ESR of Gamma Irradiation Damage Centers in Single Crystals of Some Phenol Derivatives

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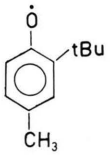
Phenoxy radicals have been observed and identified in gamma irradiated 2-t-bu-4-methylphenol, 2,6-di-t-bu-4-methylphenol and 2-amino-4-methylphenol single crystals.

Gamma irradiated 2-t-bu-4-methylphenol single crystal gave three distinct spectra with approximate intensity distributions of 1:3:3:1, 1:4:6:4:1 and 1:1:3:3:3:3:1:1, the last two being shown in Figure 1 a, b. These indicate that the radical is



When $B \| c$, then only the hyperfine interaction of the methyl protons is observable. When $B \| a^*$, the hyperfine interaction of one of the meta protons becomes equal to the methyl protons and therefore the intensity distribution of 1:4:6:4:1 in Fig. 1 a appears. However, in the case of $H \| b$ this splitting becomes smaller than the one of the methyl group protons and hence approximately an intensity distribution of 1:1:3:3:3:3:1:1 occurs as in Figure 1 b. The g tensor of the radical is anisotropic and its principal values and direction cosines are given in Table 1. The hyperfine splitting of the methyl protons is isotropic and $a = 10.5$ G. The hyperfine splitting of the meta proton is anisotropic and changes between 2 and 10.5 G depending on the orientation of the magnetic field. The hyperfine splitting of the ortho proton is smaller than 2 G and therefore unobservable. When the temperature is increased to 333 K, the signal disappears and a better resolved spectrum cannot be obtained. These results are in agreement with the literature values which were obtained by different methods [1, 2].

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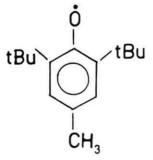
Gamma irradiated 2,6-di-t-bu-4-methylphenol single crystal exhibited a spectrum with an intensity distribution of 1:3:3:1 as in Figure 2 a. This indicates that the radical is



The principal values of the g tensor and direction cosines are given in Table 2. The hyperfine splitting for the two meta protons could not be seen in the solid, but when the temperature is increased to 353 K the crystal melts, and then each line splits into three and a spectrum with an intensity distribution of 1:2:1:3:6:3:3:6:3:1:2:1 is obtained as shown in Figure 2 b. This pattern is, obviously, due to the hyperfine interaction of the unpaired electron with methyl and meta protons. The hyperfine splitting of the methyl protons is $a_{CH_3} = 11.0$ G and of the meta protons $a = 1.7$ G. These results are in agreement with the lead dioxide oxidation results [3, 4].

Gamma irradiated 2-amino-4-methylphenol single crystals exhibited only a broad e.s.r. line with a total spreading of 58 G, as shown in Figure 3 a. But when

Table 1. The principal values and direction cosines of the g tensor of the radical obtained after gamma irradiation of 2-t-bu-4-methylphenol.

Principal values	Direction cosines		
$g_{xx} = 2.0056$	0.3596	0.5377	−0.8240
$g_{yy} = 2.0049$	0.3688	0.7445	−0.8240
$g_{zz} = 2.0043$	0.8571	−0.5041	0.1063
$g_{av} = 2.0050$			

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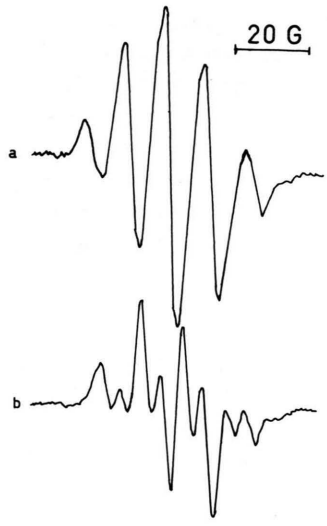


Fig. 1. ESR spectra of gamma irradiated 2-t-bu-4-methylphenol single crystal, a) $B \parallel a^*$ and b) $B \parallel b$.

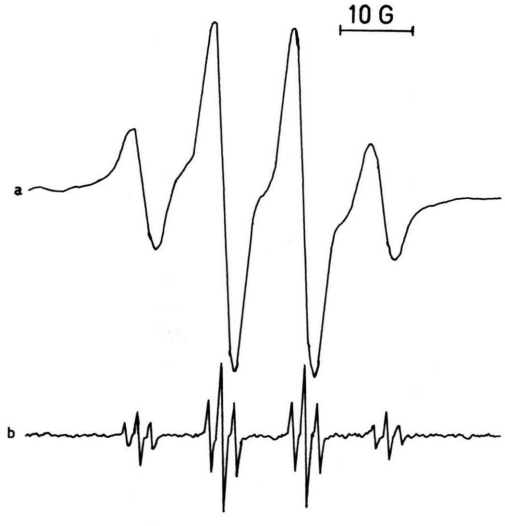


Fig. 2. ESR spectra of gamma irradiated 2,6-di-t-bu-4-methylphenol, a) single crystal, $B \parallel c$, at 293 K and b) after melting at 353 K.

Table 2. The principal values and direction cosines of the g tensor of the radical obtained after gamma irradiation of 2,6-di-t-bu-4-methylphenol.

Principal values	Direction cosines		
$g_{xx} = 2.0053$	−0.7425	0.6896	−0.0137
$g_{yy} = 2.0027$	0.6648	0.7393	0.1066
$g_{zz} = 2.0074$	0.0816	0.0700	−0.9942
$g_{av} = 2.0052$			

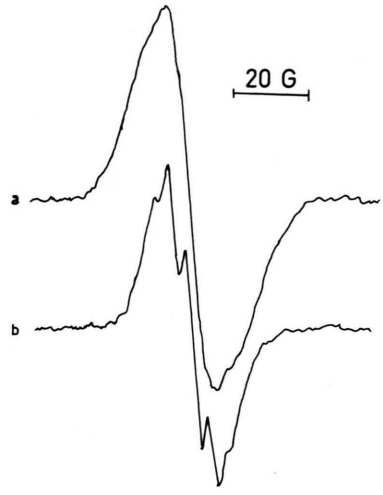
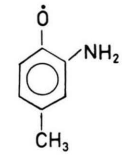


Fig. 3. ESR spectra of gamma irradiated 2-amino-4-methylphenol, a) single crystal, $B \parallel c$, at 293 K and b) after melting at 423 K.

the temperature is increased to 423 K the crystal melts and this resolves into five narrow lines, as shown in Figure 3 b. This can be attributed to the



radical. The g values of the single crystal and liquid spectra are the same: $g = 2.0049 \pm 0.0005$. The hyperfine splittings of the methyl and one of the meta protons are equal: $a = 5.2$ G at 423 K. The N nucleus does not give hyperfine splitting due to the electron rejecting behavior of the $-NH_2$ group. As a result, this study identifies the gamma irradiation damage centers in three different compounds.

Experimental

The single crystals were grown from concentrated aqueous solutions of the compounds the single crystal of 2-t-bu-4-methylphenol is monoclinic with space group P. The unit cell dimensions are $a = 6.337$, $b = 16.921$, $c = 19.090$ Å and $\beta = 94°19'$. The unit cell of the crystal contains four molecules [5]. The single crystal of 2,6-di-t-bu-4-methylphenol is orthorhombic with space group $P2_12_12_1$, and its unit cell dimensions

are $a = 10.38$, $b = 15.50$, and $c = 8.82$ Å. The unit cell contains four molecules [6]. The single crystal of 2-amino-4-methylphenol is orthorhombic with space group P_{bca}, and its unit cell dimensions are $a = 7.78$, $b = 22.90$, and $c = 7.59$ Å. The unit cell contains 8 molecules [7].

The samples were irradiated at room temperature with a ^{60}Co γ-ray source 0.3 Mrad/h for 12 hours. The e.s.r. spectra were recorded at room temperature using a Varian E109 e.s.r spectrometer equipped with a Varian temperature controller. The crystals were rotated on a Lucite pillar about their crystallographic axes, and the angles of rotations were read on a scale graduated in degrees. The a^* axis is chosen perpendicular to the bc plane. The g factors were found by comparison with a DPPH sample ($g = 2.0036$).

[1] N. M. Atherton, E. J. Land, and G. Porter, Trans. Faraday Soc. **59,** 818 (1963).
[2] N. M. Atherton and R. S. F. Harding, J. Chem. Soc. (A), 2352 (1968).
[3] J. K. Becconsall, S. Clough, and G. Scott, Trans. Faraday Soc. 459 (1960).
[4] K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi, and H. Takaki, Bull. Chem. Soc. Japan **40,** 2731 (1967).
[5] O. Büyükgüngör and Ş. Osmanoğlu, to be published.
[6] P. M. Maze-Boudet, Acta Cryst. B **29,** 602 (1973).
[7] S. Kashino, M. Tomita, and M. Haisa, Acta Cryst. Sec. C **44,** 730 (1988).