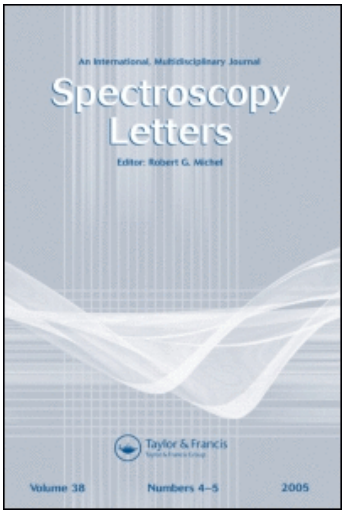


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# Synthesis, Spectroscopic Characterization and Redox Reactivity of Some New N-(2,6-Di-Tert-Butyl-L-Hydroxyphenyl) Salicylaldimines

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SPECTROSCOPY LETTERS, 32(3), 485-495 (1999)

# SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND REDOX REACTIVITY OF SOME NEW N-(2,6-DI-TERT-BUTYL-1-HYDROXYPHENYL) SALICYLALDIMINES

Key words: N- (2.6-Di-tert-butyl-1-hydroxyphenyl) Salicylaldimines, $^1$H NMR Spectrophotometry, ESR, Phenoxyl Radicals.

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## ABSTRACT

New substituted N- (2,6-Di-tert-butyl-1-hydroxyphenyl) Salicylaldimines ($L_xH$) were prepared by the condensation of various hydroxy and methoxy salicylaldehyde derivatives and 2,6-Di-tert-butyl-4-aminophenol and characterized by elemental analysis, IR, UV-Vis, $^1$H NMR spectroscopy, as well as ESR studies of the oxidation products of $L_xH$. It was found that $L_xH$, unlike analogous electron-withdrawing Cl, Br, $NO_2$ bearing derivatives, in the solid state exist both in associated and non-associated forms. UV-Vis and $^1$H NMR studies show that $L_xH$ in solutions exists both in phenolimine and ketoamine tautomer forms. In addition, alcohol solutions of $L_xH$ exhibited a new band in the region of 630-675 nm. The ESR studies of one - electron oxidation of $L_xH$, in the condition of THF, $CHCl_3$ and toluene solutions at 300 K, indicate the formation of corresponding primary or secondary phenoxyl radicals. It was found that the stability and conversion pathway of the primary phenoxyl radicals are dependent upon both kind and position of the substituents in salicylaldehyde moiety of $L_xH$. For some $L_xH$

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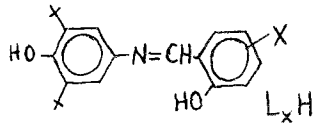
without observation of primary phenoxyl radicals, the secondary Coppinger's type radical was detected. The ESR parameters of all radical intermediates have been determined.

## INTRODUCTION

The oxidation of organic compounds containing sterically hindered phenols has been extensively investigated in the light of not only industrial benefits, but also in view of

modeling electron-transport systems for elucidation of functions and mechanisms in which radical intermediates are often involved [1,2].The oxidation processes catalyzed by transition-metal complexes include activation of substrates and / or reactants and often involve electron transfer reactions from the substrates to the metal centers [3,5]. Specific questions concerning the nature of the organic radical species, which is often the initial product of an electron transfer process [5]. The fact that sterically hindered phenol and its derivatives can undergo one or two-electron oxidation to the phenoxyl or p-quinone, respectively, offers the possibility of preparing chelates with unusual oxidation states [2,5].

As a part of our systematic work on redox-active ligands and their complexes of various bivalent transition metals [7-11], we report preparation, spectroscopic characterization and redox reactivity of some new N-(2,6-di-tert-butyl-1-hydroxyphenyl) salicylaldimines ($L_xH$) obtained by the condensation of hydroxy and methoxy substituted salicylaldehydes and 2,6-di-tert-butyl-4-aminophenol. At the same time their one-electron oxidation radical intermediates ($L^{\cdot}_xH$) were studied by ESR.




X=3-OH (I), 3-$OCH_3$(II), 4-OH(III), 4-$OCH_3$(IV), 5-$OCH_3$(V), 5-OH (VI), 4,6-di-OH(VII); $\dagger = C(CH_3)_3$

## EXPERIMENTAL

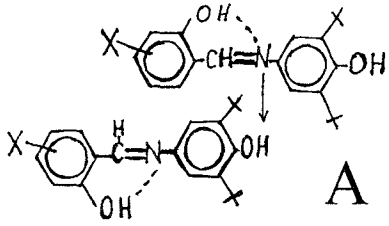
All the solvents were reagent grade and used without further purification. Salicylaldehyde derivatives used for ligand preparation were purchased from the Fluka Chemica Co. and used without further purification. 4-amino-2,6-di-tert-butylphenol was synthesized by the procedure described in [12]. Schiff bases were prepared by the condensation equimolar amounts of hydroxy and methoxy derivatives of salicylaldehyde and 4-amino-2,6-di-tert-butylphenol as described earlier [4]. The oxidation of $L_xH$ were carried out by mixing of degassed solutions of salicylaldimins and $PbO_2$ under high vacuum ($10^{-3}$-$10^{-4}$ mm Hg) in a 25-ml vessel equipped with 3-4-mm quartz tubes at one end for taking ESR spectra.

Elemental analyses were performed by the Microanalyses Laboratory of Marmara Research Center of TÜBITAK, Gebze. Infrared spectra were recorded on a MATTSON 1000 FTIR Spectrophotometer in the region 4000-400 $cm^{-1}$ using KBr disks. Electronic spectra were measured on a Shimadzu UV 160 A Spectrophotometer in the 200-800 nm region in the various

solvents. $^1H$ NMR recorded on a BRUKER AC 200 Spectrometer with TMS an internal standard in $CDCl_3$ and $C_6D_6$ solutions. The ESR spectra were recorded on a Varian E-109 C model X-band spectrometer with 100 kHz modulation. The g-values were determined by comparison with a DPPH sample of g=2.0036.

## RESULTS AND DISCUSSION

The composition and structure of the compounds synthesized were identified according to their C.H.N. analysis and IR, UV-vis , $^1H$ NMR spectroscopic studies. The more characteristic IR frequencies along with tentative assignments are given in Table 1. It can be seen from these data that the characteristic peaks for free sterically hindered hydroxyl groups ($\nu_{OH}$ =3620-3650 $cm^{-1}$) were observed only for I, III, V and VII compounds. On the other hand, except VII, all compounds exhibit the sharp-strong band in the region of 3300-3580 $cm^{-1}$. Two sharp and strong bands at 3437 and 3635 $cm^{-1}$, 3304 and 3631 $cm^{-1}$, 3443 and 3618 $cm^{-1}$ were observed for each of I, III, V salicylaldimines, respectively. At the same time, in the spectra of II, IV, VI and VII only single strong-sharp bands appeared at 3440, 3580, 3490 and 3632 $cm^{-1}$, respectively. In order to investigate the reasons, which cause the appearance of the lower frequency peaks we have measured the IR spectra of $L_1H$ and $L_2H$ in $CCl_4$ solutions in the range 3000-4000 $cm^{-1}$. Interestingly, in the solution spectrum of $L_1H$ and $L_2H$ only one peak was observed at 3620 and 3630 $cm^{-1}$, respectively. This fact unsuspectedly indicates that the lower frequency peaks observed in the solid state IR spectra of $L_XH$ may be caused by intermolecular associates such as A.




A

It is necessary to note that similar shifts of $\nu_{OH}$ bands previously were observed for 4-(N-Arylmethylideneamino) 2,6-di-tert-butylphenols in the solid state IR spectra [13].

Interestingly, the lower frequency shifts of sterically hindered hydroxyl vibrations, previously had been found in the IR spectra of N-( 2,6-di-tert-butyl-phenol)-2-hydroxy-1-Naphthaldimine obtained by using KBr pellet ($\nu_{OH}$ =3400 $cm^{-1}$ ). But in the spectrum of this compound in $CHCl_3$ solution the solid state $\nu_{OH}$~3400 $cm^{-1}$ band disappeared and a single sharp peak was observed at 3600 $cm^{-1}$ [10]. Note that in our previous work similar salicylaldimines, bearing electron withdrawing (Cl, Br, $NO_2$) groups on the salicylaldehyde moiety did not lower frequency shifts of $\nu_{OH}$ in the IR spectra [4]. Thus, we conclude that the observed lower frequency shifts in the ν

**TABLE 1**

**Melting point and analytical data for the $L_xH$ salicylaldimines.**

| X | Tm. °C | IR Spectra, $cm^{-1}$ $\nu_{C=N}$ | $\nu_{OH}$ | found (cal) % | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| 3-OH | 193 | 1649 | 3635, 3437 | 72.17 (73.90) | 8.03 (7.91) | 3.80 (4.11) |
| 3-$OCH_3$ | 123 | 1614 | 3440 | 73.44 (74.36) | 8.30 (8.16) | 3.78 (3.94) |
| 4-OH | 156 | 1620 | 3631, 3304 | 71.84 (73.90) | 7.91 (7.91) | 3.44 (4.11) |
| 4-$OCH_3$ | 151 | 1620 | 3580 | 72.37 (74.36) | 8.02 (8.16) | 3.36 (3.94) |
| 5-OH | 187 | 1618 | 3618, 3443 | 72.14 (73.90) | 8.15 (7.91) | 3.87 (4.11) |
| 5-$OCH_3$ | 134 | 1608 | 3490 | 74.12 (74.36) | 8.13 (8.16) | 2.51 (3.94) |
| 4,6-di (OH) | 225 | 1618 | 3632 | 68.99 (70.58) | 7.35 (7.56) | 3.44 (3.92) |



$_{OH}$ may be assigned to the vibrations of associated sterically hindered phenol groups of $L_xH$ in the solid state.

Electronic absorption spectra of $L_xH$ in various alcohols are shown in Table 2. In general, the band positions are almost similar to each other in alcohol solutions. All $L_xH$ in alcohol solutions show four group bands at about the 207-240, 240-280, 340-370 and 420-512 nm regions as maximum or shoulder bands (Table 2). The bands at the first two regions are attributed to $\pi \rightarrow \pi^*$ transitions in the aromatic ring and the CH=N chromophore. This assignment is on the basis of the high intensity of the bands and the solvent dependence of the band positions. The band at 340-370 nm is assigned to $n \rightarrow \pi^*$ transitions. The intensity of 420-512 nm region band, which is more sensitive to polarity of solvents than other bands. is attributed to ketoamine tautomer of $L_xH$ [14, 15]. Surprisingly, when we study the solvent dependence behavior of $L_xH$ in the high concentration of alcohol solutions we have, unexpectedly, observed the appearance of a new less intense band at ca. 630-675 nm which is not characteristic for arylsalicylaldimines. But in the case of the polar solvents, such as acetone, DMF, DMSO, dioxane, $CHCl_3$, $CH_2Cl_2$, no bands were observed in the same region. Our investigation shows that this band appears only in alcohol solutions.

It is difficult to explain the reason for the appearance of the 630-675 nm band. However it is well known that the electronic spectra of radical anions of type B, and some sterically hindered phenoxyl radicals, there are observed low intensity bands at 670 nm [ 17, 18, 19 ]. By analogy, one may suggest that the 630-675 nm band observed in the alcohol solutions of our compounds $L_xH$ probably was caused by the dipolar resonance structures that is stabilized by a polar hydrogen bonded alcohol molecule.

**TABLE 2**

**Electronic absorption spectral data of salicylaldimines I-VII.**

| X | solution | Electronic spectrum, $\lambda_{max}$ ($\varepsilon x10^{-4}$) nm |
|---|---|---|
| 3-OH | EtOH | 453 (0.95), 341 (10.9, 276 (7.5), 222 (135) |
| | MeOH | ~630 (0.0027), 451, 341, 274, 218 |
| | iso-PrOH | 457 (0.63), 348 (0.46), 277 (0.31), 208 (1.1) |
| | aseton | 456, 339 |
| 3-$OCH_3$ | EtOH | 676 (0.0025), 447 (0.81), 342 (4.23), 275 (2.77), 220 (6.82) |
| | MeOH | ~620 (0.0023), 451, 341, 274, 218 |
| | iso-PrOH | 451 (0.069), 343 (0.444), 274 (0.28), 207 (0.775) |
| 4-OH | EtOH | 664 (0.0092), ~500 (0), 416 (2.41), 348 (5.44),285 (2.47), 220 |
| | MeOH | (6.16) |
| | iso-PrOH | ~640 (0.0045), ~500 (0), 418, 348, 284, 238, 209. |
| | | ~625 (0.0032), ~500 (0), 421 (0.75), 348 (3.88), 285 (1.81), 240 |
| | | (3.01), 209 (7.83) |
| 4-$OCH_3$ | EtOH | 420 (1.44), 348 (3.684), 284 (1.8), 241 (2.92), 218 (3.55) |
| | MeOH | 419, 348, 283, 240, 212 |
| | iso-PrOH | 422, 348, 283, 243, 214 |
| 5-OH | EtOH | 677 (0.0029), 465 (0.053), 370 (7.02), 272 (4.03), 237 (10.79), 220 |
| | | (10.39) |
| | MeOH | ~469 (0), 371, 272, 239 |
| | iso-PrOH | ~620 (0) (0.0027), ~500 (0.0296), 373 (4.93), 344 (4.62), 9.39 |
| | | (8.33), 207 (15.14) |
| 5-$OCH_3$ | EtOH | 670 (0.0019), 467 (0.0545), 370 (7.65), 227 |
| | MeOH | ~630 (0), 470, 369, 272, 237, 210 |
| | iso-PrOH | ~630 (0.3 ), 471 (0.031), 371 (0.535), 237 (8.26), 209 (1.34) |
| 4,6-di-OH | EtOH | 675 (0.0242), 512 (9.7), 392 (9.69), 218 (12.4) |
| | MeOH | ~500, 399, 261, 206 |
| | iso-PrOH | ~630, ~500, 399, 209 |

The $^1H$ NMR spectra of $L_xH$ salicylaldimines show some interesting features (Table 3). The influence of solvent polarity is manifest in the $^1H$ NMR spectra of $L_xH$ recorded in both $CDCl_3$ and $C_6D_6$. The spectra of $L_1H$, $L_4H$, $L_6H$ ($CDCl_3$) and $L_1H$, $L_2H$, $L_6H$ ($C_6D_6$) show that the methyl groups of the tert-butyl substituents on 2 and 6 positions are equivalent. Other $L_xH$ methyl protons resonances occur as multipletes across the ranges δ 1.18-1.41 ($C_6D_6$) and 1.26-1.59 ppm ($CDCl_3$), which shows that the methyl groups of tert-butyl substituents of these

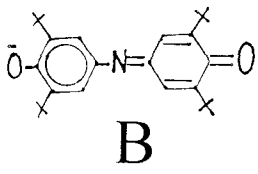
**TABLE 3**

**Effect of solvent polarity on $^1H$ NMR**

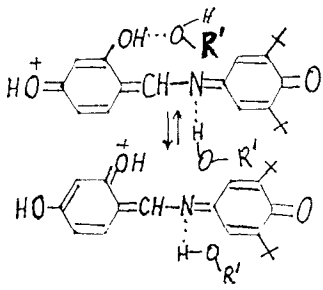
| X | δ OH/NH | δCH=N | δOH | δ $OCH_3$ | Sal.δH | Fen δH | δt-Bu | Solu tin |
|---|---|---|---|---|---|---|---|---|
| 3-OH | - | 8.23 | 4.95 | - | 7.14 | 6.55-6.60 | 1.31 | a |
| | 14.25 | 8.55 | 5.32 | - | | | 1.49 | b |
| 3-$OCH_3$ | 14.13 | 8.39 | 4.96 | 3.51 | 7.13 | 6.69 | 1 18,1.31 | a |
| | 1418 | 8.60 | 5.29 | 3.93 | 7.03-7.15 | 6.88-6.99 | 1.47 | b |
| 4-OH | 11.95 | 9.14,8.17 | 4.92 | - | 7.10-7.15 | 6.50-6.78 | 1.06-1.43 | a |
| | 11.45 | 9.65,8.40 | 5.26 | - | 7.10-7.26 | 6.46 m. | 1.26,1.47 m | b |
| 4-$OCH_3$ | 14.86 | 8.33 | 4.91 | 3.22 | 7.12-7.15 | 6.35-6.44 | 1.32 1.47-1 56 | a |
| | 14.15 | 8.48 | 5.29 | 3.84 | 7.13-7.26 | 6.89 | | b |
| 5-OH | 13.2 | 8.23 | 4.95 | - | 7.12-7.15 | 6.35-6.44 | 1.31-1.41 | a |
| | 13.15 | 8.50 | 5.28 | - | 7.13-7.26 | 6.89 | 1.42-1.59 | b |
| 5-$OCH_3$ | 13.42 | 8.31 | 4.96 | 3.31 | 7.87 m | 6.61-6.80 | 1.32 1.48 | a |
| | 13.11 | 8.55 | 5.27 | 3.81 | 7.14 m | 6.95 m | | b |

A- $C_6D_6$, b-$CDCl_3$

compounds are not equivalent. All the OH-substituted derivatives show a broad and low intensity singlet in the range δ 11.45-14.86 ppm, this is due to the exchangeable protons of hydroxyl of the salicylaldehyde and NH groups type [18]. The ring protons of salicylaldehyde and phenol moieties of $L_3H$ display multiplets across the ranges δ 6.35-7.15 ($C_6D_6$) and 6.46-7.26 ($CDCl_3$) ppm. The CH=N, $OCH_3$ and PhOH protons resonance's are manifested as a singlet in the ranges δ 8.23-8.60 , 3.22-3.84 and 4.96-5.29 PPM, correspondingly. The CH=N resonance of $L_4H$ appears as doublet centered at δ 8.17, 9.14 ($C_6D_6$) and 8.40, 9.65 ($CDCl_3$) ppm.



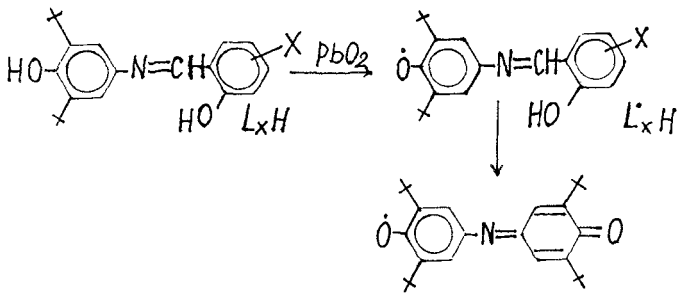
B



The one-electron oxidation of the compounds $L_xH$ with $PbO_2$ in toluene or toluene/$CHCl_3$ mixture solutions leads to formation of the stable phenoxyl ($L^{\cdot}_xH$) radicals. The ESR spectra of $L^{\cdot}_xH$ radicals, at room temperature are shown in Fig. 1-2. The hyperfine structure (hfs) of the ESR spectra for $L^{\cdot}_1H$, $L^{\cdot}_2H$, $L^{\cdot}_3H$, $L^{\cdot}_4H$, $L^{\cdot}_5H$, and $L^{\cdot}_6H$ radicals can be interpreted if it is assumed that the splitting arises from the interaction of the unpaired electron spin density of two equivalent meta protons of the phenoxyl fragment $\left(A_H^m\right)$, with the hydrogen atom of the CH in azomethin group $\left(A_H^{CH}\right)$, and with the nitrogen nucleus ($A_N$). The coupling constants and g-factors for the phenoxyl radicals are given in Table 4.

The interaction of the ligand $L_1H$ with $PbO_2$ in toluene solution leads to the formation of the stable radical (g=2.0053). The spectrum is shown in Fig. 1a and has eleven lines, some of them show additional unresolved splittings ($A_H$ = 0.85 G). This spectrum was analyzed in terms of an interaction of the unpaired electron with one nitrogen ($A_N$ =3.26 G) and two sets of protons ( $A_H^{CH} = 6.25G(H)$), and ( $A_H^m = 1.63G(2H)$).

The oxidation of $L_2H$ in toluene results in an ESR spectrum (g=2.0045) which consists of nine resolved lines with the coupling constants $A_N = A_H^m = 1$ G, $A^{CH} = 2$ G. Several low field lines of this spectrum also show additional unresolved splitting (A=0.375 G), which may have arisen by t-Butyl protons [21]. The one-electron oxidation of compounds of $L_3H$ and $L_7H$ with $PbO_2$ in toluene solution leads to the formation of the stable phenoxyl radicals $L^{\cdot}_3H$ and $L^{\cdot}_7H$. The ESR spectra of which consist of equidistant well-resolved lines with an intensity of 1:4:8:8:8:8:4:1 (Fig. 2). The hfs of these signals may be easily interpreted in terms of the interaction of an unpaired electron spin density with one nitrogen and four equivalent protons in these radicals, which have hyperfine coupling constants $A_H^m$ = 1.05$G$, $A_N$ = 2.12$G$ and $A_H^m$ = 1.06$G$, $A_N$ = 1.06$G$ for $L^{\cdot}_3H$ and $L^{\cdot}_7H$, respectively. It is not necessarily that these signals were identical in shape, yet the relative intensity of the hfs lines, the values of g-factors, and the hyperfine coupling constants agree with those that are observed for Coppinger's radical [20]. On the basis of these experimental results we suppose that the Coppinger type radical has been generated in the one-electron oxidation of $L_3H$ and $L_7H$, by the following pathways:



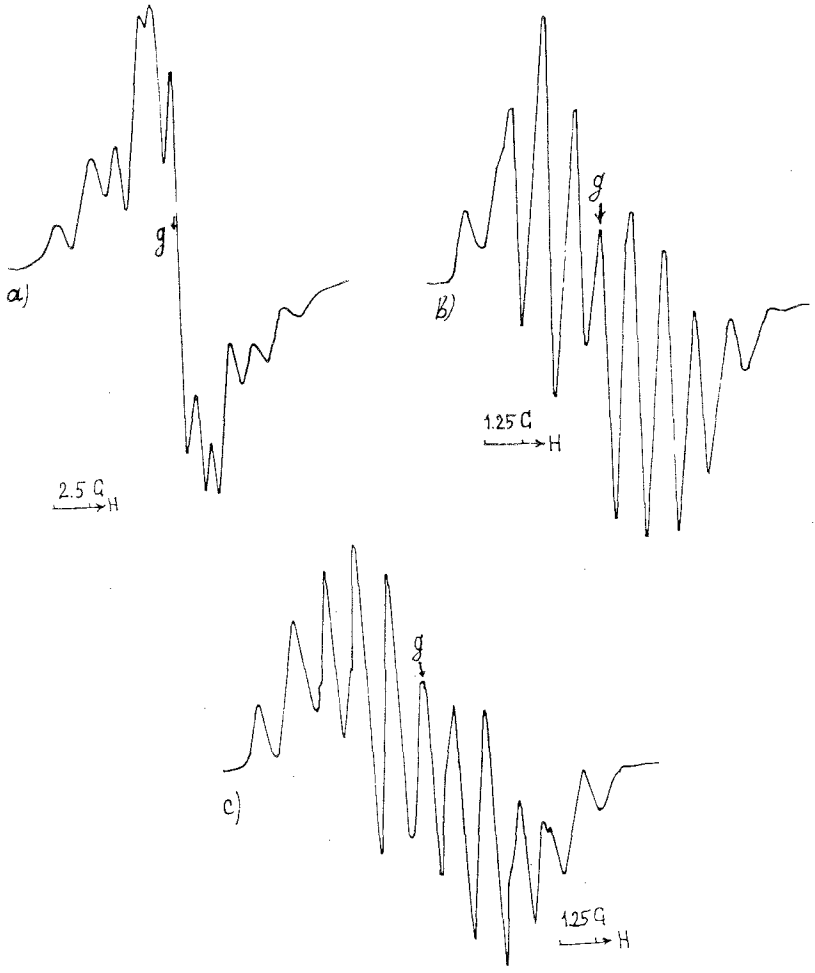



Fig. 1 ESR spectra obtained after oxidation of $L_1H$ with $PbO_2$ at 300 K in toluene solutions. $L^{\cdot}{}_1H$ (a), $L^{\cdot}{}_4H$ (b), $L^{\cdot}{}_6H$ (c).

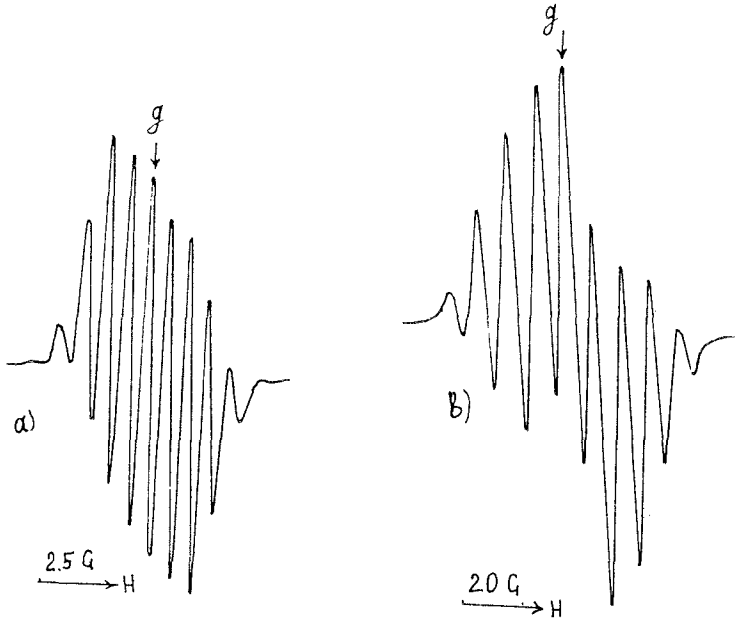



Fig. 2. ESR spectra obtained after oxidation of $L_3H$ and $L_7H$ with $PbO_2$ in toluone/CHCl3 mixture at 300 K $L'_3H$ (a), $L'_7H$ (b).

**TABLE 4**

**ESR coupling constants and g-factors of $L'_XH$**

| Compound | g- factor | $A^m{}_H$ | $\rho_H{}^m$ | $A_N$ | $A^{CH}{}_H$ | $\rho_H^{CH}$ |
|---|---|---|---|---|---|---|
| 3-OH | 2.0053 | 1.625 | 0.071 | 3.25 | 6.5 | 0.2826 |
| 3-$OCH_3$ | 2.0045 | 1.0 | 0.0435 | 1.0 | 2.0 | 0.08695 |
| 4-OH | 2.0045 | 1.05 | 0.0457 | 2.1 | | |
| 4-$OCH_3$ | 2.0042 | 1.06 | 0.046 | 2.42 | 2.12 | 0.092 |
| 5-OH | 2.0049 | 1.38 | 0.061 | 3.13 | 3.13 | 0.13608 |
| 5-$OCH_3$ | 2.0048 | 1.01 | 0.0439 | 2.02 | 4.04 | 0.17565 |
| 4,6-di-OH | 2.0044 | 1.06 | 0.046 | 2.12 | | |

The ESR spectrum that indicates the formation of Coppinger's radical has also been observed previously in the oxidation of N-(2,6-di-tert-butyl-1-hydroxyphenyl) salicyaldimine by $PbO_2$ in toluene/$CHCl_3$ solution [4].

The interaction of the salicylaldimines $L_4H$ and $L_6H$ by $PbO_2$ in the toluene/$CHCl_3$ mixture leads to the formation of the stable radicals $L'_4H$ and $L'_6H$ , respectively. The spectra of these radicals consist of nine and eleven lines with various character distribution of the spin density on the paramagnetic nucleous in these particulars (Figure 1b,c ). Thus, ESR spectra, recorded at room temperature in toluene/$CHCl_3$ mixture, indicate that in the one-electron oxidation of salicylaldimines containing sterically hindered phenol groups depending on substitution positions of X generates two type phenoxyl radicals: the primary phenoxyl radicals by one-electron oxidation of the $L_xH$ (g = 2.0042 - 2.0053, $A_H^m$ =1.000-1.025 G, $A_N$= 1.00-3.25 G, $A_H^{CH}$ = 2.0-6.5 G) and secondary Coppinger's type radical (g = 2.0044, $A_H^m$ = 1.06, $A_N$ = 2.125G. It is necessary note that the intensity of the ESR signal of $L'_xH$ unlike the Coppinger's radical is slowly decreases over period of several hours. The unstablety of $L'_xH$ in the absence of atmospheric oxygen, probably, may be explained by the dimerization or disproportion of these radicals [2,13]. It is intersting that in the spectra some $L'_xH$ also appears additional poorly resolved splitting with coupling constants about 0.375 G, which may be arises from protons of tert-butyl groups in $L'_xH$ [21].

Thus, we have observed that upon depending on the nature and positions of subtituents on salicylaldehyde moiety, salicylaldimines containing 2,6 - di - tert-butyl -1-hydoxyphenyl in the solid state may exist both in associated and non-associated phenolimine forms. It was found that alcohol solutions of $L_xH$ exhibited a new band in the region of 630-675 nm. The ESR study indicate that the oxidation of these compounds leads to the formation of primary or secondary phenoxyl radicals depending on nature and positions of substituents on salicylaldehyde.

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