	159.3, 148.5, 141.3, 136.9, 133.8, 129.7, 129.6, 129.3,	15.6	_	-	-
		129.0, 128.1, 126.2, 122.6, 118.5				
3	160.9	158.8, 158.5, 141.5, 137.0, 133.7, 132.1, 129.6, 129.3,	20.4	-	-	_
		129.0, 128.1, 122.6, 119.0, 117.0				
4	161.0	151.2, 148.6, 148.4, 141.1, 136.3, 129.7, 129.3, 129.0,	_	56.2	-	_
		128.1, 123.6, 122.6, 119.2, 118.5, 114.5				
5	163.7	160.0, 148.2, 141.3, 137.1, 133.3, 129.6, 129.3, 128.9,	_	55.5	-	_
		128.0, 122.4, 107.1				
6	160.6	155.3, 152.2, 148.6, 141,3, 136.9, 129.7, 129.3, 129.0,	-	55.9	_	_
		128.1, 122.6, 120.1, 118.9, 117.9, 115.1				
7	161.5	160.5, 148.4, 141.2, 137.6, 137.0, 130.4, 130.1, 129.6,	-	_	34.9	29.4
		129.3, 129.0, 128.1, 122.6, 119.2, 118.3				
8	161.3	158.7, 148.4, 141.6, 141.4, 136.9, 130.3, 129.6, 129.2,	-	_	33.9	31.4
		128.9, 128.4, 127.9, 122.5, 118.5, 116.7				
9	161.8	158.11, 148.26, 141.30, 140.41, 136.99, 136.82, 129.63,	-	_	35.1, 34.1	31.5, 29.4
		129.22, 128.90, 127.91, 127.62, 126.60, 122.52, 118.36				
10	154.2	148.3, 138.7, 136.8, 136.0, 133.1, 129.9, 129.3, 129.1,	_	_	_	_
		128.2, 127.9, 127.3, 123.4, 121.8, 119.0				

the enol-imine tautomer form; in addition, the N1–C19 distance of 1.280(2) Å is in accordance to lengths of double C=N bonds, as in *N*-(*m*-hydroxyphenyl)-5-methoxysalicylaldimine  $d_{O-C} = 1.362(2)$  Å and  $d_{C=N} = 1.279(2)$  Å [17]. Salicylaldimine part of structure preserves planarity by intramolecular hydrogen bond formation, whereas the phenyl-substituted phenol ring twisted around N1–C1 single bond [torsion angles of C19–N1–C1–C6 and N1–C19–C20–C21 are 21.5(2)° and -1.3(2)°, respectively]. These torsion angles suggest delocalization of electron density between the aromatic phenols. However, the substituted phenyl and *tert*-butyl groups will probably causes the phenol moieties to rotate out conjugation with each other, thus leading to a loss of planarity. The dihedral angle of two phenols mean plane (C1/C6 and C20/C25) is 24.23(6)°. The dihedral angles between the phenol (C1/C6) and the phenyl groups (C13/18 and C7/C12) mean planes are 69.75(5)° and 46.88(6)° while that between the phenyls (C13/18 and C7/C12) mean planes is 49.62(6)°. In the chelate ring two other C–C bonds are different; C19–C20 bond distance [1.452(2) Å] is longer than C20–C21 bond distance [1.407(2) Å].



Fig. 1. Electrospray mass spectrum of a methanol solution of 5.

Table 5			
$IR (cm^{-1})$	) and electronic absorption spectral data for	X	compound

Compound	IR spectra		Electronic spectra $\lambda_{max}$ (log $\varepsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
	V <sub>CH=N</sub>	VOH	
1	1618	3532	208(4.78), 267(4.53), 350 <sup>a</sup> , 355(4.36), 440 nm (2.44)
2	1613	3505	210(4.7), 225(4.7), 268(4.6), 322(4.4), 354(4.4), 447(2.6)
3	1618	3508, 3534	210(4.7), 233(4.73), 267(4.42), 313 <sup>a</sup> , 332 <sup>a</sup> , 447 <sup>a</sup> (2.33)
4	1614	3377	209(4.7), 230(4.83), 269(4.65), 339(4.28), 453(2.73)
5	1617	3430	210(4.67), 235(4.66), 348(4.53), 419(3.78), 456(2.77)
6	1617	3386	209(4.7), 235(4.7), 348(4.5), 343(4.3), 369(4.3), 468(2.1)
7	1614	3533	230(4.72), 268(4.63), 330(4.42), 355(4.46), 447(2.07)
8	1618	3539	208(4.64), 232(4.63), 267(4.49), 358(4.29), 447(2.37)
9	1615	3535	230(4.76), 271(4.60), 336(4.38), 361(4.40), 480 <sup>a</sup>
10	1619	3524	234(4.69), 316(4.15), 396(4.19), 467(3.91)

<sup>a</sup>Shoulder.

The six-membered pseudoaromatic chelate OH–C=C–C=N ring is formed by heteronuclear intramolecular hydrogen bond O–H···N which is enhanced by delocalization of the  $\pi$ conjugated system (resonance assisted hydrogen bond, RAHB). RAHB is formed between the phenol O–H group and imine N atom [O–H···N (O1···N1: 2.575(2) Å)]. The N1···O1 distance in the intramolecular hydrogen bond is in accordance to lengths of RAHB heteronuclear intramolecular hydrogen bonds in  $\beta$ -enaminones and related heterodienes (2.5–2.6 Å) [18]. The proton is localized near the oxygen atom  $d_{O-H} = 0.96(2)$  Å. The OHN angle of 152.1(18) is typical for phenol–imine tautomer structures.

In the extended structure, there are no intermolecular hydrogen bonding and  $\pi - \pi$  stacking interactions. The crystal packing of **7** is formed via C-H··· $\pi$  and short contacts. It can be seen from Fig. 3 that the two molecules are joined by two C-H··· $\pi$ interactions, which leads to the formation of a centrosymmetric

Table 6

Electronic spectral data for some	$\mathbf{X}$ and $\mathbf{X} + ACN$	system in acetonitrile
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Compound	Solvent	Electronic spectra, $\lambda$ (nm) (log $\varepsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
1	MeCN	230, 268, 329, 356, 376(sh)
1 + ACN	MeCN	264(sh), 283(sh), 340(sh), 441
2	MeCN	232(3.71), 266(3.62), 317(3.39), 352(3.42)
<b>2</b> +CAN	MeCN	231 <sup>a</sup> , 262, 347, 450 <sup>a</sup>
3	MeCN	231(4.690), 265(4.55), 329(sh)(4.31),
		355(4.36)
3 + CAN	MeCN	250 <sup>a</sup> , 340 <sup>a</sup> , 450(3.21)
4	MeCN	229(4.83), 268(4.64), 325(4.49)
<b>4</b> +CAN	MeCN	255(sh), 345(4.03), 447(3.43)
5	MeCN	231(4.61), 267(4.43), 347(4.54)
5+CAN	MeCN	274(4.45), 361(4.19), 485 <sup>a</sup> (3.27)
6	MeCN	235(4.87), 319(4.45), 340(4.40), 365(3.27)
<b>6</b> +CAN	MeCN	232 <sup>a</sup> , 255 <sup>a</sup> , 365(4.03), 440(3.51)
7	MeCN	226, 266, 352, 380 <sup>a</sup>
7 + CAN	MeCN	271 <sup>a</sup> , 330 <sup>a</sup> , 390 <sup>a</sup> , 416 <sup>a</sup> , 480 <sup>a</sup>
8	MeCN	234 <sup>a</sup> , 266(4.54), 330(4.33), 354(3.39)
8+CAN	MeCN	254 <sup>a</sup> , 272 <sup>a</sup> , 347(4.03), 450 <sup>a</sup> (2.87)
9	MeCN	230, 268, 330,357
9+CAN	MeCN	280, 310, 490 <sup>a</sup>
10	MeCN	232(4.61), 319(4.08), 384(4.13), 438(3.65),
		459(3.58)
10 + CAN	MeCN	311(4.18), 356(3.92)

<sup>a</sup>A broad shoulder.

dimer of **7** in the crystal unit cell. For the C23–H23···A<sup>i</sup> contact, the distance between atom H23 and the centre of the phenyl ring (ring A<sup>i</sup>: C13–C18; symmetry code (i) -x, 1 - y, 1 - z) is 3.103 Å, the distance between atom H23 and the plane of ring A is 3.018 Å, and the C23–H23···A<sup>i</sup> angle is 141.42°. Dimers are assembled by short contact between the two symmetry related O1 atoms [O1···O1<sup>ii</sup>: 3.735(2) Å; symmetry code (ii) 2 - x, -y, 1 - z], forming polymeric chain in the *ab* plane. In addition there is also strong short contact between symmetry related C28 and O2 atoms [C28<sup>iii</sup>···O2<sup>ii</sup>: 3.508(2) Å; symmetry code (iii) 1 - x, 1 - y, -z; which forms centrosymmetric dimer of (I).

## 3.3. Chemical oxidation of X

One-electron oxidation of **1** with PbO<sub>2</sub> at 300 K in deoxygenated PhMe/CHCl<sub>3</sub> mixtures under vacuum leads to the formation of poorly resolved phenoxyl radical signals centered at g = 2.0045 with a line width of 5.5 G. One-electron oxidation of **9** under similar conditions immediately leads to the formation



Fig. 2. An ORTEP representation of the molecular structure of **7** shows the atom-numbering scheme.

Table 7	
Some selected bond distances (Å) and bond angles (°) for the compo	und 7

Bond distances (°)					
C1C2	1.385(2)	C9-C10	1.369(3)	C19–N1	1.280(2)
C2–C3	1.391(2)	C5-C13	1.494(2)	C21–O2	1.351(2)
C3–C4	1.402(2)	C2-H2	0.93	C26–C28	1.528(2)
C401	1.3643(2)	C8–H8	0.93	C22–C26	1.539(2)
C1-N1	1.418(2)	C28–H28A 0.96		C21–C22	1.409(19)
C3–C7	1.487(2)	C13–C14 1.378(2)		C22–C23	1.390(2)
C7–C8	1.389(2)	C14–C15	1.383(2)	C19–C20	1.450(2)
C8–C9	1.384(2)	C15-C16	1.360(3)	C20-C21	1.406(2)
Bond angles (°)					
C19-N1-C1	121.90(13)	C401H1A	109.5	C1-C2-C3	122.39(13)
O1-C4-C5	120.19(13)	C21-O2-H2A	109.5	C3C4–C5	120.95(13)
C28-C26-C29	107.55(14)	O2-C21-C20	119.74(12)	C2-C1-C6	118.46(13)
C28-C26-C27	109.66(14)	O2-C21-C22	118.66(12)	C21-C20-C19	121.70(13)
C6-C1-N1	124.62(14)	C12-C7-C8	118.03(15)	N1-C19-C20	122.18(14)
C4–C3–C7	122.62(13)	C18-C13-C14	118.10(14)	C25-C20-C21	119.04(13)

of the phenoxyl radical species displaying a well-resolved ESR spectrum (g = 2.0045) with hfsc of 1.125 G at the central part of the spectrum (Fig. 4). Both sides of this spectrum exhibits a low intense of a broad satellite lines spacing of ca. 4 G, probably, due to coupling to <sup>13</sup>C (I = 1/2) isotopes in natural abundance have been observed. We were unsuccessful to generate phenoxyl radicals from other **X** by using of PbO<sub>2</sub> as oxidizer. But our preliminary studies revealed that the above compounds could be readily oxidized by (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] (ACN) in MeCN, CHCl<sub>3</sub>, EtOH and other solvents. Recently, we demonstrated that ACN could be used as good oxidant for oxidation of some sterically demanded SA and their metal complexes [7g,8d].

The spectral changes for  $\mathbf{X}$  + ACN systems were monitored by UV–vis spectroscopy during the progress of the oxidation of **X** in solvents. As soon as ACN and **X** were soluble in MeCN the oxidation of the ligands was carried out with one equiv. molar amount of ACN. The results of these experiments show that upon mixing of equiv. molar amount of **X** SA and ACN in MeCN, their yellow color simultaneously or for 5-10 min turns to red along with the disappeared initial long wavelength absorption bands at ca. 325-380 nm of non-oxidized **X**, and a new maximum peak appears around 440–490 nm for oxidized **X** (Table 6). On standing the red color of these oxidized systems remains unchanged for ca. 2-3 in air and then gradually converted to light yellow. Note that the observed a strong absorption at ca. 430 nm detected in the spectra of the oxidized **X** compounds (Table 6) are characteristic for phenoxyl type radicals (PhO<sup>•+</sup>H, PhO<sup>•</sup>) generated by chemical or electrochemical one-electron oxidation of



Fig. 3. View of the packing in 7 along the axis shows the possible intermolecular short contact interactions  $O \cdots O$ ,  $C \cdots O$  and  $C-H \cdots \pi$  contacts (dashed lines) at 10% probability displacement ellipsoids.



Fig. 4. ESR spectrum of radical generated from **1** in toluene at 300 K. Experimental conditions: frequency, 9.52 GHz; microwave power, 5 dB; modulation amplitude, 0.8 G; gain, 630; scan range, 100 G.

PhOH fragments [6b,d]. The absorption at ca. 440–490 nm is assigned to a  $\pi \rightarrow \pi^*$  transition of the phenoxyl radical ligand, **X**<sup>•</sup>, as described in UV–vis spectra of the oxidized bulky phenol bearing ligands and their complexes, in which the existence of phenoxyl radicals were demonstrated by ESR spectroscopy [6,7e,g,8d].

We have found that some OCH<sub>3</sub> and *t*-Bu substituted ligands (6–8), when they are oxidized by ACN in CHCl<sub>3</sub>, even in the presence of atmospheric O<sub>2</sub> condition, their ESR spectra at 300 K exhibit low resolved radical signal with g-factors of 2.003–2.004 and line widths,  $\Delta$ H = 6.0–6.7 G. For other ligands under similar conditions no radical species were detected. It is interesting that in the chemical oxidation of *N*-alkyl(cycloalkyl)-3,5-<sup>*t*</sup>Bu-salicylaldimines and their complexes under above oxidative conditions, to generate uncomplexed and coordinated phenoxyl radical species which display absorption band around 720 nm [7e,8d].

### 3.4. Electrochemistry of X

The electrochemical electron transfer behavior of **X** was studied by cyclic voltammetry technique using a Pt working electrode in acetonitrile (MeCN) in the potentials ranging from -1.85 to +1.85 V versus Ag/AgCl at 293 K under N<sub>2</sub> containing Et<sub>4</sub>NBF<sub>4</sub> (0.05 M) as the background electrolyte. The main electrochemical data are given in Table 8 and some

Table 8 Cyclic voltammetric potentials (in V vs. Ag/AgCl) for some **X** SA in MeCN



$$CCH=NR^2 + DH \longrightarrow R^2CH_2-NR^2 + \overline{D}$$
 (3)  
Scheme 2.

representative voltammograms of X are presented in Fig. 5. It is interesting to note that a single quasi-irreversible reductive wave observed for 5–8 in the initial first scan with  $E_{1/2}$  at -0.96(5), -0.98(6), -0.97(7) and -0.99(8) V (Fig. 5a), is converted to another CV waves in the subsequent second and third scanning (Fig. 5b). This behavior suggests that the initially reduced species are unstable or they are involved to side irreversible chemical process on the timescale of the electrochemical experiment [19]. The anodic and cathodic redox processes for the presented X compounds are strongly dependent upon scan rate (Fig. 5e and f). The analyses of the voltammograms indicate that with the increasing of sweep rates from 0.02 to  $1.2 \,\mathrm{V \, s^{-1}}$  of the values of the peak potentials, the peak currents and the standard potential determined as  $(E_{pc} + E_{pa})/2$  are increased. They also tend to become diffusion controlled as evident from the linearity of the  $i_{pc}$  versus  $v^{1/2}$  plot passing through the origin. The  $i_{pc}/i_{pa}$  ratios are less (0.4–0.7) than unity and increases as the scan rate is increased. The CV of the OCH<sub>3</sub> and <sup>t</sup>Bu substituted **X** exhibit irreversible oxidation peak centered at ca. 0.0 V (Fig. 5b and e). The CV waves observed in the range of -1.85 to 0.0 V region are tentatively assigned to the reduction of the imine moiety of the molecule as suggested by Dmitreva et al. [20] and Scott [21] is shown in Scheme 2. The second step is chemically irreversible because of fast

protonation of the dianion (Eq. (3)) where DH is any proton donor in solution. Oxidation of the resulting monoanion is often observed at the potential of more positive than the first reduction peak [21]. The electrochemical reduction of SA involves hydrogenation of CH=N bond, leading to saturated amines [19,20]. The overall two-electron process gives rise to a single reduction wave, but for some *N*-benzylideneanilines, a wave splitting is invariably observed [19–21]. This behavior suggests that the latter waves are originated from the two-electron reduction intermediates in Scheme 2 or of their conjugate bases [20]. The CV of **X** recorded in the anodic potential range from 0.0 to 1.75 or -1.5 to +1.85 V versus Ag/AgCl exhibits various

Compound	$E_{\rm pa}^1/E_{\rm pc}^1$	$E_{1/2}^{1}$	$\Delta E$	$E_{\rm pa}^2/E_{\rm pc}^2$	$E_{1/2}^2$	$\Delta E$	$E_{\rm pa}^3/E_{\rm pc}^3$	$E_{ m pa}^{ m ir}$	$E_{\rm pc}^{\rm ir}$
2	-0.23/-0.67	-0.45	0.44	1.26/1.07	1.16	0.19	_	1.01	-0.28
3	-0.63/-1.05	-0.84	0.42	1.08/0.88	0.98	0.20	-	0.72, 1.52	0.43
4	-0.85/-1.31	-1.08	0.46	0.08/-0.02	0.03	0.10	-	1.03	-0.76
5	-1.05/-0.56	-0.81	0.49	1.67/1.44	1.56	0.23	-	1.08, 1.31	-
6	-1.04/-0.61	-0.84	0.40	1.06/0.94	1.0	0.12	-	0.9, 1.1, 1.5	0.28
7	-0.74/-1.15	-0.94	0.41	1.28/1.04	1,16	0.24	-	-0.36, 1, 16, 1.67	_
8	-0.59/-1.18	-0.89	0.59	1.29/1.16	1.23	0.13	-0.22/-0.38	0,02, 1.05	0.33
9	-0.89/-1.03	-0.96	0.14	-0.44/-0.73	-0.58	0.29	-	-	0.39
10	-1.36/-1.02	-1.19	0.34	1.39/1.08	1.24	0.31	-0.34/-0.44	0.05	-



Fig. 5. Representative CV of **X**: **6** (a) initial; (b) third scan waves; (c) **6** from -1.5 to +1.85 V range; (d) **5** from 0.0 to 1.85 V; **3** anodic waves with scan rates of 0.4 V s<sup>-1</sup>; (e) 0.02 V s<sup>-1</sup>; (f) all other CV recorded at a scan rate of 0.1 V s<sup>-1</sup> in MeCN containing [Net<sub>4</sub>][BF<sub>4</sub>] at 290 K.

quasi-reversible and irreversible oxidation process (Fig. 5c–f and Table 8). The observed I–III curves in this voltammograms were assigned to an irreversible anodic oxidation process of phenolate/phenoxyl couples. This scan rate dependent behavior appears typical of CE process. Taking into account that the investigated **X** compounds involve two different oxidasible phenolic OH and their oxidation could generate PhO<sup>•</sup>, and because that this radical is easier to oxidize than the parent phenol and undergoes a one-electron oxidation to produce the phenoxonium ion, [PhO<sup>•+</sup>] [22], the complexity of the anodic process is not surprise.

# 4. Conclusions

Α series of new redox-active bulky 4-(N-Rsalicylideneimine)-2,6-di-phenylphenols chelating compounds have been synthesised and characterized by structural and spectroscopic techniques, as well as their chemical and electrochemical electron transfer properties were studied. The presented compounds have non-planar enol-imine tautomer structure in solid state as evidenced by an X-ray crystallographic study of one of the salicylaldimines, 7. As evidenced by EPR and UV-vis studies of the chemical oxidation of the presented compounds to generate stable phenoxyl radical species. Their CV display rate dependent on irreversible and

quasi-reversible redox waves in the anodic and cathodic regions due to the oxidation and reduction of phenolic and iminic groups, respectively.

### Supplementary data

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 632165. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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