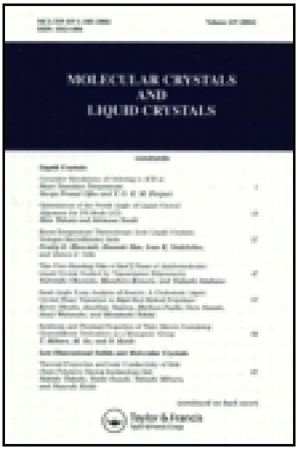

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

An EPR Study of Hydronaphthyl Radicals in Naphthalene Single Crystals

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Version of record first published: 21 Mar 2007.

To cite this article: Noriaki Itoh & Takenori Okubo (1972): An EPR Study of Hydronaphthyl Radicals in Naphthalene Single Crystals, Molecular Crystals and Liquid Crystals, 17:3, 303-314

To link to this article: http://dx.doi.org/10.1080/15421407208083176

Molecular Crystals and Liquid Crystals. 1972. Vol. 17, pp. 303–314

Printed in Great Britain

An EPR Study of Hydronaphthyl Radicals in Naphthalene Single Crystals

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Received October 1, 1971

Abstract—Angular dependence of the EPR spectra of naphthalene single crystal irradiated at room temperature is measured and explained on the basis that the 1- and 2-hydronaphthyl radicals are present. The spin densities of π-electrons in these radicals and the principal values of the hyperfine tensor of indirect, or α-proton coupling, are determined by the least-squares fit. The values are compared with the theoretical values obtained by Shida and Hanazaki.

1. Introduction

Attention has been paid to clarify the radiation-chemical processes in aromatic hydrocarbons.(1,2) In order to make the nature of the radiation products clear, it is of interest to study radiation effects on single crystals, in which radicals and other radiation products are oriented regularly. Recent EPR studies(3–6) of radiation products in aromatic hydrocarbon single crystals have suggested that the irradiation of an aromatic hydrocarbon single crystal produces the cyclohexadienyl-type radicals, the structure of which in naphthalene is shown in Fig. 1. This suggestion has been made using the EPR spectra obtained in polycrystals(7) or those obtained in single crystals without a detailed analysis of the angular dependence. Therefore the constants for the EPR spectrum, such as the anisotropic hyperfine splitting parameters and the spin densities, have not been obtained exactly.

The cyclohexadienyl radical has been considered as the reaction intermediate in radical substitution reactions and a few theoretical works on them have been made.(8) The radical has a π-electron system consisting of the carbon π-orbits and of the pseudo-π-orbit

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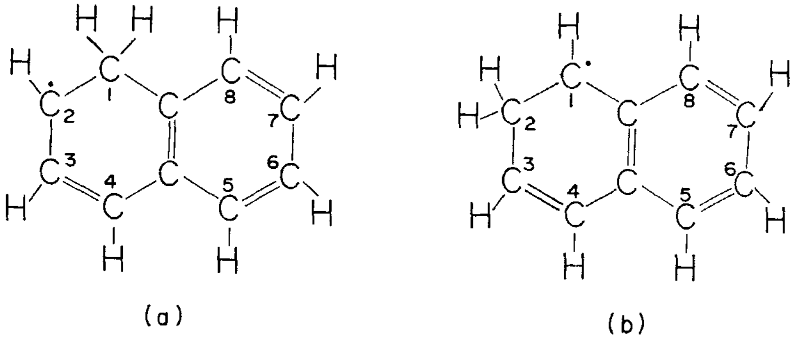

Figure 1. Hydronaphthyl radicals.

of the methylene group interacting through hyperconjugation. A comparison between the theoretical and experimental optical transition energies in 1- and 2-hydronaphthyl radicals has been made and good agreement has been obtained.(9) It is also interesting to compare the experimental spin densities with the theoretical values. Such a comparison may give further insight into the molecular structure of these radicals.

The purpose of the present paper is to analyze the angular dependence of the EPR spectrum. It is clear that the 1-hydronaphthyl radical (Fig. 1(a)) is produced. It is also shown that another radical which is suggested to be the 2-hydronaphthyl radical (Fig. 1(b)) is produced.

2. Experimental Technique

Naphthalene powder of reagent grade was purified by vaporization. Crystals were grown by the Bridgeman technique in an evacuated cell. The crystal orientation was determined with a polarizing microscope, Specimens of $3 \times 3 \times 10$ mm^3 in dimension were sealed off in an evacuated sample cell. They were irradiated at room temperature with X-rays from an X-ray tube operated at 50 kV, 40 mA.

EPR spectra were obtained at room temperature with an X-band spectrometer JES-ME. The specimens were set in the magnetic field, with the *b*-axis perpendicular to the field and were rotated around the *b*-axis and the angular dependence of the EPR spectrum was obtained.

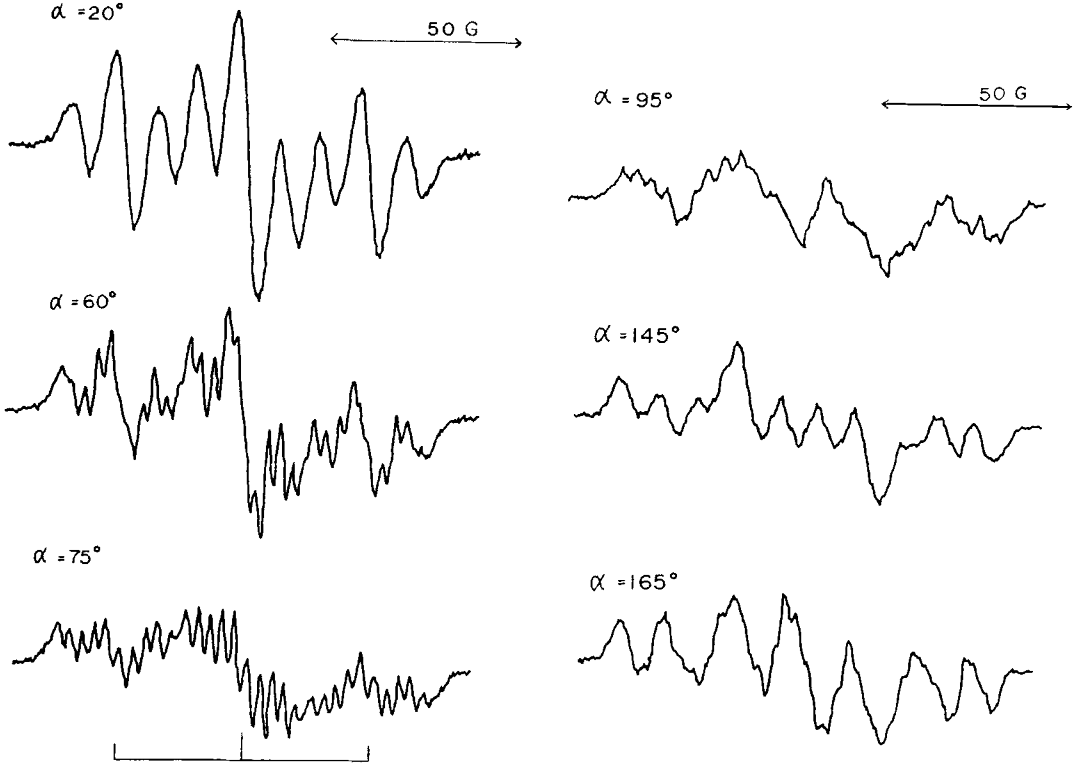

Figure 2. EPR spectra of naphthalene single crystal irradiated at room temperature. The magnetic field is perpendicular to the b-axis and α denotes the angle between the magnetic field and the a-axis.

3. Experimental Result and Discussions

Typical EPR spectra are shown in Fig. 2. They provide the angular independent g-value of 2.0016. These spectra were obtained with the magnetic field in the *ac*-plane and at a given angle α from the *a*-axis. The angle α for the *c*-axis is 122.55°. The spectra at $\alpha = 25° \sim 35°$, where the magnetic field is nearly perpendicular to the molecular plane, consist of a triplet which is further split into another triplet. The spectra are similar to those obtained in glassy systems and have been assigned to the hydronaphthyl radical.(7)

As seen from Fig. 2, the spectra show a strong angular dependence. Inspection of spectra, however, indicates that many of them can be divided into three groups, as shown in Fig. 2 for the case of $\alpha = 75°$, and that the magnitude of the splitting into three groups is almost angular independent. The intensity ratio of each component of the triplet signal is 1 : 2 : 1, and it is clear that this splitting is caused

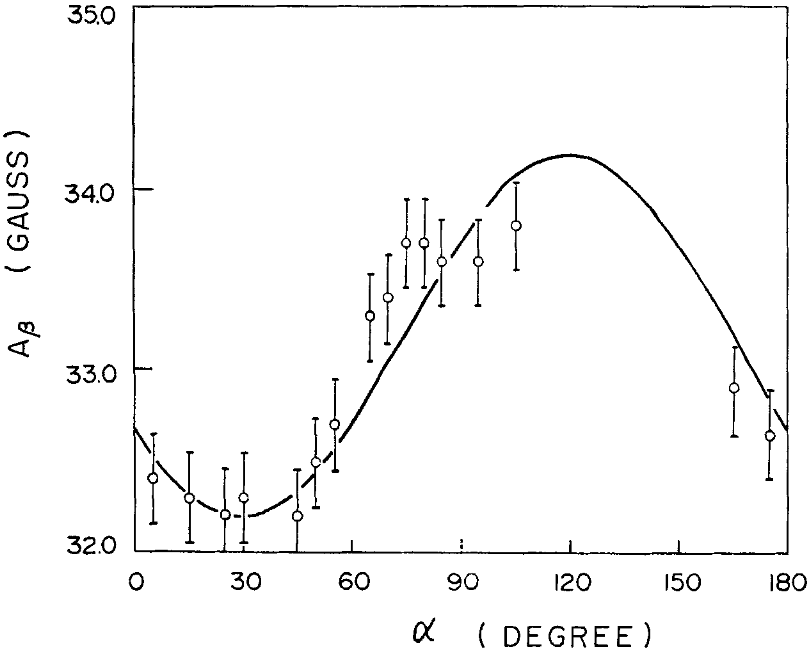

Figure 3. The angular dependence of the hyperfine splitting caused by the β-proton coupling in 1-hydronaphthyl radical.

by the coupling of the π-electron with two protons. The magnitude A_β of this splitting is obtained as the function of α and shown in Fig. 3. The angular dependence of A_β can be described as

$$A_\beta = 33.2 - 2.0 \cos(\alpha - 30^\circ) \quad \text{gauss.} \tag{1}$$

Owing to the small angular dependence this splitting is considered to be caused by the methyl, or β-proton coupling. The values of A_β in the glassy or polycrystalline system obtained by other authors$^{(7)}$ agree with the present result.

The splitting in each group is highly angular-dependent. For $\alpha = 75^\circ$, ten lines with the width of about 2.5 gauss and with nearly the same intensity can be identified. Instead of these sharp lines, broad lines are observed when α is at the outside of the angular region from 65° to 110°. Angular dependence of the positions of these ten lines in the central group of the triplet is shown in Fig. 4.

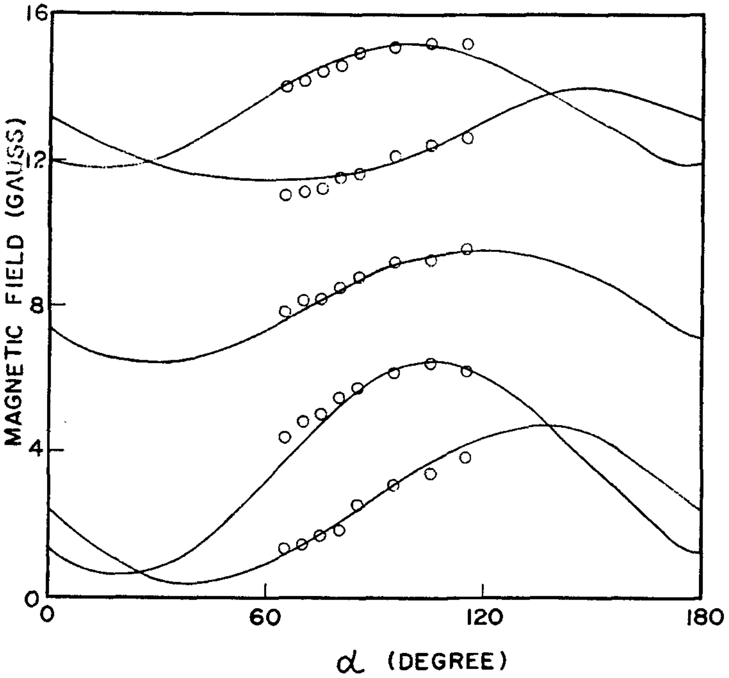

Figure 4. The angular dependence of the hyperfine lines caused by the α-proton coupling. Curves are obtained using the parameters determined by the least squares fit to the experimental values, which are denoted by dots.

The curves in the figure are drawn using the hyperfine parameters obtained, with the method described below.

Since the complete spectrum is obtained only in a limited region of the angle, the principal values of the hyperfine tensor and normal coordinates can not be obtained independently. Therefore the observed spectrum is analyzed, assuming that the spectrum is caused by the hydronaphthyl radical, which may be the most probable radical created by irradiation in naphthalene single crystals.† It is also assumed that the radical has the same orientation as the host molecule. The disorientation of the radical, if any, may be very small since general features of the angular dependence of the EPR spectra can be described fairly precisely with this assumption.

It is known that the exchange interaction between the π-electron and the carbon σ electron in the C—H σ bond causes angular-dependent hyperfine coupling, which is called the α-proton coupling. If the direction cosines of the magnetic field in the coordinates fixed to the nth C—H bonds (Fig. 5) in the hydronaphthyl radical are designated by l_{nx}, l_{ny}, l_{nz}, the contribution of the proton to the hyperfine coupling is expressed as

$$A_n = \rho_n \sqrt{{A_x}^2 l_{nx}^2 + {A_y}^2 l_{ny}^2 + {A_z}^2 l_{nz}^z}, \tag{2}$$

where A_x, A_y and A_z are the principal values of the hyperfine tensor of the α-proton and ρ_n is the spin density of the π-electrons at the nth proton.

The direction cosines (l_{nx}, l_{ny}, l_{nz}) at a given magnetic field direction may be calculated in terms of the orientation tensor of the molecule in the crystal lattice and the orientation tensor of a given C—H bond in the molecular coordinates. The orientation tensor of the molecule has been obtained by Abraham *et al.*(10) With reference to Fig. 6, which shows two different molecules in a unit cell, it is easily shown that the absolute values of the direction cosines for protons at 2 and 6, those for protons at 3 and 7 and those for protons at 1, 4, 5 and 8 are the same, when the direction of the magnetic field is in the ac-plane. Since the spin densities of π-electrons in 1-hydronaphthyl radical are the highest at the positions

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† It is considered that the isotropic splitting is caused by the β-proton coupling at position 1 in Fig. 1(a), or at position 2 in Fig. 1(b).

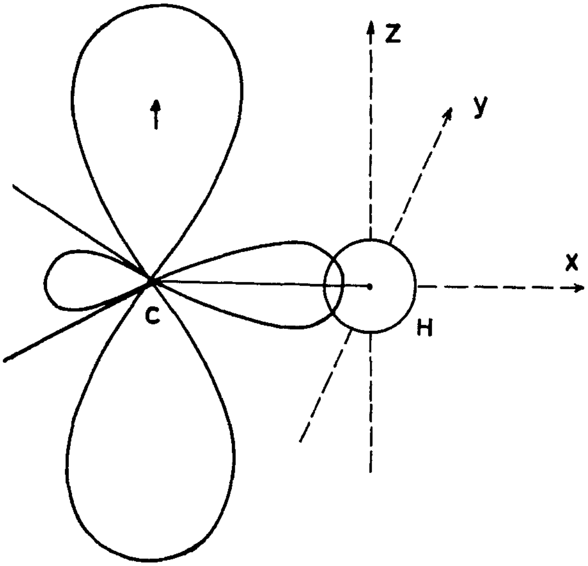

Figure 5. Coordinates for α-proton coupling.

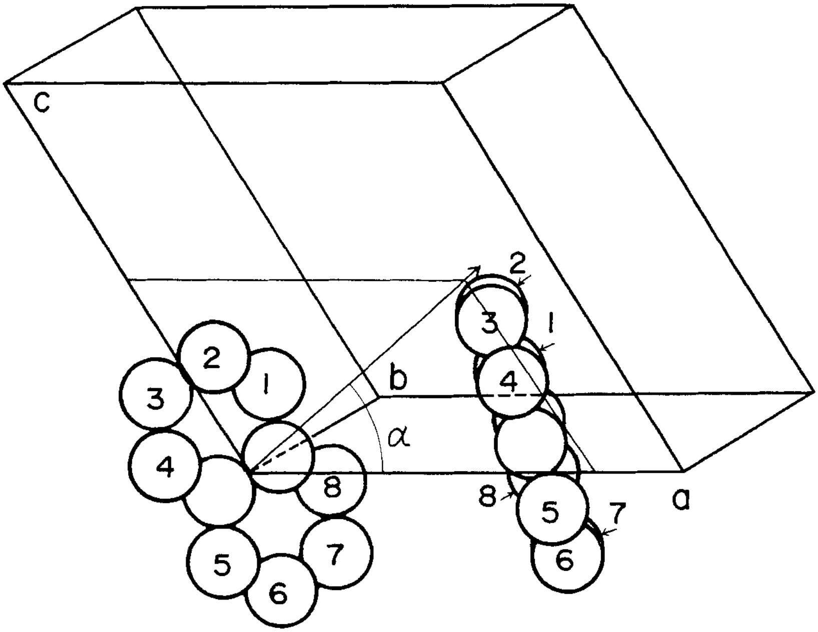

Figure 6. A unit cell of naphthalene single crystal.

2 and 4 among other positions, the α-protons at positions 2 and 4 give the highest contribution to the hyperfine splitting and four distinct hyperfine lines may be observed. The 1-hydronaphthyl radical at an additional proton at position 5 may display the same four lines. The 1-hydronaphthyl radical with an additional hydrogen at position 8 may give different hyperfine splitting. Since the contribution from the α-protons at 4 and 5 is the same, the 1-hydronaphthyl radical at position 8 produces another four hyperfine lines: one of the doublet splittings for the 1-hydronaphthyl radical at position 8 is the same as that for the 1-hydronaphthyl radical at position 1. The hyperfine splittings which are caused by the hydronaphthyl radicals formed in another molecule in the unit cell are the same as those formed in the first molecule.

Experimental results shown in Fig. 4 indicates that there are ten lines with nearly the same intensities in each group. Among these ten lines in each group, eight lines may be considered to be associated with the 1-hydronaphthyl radical. The assignment of the splitting is shown in Fig. 7, where A_2 and A_4 designate the hyperfine splitting caused by the α-protons at positions 2 and 4 in the 1-hydronaphthyl radical and A_7 that caused by α-protons at position 7 in the 1-hydronaphthyl radical at position 8. The choice of four lines shown in Fig. 7 is most appropriate, since the center of two pairs split by A_2 and A_7 falls in the same position and the dependence of the center position on α is the same as expected for splitting due to A_4 (Fig. 4).

The origin of the lines which have not been assigned in the spectrum shown in Fig. 7 is now discussed. The spectrum is composed of six lines: a triplet with nearly the same separation as A_β of 1-hydronaphthyl radical, which further split into two by A' as shown in Fig. 7. The angular dependence of the splitting A' is in parallel with that of the splitting A_4. This result may indicate that the splitting A' is produced by the α-proton coupling at the positions 1, 4, 5 or 8. Such an angular dependence may be produced by the 2-hydronaphthyl radical, which is shown in Fig. 1(b). From the intensity of the EPR spectra the concentration of the 2-hydronaphthyl radical is estimated to be about $\frac{1}{4}$ of that of 1-hydronaphthyl radical.

The spin densities in the π-electron systems of 1- and 2-hydronaphthyl radicals and the principal values of the hyperfine tensor

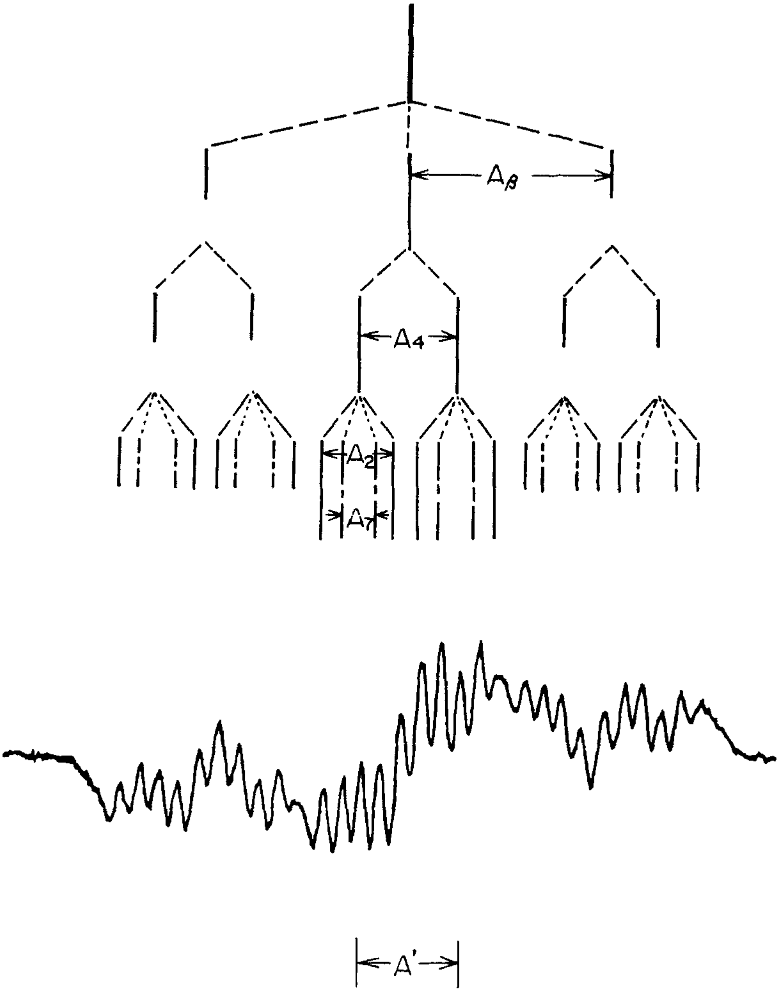

Figure 7. Assignments of the EPR lines for the 1- and 2-hydronaphthyl radical (see text).

may be obtained from the angular dependence of the hyperfine splitting. Eq. (2) may be transformed into

$$A_x{}^2 l_{nx}^2 + A_y{}^2 l_{ny}^z - A_n{}^2 \cdot \frac{1}{\rho_n{}^2} = -A_z{}^2 l_{nz}^z. \tag{3}$$

The values of A_n in Eq. (3) is replaced by the values of A_2, A_4 and A_7 obtained experimentally at various angles for the 1-hydronaphthyl radical. Regarding that A_z is known, Eq. (3) gives simultaneous equations for four unknowns, A_x, A_y, $\rho_2(=\rho_7)$ and ρ_4. The value of A_z is assumed to be -30 gauss(8) and the least-squares method is used to obtain the most appropriate values for these unknowns. This value of A_z has been used by other authors(8) in the discussion of cyclohexadienyl radical and is considered to be appropriate on the basis of the value of spin density as discussed later. The values of A_x and A_y obtained by the least-squares fit are

$$A_x = -13 \pm 1.5 \quad \text{gauss}$$

and

$$A_y = -42 \pm 1.5 \quad \text{gauss.}$$

Table 1 shows the spin densities obtained both from the least squares fit and from theory. In obtaining the spin density at the pseudo-π orbits, the values of A/ρ is assumed to be 353 gauss.(8)

TABLE 1 Spin Densities in 1 – and 2-Hydronaphthyl Radicals

Radical	Position	Experiment	Theory(a)
1 – hydronaphthyl radical	1	0.094	0.084
	2	0.36	0.48
	4	0.46	0.38
2 – hydronaphthyl radical	1	0.47	0.58
	2	0.094	0.11

(a) Reference (8)

The close agreements between the experimental spin densities at position 4 of the 1-hydronaphthyl radical and that at position 1 of the 2-hydronaphthyl radical and between the spin densities at the β-protons of both radicals may be accidental.

The width of the spectrum may originate in the hyperfine splitting caused by other protons. The largest contribution will arise from the proton at position 5 for the 1-hydronaphthyl radical and the width is estimated as 3 gauss at 60°, by using the theoretical spin density 0.092. This value agrees well with the experimental value. The above results substantiate the assumption that A_z is -30 gauss. As α increases, the hyperfine splitting due to the proton at position 5 increases, which is consistent with the experimental result that the width increases as α increases.

It was tried to simulate the EPR spectra at the magnetic field directions at the angle, where the spectra can not be resolved clearly. Although qualitative agreement between the simulated and experimental spectra was obtained, quantitative agreement has not been attained, mainly because of the overlap of the spectrum with another spectrum. The mixing of another spectrum is clearly verified by using the difference in the saturation characteristics to the microwave power. By increasing the microwave power, the spectrum due to the hydronaphthyl radical disappears and only a new spectrum is observed. The nautre of this spectrum will be treated separately. It has already been shown(11) that the hydrobinaphthyl radical exists in the specimen which has been irradiated at liquid nitrogen temperature and subsequently warmed to room temperature, or in the specimen irradiated at room temperature.

Agreement between the experimental and theoretical values of the spin densities of the hydronaphthyl radical is not very satisfactory. As was already discussed, the agreements between the experimental and theoretical values of the transition energies are fairly good. The direction of the dipole moment obtained theoretically, however, does not predict the polarization of optical transition precisely. The disagreement between the experimental and theoretical spin densities may have a correlation with the disagreement of the direction of the transition dipoles. Theoretical computations are made using the semi-empirical method developed by Pariser and Parr combined with the SCF method for an open shell.(8) The origin of the discrepancy is not clear yet. The assumptions made in the theoretical calculation may be responsible for the discrepancy. The principal values of the hyperfine tensor for α-protons obtained experimentally would be of use in analyzing similar EPR spectra produced in irradiated aromatic hydrocarbons.

Acknowledgement

Numerical calculation is made with HITAC 5020E at the computer center, University of Tokyo.

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