

## Intermolecular Hydrogen Bonds between a Radical and a Diamagnetic Matrix: CW-ESR Investigations of 2,6-Di-*tert*-butyl-4-hydroxymethylphenol

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We propose a novel formation model of an intermolecular hydrogen bond between radicals and a diamagnetic matrix in the condensed phase. W-band and multi-frequency ESR studies revealed that the polycrystalline radical sample generated from PbO<sub>2</sub> oxidation of 2,6-di-*tert*-butyl-4-hydroxymethylphenol in toluene solution in vacuum at room temperature has an anomalously large <sup>1</sup>H-hyperfine interaction. It was concluded that this interaction is attributed to hydrogen bonding between the O• which is a paramagnetic center in the molecular structure of the radicals and the *para*-OH or the phenolic OH of the primary phenol. Although the phenol shows interesting radical chemical reactions unlike other 2,6-di-*tert*-butylphenol derivatives, the generated radical species were successfully defined by the solution ESR investigations. This may be the first ESR observation of an anomalously large hyperfine doublet structure coming from a proton on an intermolecular hydrogen bond between a radical and a diamagnetic phenol.

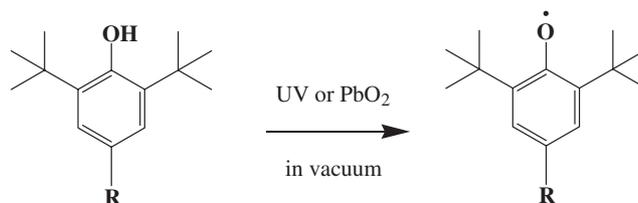
Historically, most commercial spectrometers have always operated around 10 GHz at magnetic fields around 0.3 T using electromagnets. However, over the last ten years, there has been an increasing interest in achieving the ability to make multi-frequency measurements at much larger magnetic fields using super-conducting magnets.<sup>1–14</sup> A higher-frequency operation potentially offers much greater absolute sensitivity as well as higher *g*-factor resolution. More generally, multi-frequency measurements often allow the field-dependent and field-independent terms of the spin Hamiltonian to be separated and characterized.

In *The Journal of Physical Chemistry A*, we recently reported a multi-frequency ESR study of the polycrystalline phenoxyl radical of  $\alpha$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitron in a diamagnetic matrix,<sup>15</sup> which is very useful as a spin-trapping technique. As reported, we successfully interpreted the powder-pattern ESR spectra and determined the ESR parameters (*g*-tensor and hyperfine tensor) using high-frequency ESR (Q- and W-band ESR) techniques in addition to the conventional X-band ESR. Thus, this study showed the significant potential of a multi-frequency ESR approach to powder-sample radicals, in particular samples that are difficult to acquire as single crystals, because of their high resolution with a *g*-value, confirming the electronic structure of the phenoxyl radical in terms of the ESR parameters.

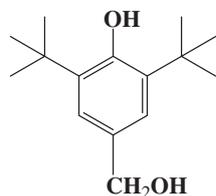
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At this point, we have systematically interpreted the powder-pattern ESR spectra of a series of the phenoxyl radical derivatives with *tert*-butyl groups at both *para* positions, including the above radical, and obtained the *g*-tensors data from X-, Q-, and W-band multi-frequency ESR investigations.<sup>16</sup> The polycrystalline samples of phenoxyl radical derivatives diluted in the corresponding phenol matrix can be prepared either by method 1; UV-irradiation of corresponding phenol matrix,<sup>16</sup> or by method 2; mixing corresponding primary phenol matrix with phenoxyl radical derivative generated from chemical oxidation (PbO<sub>2</sub> oxidation) of corresponding phenol (shown in Figure 1).<sup>15,16</sup>

However, in these studies, the X-band ESR spectrum of a polycrystalline radical sample derived from a PbO<sub>2</sub> oxidation of 2,6-di-*tert*-butyl-4-hydroxymethylphenol in toluene solution in vacuum at room temperature showed a singular pattern, that is to say, anomalously large doublet structure. The generated compound was not evidently the corresponding radical, that is 2,6-di-*tert*-butyl-4-hydroxymethylphenoxyl radical, from the splitting in the X-band spectrum. In this paper, we would like to report the results of the CW-ESR studies of the polycrystal-



**Figure 1.** Oxidation scheme of a series of 2,6-di-*tert*-butylphenol derivatives.



**Figure 2.** Structural formula of the phenol parent compound, 2,6-di-*tert*-butyl-4-hydroxymethylphenol.

line radical sample generated from  $\text{PbO}_2$  oxidation of 2,6-di-*tert*-butyl-4-hydroxymethylphenol and propose a hydrogen-bond scheme between radicals and the phenol. As seen later, the powder-pattern X-, Q-, and W-band ESR spectra are clearly showing a doublet structure as typical textbook data. It goes without saying that the hydrogen-bond model proposed in this paper can be referred in many studies related to radicals such as phenol science and bionics.

We previously reported “Pulsed ESR study of electron spin relaxation times of polycrystalline phenoxyl radical derivative in a diamagnetic crystal” in the journal, *Solid State Ionics*.<sup>17</sup> In that study, the analysis of a temperature dependence of the electron spin relaxation times from the viewpoint of the molecular motions is correct, however, we regarded a radical generated by  $\text{PbO}_2$  oxidation as the corresponding radical, since in the case of the other phenols,<sup>15,16</sup> the corresponding phenoxyl radicals can be derived by a similar way. Thus, the present paper also corresponds to the errata of the previous report. The details will be written in the Conclusion section.

### Materials and Methods

The structural formula of 2,6-di-*tert*-butyl-4-hydroxymethylphenol discussed in this paper is shown in Figure 2. The phenol sample was oxidized with lead dioxide ( $\text{PbO}_2$ ) in toluene solution under vacuum at room temperature.<sup>15–17</sup> The toluene solutions including generated radicals and including the primary phenol were mixed. We then obtained the polycrystalline radical sample diluted in a diamagnetic matrix, the primary phenol by grinding the remaining crystal after evaporation of the toluene solvent. Finally, it was sealed in a 5 mm $\phi$  ESR sample tube under vacuum.

### Experimental

X- and Q-band ESR experiments were carried out using a JEOL FE1XG spectrometer and a JEOL FE-3X ESR spectrometer, respectively. W-band ESR measurement was performed using a Bruker E600 W-band EPR spectrometer. X-band ESR experiments were conducted with the samples in the evacuated X-band tube, whereas Q- and W-band measurements were carried out with the samples in the Q- and W-band tubes not evacuated after taking the samples out of the X-band tube. In this work, the effect of air was not considered to be a problem.<sup>16</sup> Sealing the X-band tube also contributed to maintain the vacuum before high-frequency ESR measurements. The computer simulations of the ESR spectra were conducted with the assigned spin-Hamiltonian parameters using Bruker SimFonia V.1.25.

### Results and Discussion

The experimental and simulated all band powder pattern ESR spectra are shown in Figure 3. In the W-band spectra, the assignments of the *g*- and hyperfine tensors determined later are

also presented.

From the W-band spectrum, two possibilities can be considered. One is that two radical species having different orthorhombic *g*-tensors are generated during the sample preparation in the toluene solution, resulting in the W-band spectrum being a superposition of those orthorhombic spectra having no hyperfine structure. Another is that a radical species with a large  $^1\text{H}$ -hyperfine interaction is generated, resulting in the W-band spectrum showing a doublet structure like that of 2,6-di-*tert*-butylphenoxyl radical.<sup>16</sup>

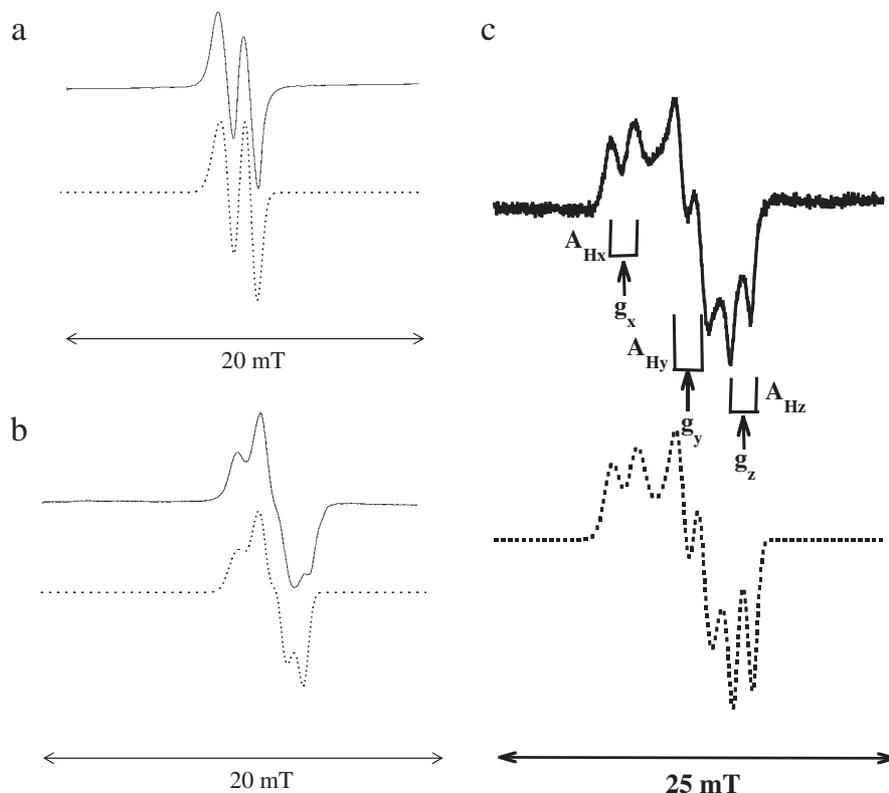
The simulated spectra at the all-band in the former case are not shown. The *g*-tensors of two species were estimated as appropriately reproducing the W-band spectrum. The simulation results may reproduce the W-band spectrum, but as the frequency becomes lower (from Q to X-band), the degree of reproducibility becomes lower. While a hyperfine structure does not change to first order on perturbation by varying the external magnetic field (band or frequency), splitting of *g*-values has a linear relationship with field strength. Consequently, the result understandably becomes a single peak on the X-band level, the peaks overlapping with each other. It may therefore be concluded that a kind of radical species was generated which has large unpaired electron-spin density on a single proton in the molecular frame. This conclusion can be reached not only through high-frequency measurement but also by carrying out multi-frequency ESR measurements. As seen in Figure 3, the simulated results successfully reproduce the experimental on the all-band of the phenoxyl radicals.<sup>15,16</sup> The ESR parameters obtained from the assignment of the W-band spectrum are summarized in Table 1. The orientation of the *g*-tensor in the radical can be defined as illustrated in a previous paper.<sup>15,16</sup>

A solution-CW-ESR measurement of a species generated from  $\text{PbO}_2$  oxidation of the phenol in toluene solution under vacuum at room temperature was also carried out. A solution spectrum generally supplies high-resolution (isotropic) data and shows electronic structure of a radical. The observed and simulated solution-CW-ESR spectra are shown in Figure 4.

From seeing the spectrum, it can be concluded that the generated species is the corresponding radical, that is, 2,6-di-*tert*-butyl-4-hydroxymethylphenoxyl radical. The assignment of the isotropic hyperfine splittings is summarized in Table 2.

From the results of this toluene solution spectrum, it is seen that the corresponding radical has notable electron spin density at the *meta*-Hs and *para*- $\alpha$ Hs and shows isotropic hyperfine structures from those protons in toluene solution, splitting to 1:2:1 by the two equivalent *para*-Hs, in addition, to 1:2:1 by the two equivalent *meta*-Hs. The proton at the *para*-OH has little electron spin density so the hyperfine structure is within the linewidth, resulting in no resolution. From the powder pattern spectra, it is thus clear that the generated radical species is not the corresponding 2,6-di-*tert*-butyl-4-hydroxymethylphenoxyl radical, because the corresponding radical does not have as large a  $^1\text{H}$ -hyperfine doublet structure.

Incidentally, in our studies it has been found that the phenol discussed in this paper shows interacting chemical reactions in solution unlike the other 2,6-di-*tert*-butylphenol derivatives, resulting in changes of the ESR spectrum. The spectrum changed by keeping in contact with  $\text{PbO}_2$ , while the spectra of



**Figure 3.** Experimental (solid lines) and simulated (dotted lines) X-, Q-, and W-band (a, b, and c) ESR spectra of the powder sample, respectively. Experimental conditions: room temperature; microwave frequency, 9.18 GHz (X-band), 36.08 GHz (Q-band), 93.743251 GHz (W-band); center field, 328 mT (X-band), 1256 mT (Q-band), 3341.65 mT (W-band); modulation amplitude, 0.1 mT (X-band), 0.2 mT (Q-band), 0.1 mT (W-band); modulation frequency, 100 kHz (X-, Q-, and W-bands); microwave power, 1 mW (X- and Q-bands), 0.1265 mW (W-band).

**Table 1.** The ESR Parameters Obtained from the W-Band Powder-Pattern ESR Spectra<sup>a)</sup>

$g_x$	$g_y$	$g_z$	$g_{ave}^b)$
2.00689	2.00423	2.00234	2.00449
$A_x$	$A_y$	$A_z$	$A_{ave}$
1.59	1.34	1.25	1.39

a) The unit of  $A$  is mT. b)  $g_{ave} = (g_x + g_y + g_z)/3$ .  $A_{ave} = (A_x + A_y + A_z)/3$ .

the other phenol derivatives do not change. Polymerization of phenoxyl radical derivatives in solution, generation of secondary radicals, and ESR spectral variations are also known.<sup>20</sup>

In our studies, it had been found that in a series of 2,6-di-*tert*-butylphenoxyl radical derivatives, 2,6-di-*tert*-butylphenoxyl radical (illustrated left in Figure 5) shows a large doublet hyperfine structure resulting from the  $^1\text{H}$  at the *para* position.<sup>16</sup> However, the spectra in the present paper are clearly different from those of 2,6-di-*tert*-butylphenoxyl radical. For example, the  $x$ -component of the hyperfine structure of the *para*-H of 2,6-di-*tert*-butylphenoxyl radical is not resolved, unlike the other components, due to the relatively small splitting within the line width. Furthermore, 2,6-di-*tert*-butylphenoxyl radical can be obtained only by UV irradiation, since in solution, the radical can instantly dimerize, becoming diamagnetic and ESR-silent.<sup>16</sup> So the generated radical discussed at this moment, indeed is not 2,6-di-*tert*-butylphenoxyl radical.

**Table 2.** The Isotropic Hyperfine Splitting Constants Obtained from the X-Band ESR Measurement of 2,6-Di-*tert*-butyl-4-hydroxymethylphenoxyl Radical in Toluene Solution<sup>a)</sup>

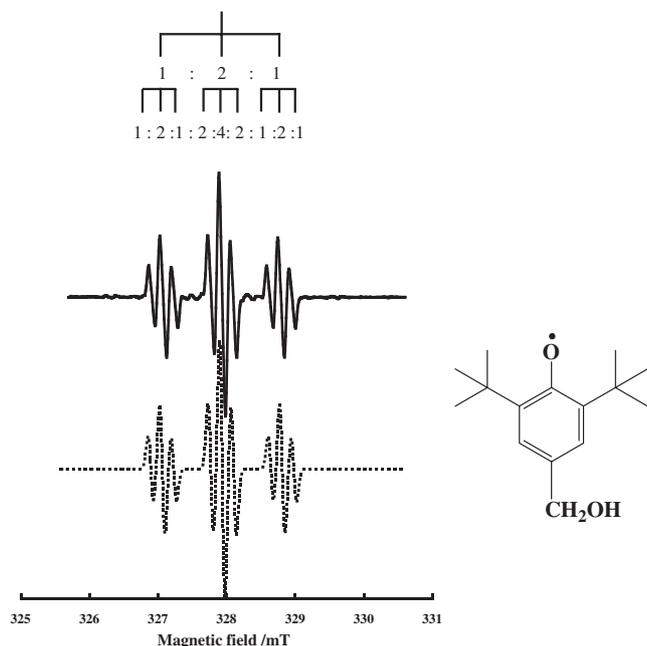
Corresponding phenoxyl radical	0.875	0.167
	(two Hs in <i>para</i> -CH <sub>2</sub> )	(two <i>meta</i> -Hs)

a) The unit of hfs is mT.

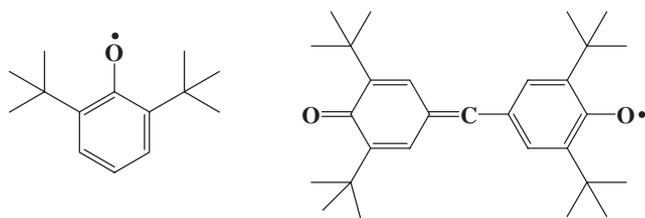
At this point, we presume that the radical species and the diamagnetic host matrix, the primary phenol forms the hydrogen bond as a kind of a stabilization effect and the anomalously large hyperfine doublet structure results from the H at the hydrogen-bond. We shall analyze the generated polycrystalline radical sample more in detail.

In order to define the generated radical species, the polycrystalline radical sample was dissolved in toluene under vacuum at room temperature. An X-band CW-ESR measurement of the toluene solution was done. The observed spectrum is shown in Figure 6.

It can be easily recognized that multi radical species exist since this experimental ESR spectrum is not symmetric at the center position. From amplitudes of the hyperfine splittings, it is found that the corresponding radical does not exist. We attempted the spectral fittings by presuming all possible combinations of multi radical species. Finally, a superposition of the ESR spectra coming from two possible radical species



**Figure 4.** Experimental (top) and simulated (bottom) X-band ESR spectra of 2,6-di-*tert*-butyl-4-hydroxymethylphenoxyl radical in toluene solution under vacuum at room temperature. The molecular structure of the radical is also illustrated. Experimental conditions: microwave frequency, 9.40 GHz; center field, 328.084 mT; sweep-width, 5.00 mT; sweep-time, 8 min; modulation amplitude, 0.1 mT; modulation frequency, 100 kHz; microwave power, 1.00 mW; amp, 100; time constant, 0.3 s.

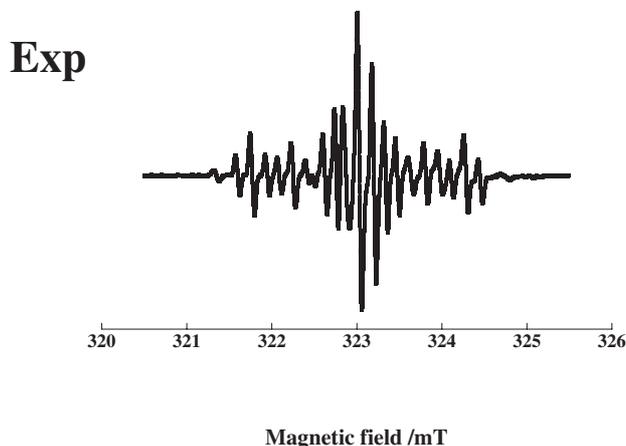


**Figure 5.** Molecular structures of 2,6-di-*tert*-butylphenoxyl radical (left) and a galvinoxyl radical (right).

successfully reproduced the observed spectrum. The results of the spectral simulation and the molecular structures of the presumed radical components are shown in Figure 7.

The isotropic hyperfine splitting constants of the two radical components obtained from the spectral simulations are summarized in Table 3. The molecular ratio of the two radical components is found to be approximately 1:1 from the comparison of the spectral amplitudes. It has been reported that the radical component II, that is 2,6-di-*tert*-butyl-4-carboxyphenoxyl radical, can be generated as a secondary radical during the chemical oxidation reactions of the primary phenol of the present work in solution, resulting in the triple line-ESR spectrum.<sup>20</sup>

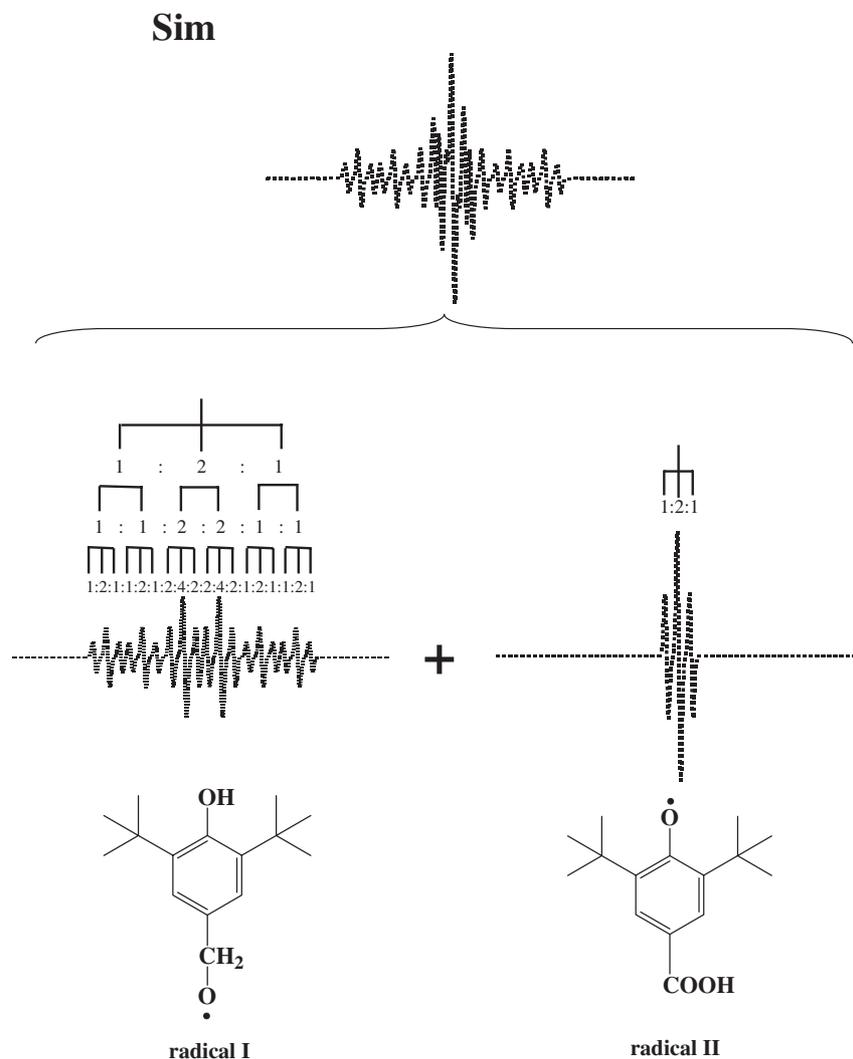
The doublet hyperfine splitting observed in the powder spectra is anomalously large. A galvinoxyl radical (illustrated right in Figure 5), which is one of the most well known organic free radicals, may have doublet hyperfine structure from its



**Figure 6.** Experimental X-band ESR spectrum of the toluene solution dissolved polycrystalline sample under vacuum at room temperature. Experimental conditions: microwave frequency, 9.066 GHz; center field, 323 mT; sweep-width, 5.00 mT; sweep-time, 16 min; modulation amplitude, 0.05 mT; modulation frequency, 100 kHz; microwave power, 1.00 mW; amp, 320; time constant, 0.3 s.

center proton. However, the interaction is small ( $\approx 0.57$  mT) compared with the value of this work. A high-field ESR spectrum of a galvinoxyl radical had been already reported, showing no hyperfine structures.<sup>21</sup> The observed W-band spectrum and the obtained  $g$ -tensors are similar to those of other phenoxyl radicals,<sup>15,16</sup> showing that the unpaired electron is delocalized over the  $\pi$ -conjugated framework. At this point, it can be assumed that the oxygen which is a paramagnetic center in the molecular structures of the generated radicals might form a hydrogen bond with the *para*-OH or the phenolic OH of the host diamagnetic matrix, primary phenol in the condensed phase and a large part of the unpaired electron spin might be distributed over the OH, resulting in the large doublet  $^1\text{H}$ -hyperfine splitting. The presumed hydrogen-bond mechanism is shown in Figure 8. It can be considered that the hydrogen bonds break in a toluene solution due to the fast Brownian molecular motions. We presume that the  $g$ -values and  $^1\text{H}$  hyperfine constants of both hydrogen-bond radical species are almost the same within the line width by considering the isotropic data from the toluene solution experiment and the powder pattern W-band spectrum.

As seen in Table 3, the two protons of the *para*-CH<sub>2</sub> in the radical I have a large electron spin density, ( $A_{\text{Hiso}} = 1.02$  mT) enough to show the visible splitting in the powder spectra. It was however, assumed that the phenol-radical I does not show visible hyperfine splitting except the center hydrogen-bonding H because the electron spin density is delocalized over the phenol and the electron spin density at the *para*-CH<sub>2</sub> in the phenol-radical I becomes small. The hyperfine coupling constants at the CH<sub>2</sub> can be estimated to be less than 0.51 mT resulting in the unresolved hyperfine structure in the powder-pattern spectra.<sup>16</sup> Since the C of the CH<sub>2</sub> is a  $\text{sp}^3$ -hybrid carbon, the  $\pi$ -conjugated system is sectioned at the point of the C. The quantum chemical calculation study was thus required to confirm the above-mentioned analysis of the electron spin



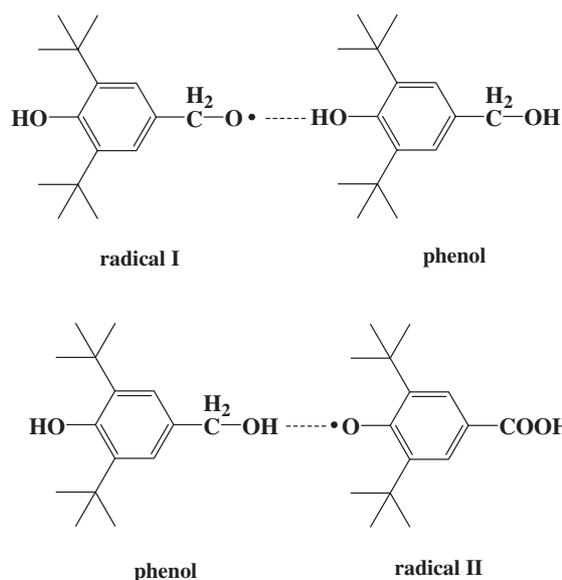
**Figure 7.** Simulated X-band ESR spectra and the molecular structure of the two radical components.

**Table 3.** The Isotropic Hyperfine Splitting Constants of the Two Radical Components Obtained from the Spectral Simulations in the Units of mT

Radical I	1.02 (two Hs in <i>para</i> -CH <sub>2</sub> )	0.481 (H in phenolic OH)	0.173 (two <i>meta</i> -Hs)
Radical II	0.169 (two <i>meta</i> -Hs)		

density of the CH<sub>2</sub>.

Density functional theory (DFT) calculations were performed using the Gaussian 03 program<sup>22</sup> to estimate the hyperfine coupling constants of some radicals appearing in this work. The B3LYP method and the 6-31G(d) basis set were used for both the structure optimizations and the parameter calculations. All opt-calculations of the radicals successfully converged. The B3LYP method is known to be applicable for the calculations of organic radicals as well as transition-metal ions.<sup>23–25</sup> The calculated results of the hyperfine coupling constants at the *para*-CH<sub>2</sub> in the phenol-radical I on the default and structure-optimized molecular models were 0.248 and 0.003 mT, respectively, decreasing from the calculated results

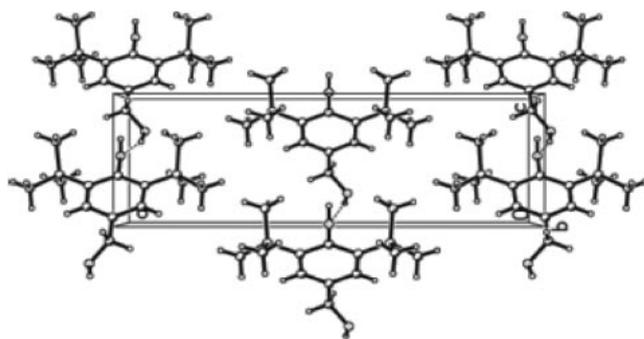


**Figure 8.** Presumed hydrogen-bond mechanism between the O• of the radicals and the phenolic or *para*-OH of the primary phenol in the condensed phase.

of the radical I model. This confirmed the above-mentioned analysis of the hyperfine coupling of the CH<sub>2</sub> in the phenol-radical I. The following were found, but not shown in detail. The calculated estimates of the hyperfine coupling constants of the protons near/away from the center (O●) of the unpaired electron were overestimated/underestimated compared to the experiment values. This shows that the electron spin densities of the radicals in the solutions are actually more delocalized over the molecules. The experimental values are between the calculated results on the default and the structure-optimized molecular models, close to the calculated results on the former. The presently used calculation modeling is a simple one (isolated)-molecular-type. It probably needs consideration of the molecular environmental effects (the intermolecular interactions or the solvent effects), such as the van der Waals force, polarization, and steric strain from the neighboring diamagnetic phenol or paramagnetic radical molecules. The calculated results of the hyperfine coupling constants on the hydrogen-bonding protons in the phenol-radical I and II were overestimated for the default molecular models, and underestimated for the structure optimized models. The reason might be that the radical molecules are actually hindered in the condensed phase, forming the hydrogen-bonding network.<sup>26</sup> The calculations done by using a basis set 6-31++G(d), that added diffuse functions to a 6-31G(d), gave just a little better results than the calculations by a 6-31G(d). Diffuse functions were thus found to be not so efficient for the evaluation of the spin density distributions or the hyperfine splitting constants at the hydrogen-bonding Hs discussed in this work. Better basis-set functions and methods need to be used for more precise evaluation. In any case, the validity of the analysis taken in this work was qualitatively confirmed by quantum chemical calculations.

The crystal structure of the host matrix phenol, 2,6-di-*tert*-butyl-4-hydroxymethylphenol is illustrated in Figure 9.<sup>26</sup> Our conclusions from the present ESR studies on the formation of the hydrogen bonding head-to-tail between the radicals and the phenol is also confirmed from the view point of the organic crystallographic data.

A re-evaporation of the toluene solvent was done. The X-band ESR spectrum of the polycrystalline sample obtained by grinding after the re-evaporation was the same as that of the



**Figure 9.** Crystal structure of the host matrix, 2,6-di-*tert*-butyl-4-hydroxymethylphenol. This crystal structure enables us to understand the abnormally large hyperfine doublet splittings from the hydrogen-bonding <sup>1</sup>Hs in the phenol radical complex I and II.

original polycrystalline sample (Figure 3a). The change between the dissolution state of the radical species in toluene solution to the hydrogen-bond formation in the condensed phase was thus found to be reversible. This result confirms the conclusion of the present work. We have not found reports that an anomalously large <sup>1</sup>H doublet hyperfine splitting is observed in ESR spectra resulting from formation of a hydrogen bond between a paramagnetic center (O●) of radicals and an OH of a diamagnetic molecule (phenol) in a condensed phase. This paper thus may supply a new physical insight for a hydrogen-bond formation between paramagnetic and diamagnetic species to, for example, studies on reactions or structures of bio molecules. Historically, it has been well known that a *p*-benzoquinone and a hydroquinone have charge-transfer interaction resulting in becoming a quinhydrone, which can be explained on the charge-transfer-complex theory established by Mulliken. Further research, for example, ab initio calculations, solution- and solid-state NMR, or UV-visible and IR spectroscopy investigations may be necessary to more strongly confirm the conclusions of the present work. Studies of frontier orbital interactions (SOMO-HOMO and SOMO-LUMO)<sup>27</sup> or thermodynamic stability might be also required for the analysis of the interesting radical chemical reaction and the hydrogen-bond formation. It can be considered that the SOMO-HOMO interaction should be predominant for the chemical reactions and hydrogen-bond formation from the viewpoint of the inter-orbital interaction since the SOMO generates from the HOMO of the precursor phenol. In solid-state NMR investigations, the proton having large electron-spin density could show the resonance-shift by the portion of the hyperfine interaction (so-called, paramagnetic shift), possibly accompanying the line broadening. Solid-state pulse-NMR methods, CPMAS and CRAMPS might be useful for more precise determination of the structures of the diamagnetic and paramagnetic molecules discussed in this paper. The states of the hydrogen bonds in a toluene solution might be investigated by solution NMR experiments (HSQC, NOESY, etc.).<sup>28</sup> The parameters are the hydrogen-exchange rates, the isotope shifts, the isotropic and anisotropic chemical shifts, the quadrupolar coupling constant of a deuteron involved in the bond, the scalar coupling constants transmitted through the hydrogen bonds and so on. These scalar couplings seem to correlate with the hydrogen-bond lengths and can be used to identify the coupling partner directly. We will carry out the above-mentioned investigations of the primary phenol and polycrystalline radical samples.

### Conclusion

The CW-ESR studies of the polycrystalline radical sample generated from PbO<sub>2</sub> oxidation of 2,6-di-*tert*-butyl-4-hydroxymethylphenol in toluene solution under vacuum at room temperature have been done.<sup>29</sup> The two generated radical species were successfully defined by analyzing the toluene dissolution spectrum. It was concluded that the radical species have an orthorhombic *g*-tensor and those paramagnetic centers O● form the hydrogen bonding with the *para*- and phenolic OH of the host matrix phenol resulting in the anomalously large <sup>1</sup>H-hyperfine splittings. These conclusions were also confirmed from the crystallographic structure data and quantum chemical calculations. It would be very interesting to further investigate

this proposed hydrogen-bond scheme from multiple eyes, i.e., other spectroscopic methods and quantum chemical calculations.

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- 29 The generated species are relatively stable radicals that have *tert*-butyl groups, but were found to be not the corresponding 2,6-di-*tert*-butyl-4-hydroxymethylphenoxy radical. Thus the present paper also corresponds to the discussion (erratum) of the our paper previously reported in the journal, *Solid State Ionics*.<sup>17</sup> In the paper, the interpretations of the pulse-ESR work had been done assuming the generated species should be the corresponding phenoxy radical as well as the case of the oxidation of the other phenols.<sup>15,16</sup> It may be however concluded that since the generated species are radicals which have *tert*-butyl groups, the assignments of the minima in the temperature variations of the relaxation times remain reasonable. We will report this discussion in the journal, *Solid State Ionics*.