

Electron Spin Resonance Study of Phenyl Radicals Isolated in an Argon Matrix at 4°K

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Abstract: A well-resolved esr spectrum was obtained from phenyl radicals generated and isolated by photolysis of phenyl iodide in an argon matrix at 4°K. Its analysis led to the assessment of both the isotropic and anisotropic parts of the hyperfine interaction terms with all the protons. The results for the isotropic coupling constants are: $A_{ortho} = +17.4 \pm 0.1$, $A_{meta} = +5.9 \pm 0.1$, and $A_{para} = +1.9 \pm 0.1$ G. The unpaired electron was found to be localized mostly in the nonbonding σ orbital centered at the 1 carbon.

The phenyl radical, the simplest member of the neutral aryl radicals, is one of the most reactive hydrocarbon radicals. Its existence and many of its characteristics have been well established through its chemical reactions. It had long evaded, however, any definitive spectroscopic detection and analysis. Until recently it was not known whether the unpaired electron was localized in the broken bond, giving rise to a σ radical, or delocalized in the six-center π -orbital system. Evidence that the phenyl is a σ radical was obtained by Porter and Ward,¹ who investigated the electronic spectrum of the radical using a flash photolysis method, and by Bennett, Mile, and Thomas² who studied the electron spin resonance spectrum of the radicals generated and trapped in various matrices at 77°K. The esr spectrum observed by the latter group was essentially a triplet of triplets, the larger triplet spacing (~ 18 G) attributed to the pair of *ortho* protons and the smaller (~ 6.4 G) to the pair of *meta* protons. No hyperfine structure due to the *para* proton was resolved.

Several attempts have been made to calculate the hyperfine coupling constants of the phenyl radical by semiempirical methods³⁻⁵ (see Table II). The coupling constants calculated by Dixon using a hyperconjugation approach,³ and those obtained by Petersson and McLachlan using an extended Hückel theory (EHT) molecular orbital⁴ are such that, while the values calculated for the *ortho* and *meta* protons are in fair agreement with the observed values, the value calculated for the *para* proton completely disagrees. The difficulty probably lies in using the result of closed-shell calculations for an open-shell system, particularly when the radical in question is a σ radical. The result of a more recent calculation by Pople, Beveridge, and Dobosh, who used an SCF method,⁵ shows a much better over-all agreement with the experimental result. The coupling constants reported by Bennett, *et al.*, however, involve large uncertainties owing to the following factors. (1) Highly polarizable materials were used as matrices; hence the spectrum varied significantly depending upon the matrix. (2) Only the isotropic coupling constants were assessed from the spectra

which were clearly distorted by the anisotropy of the hyperfine interaction and possibly of the g tensor.

In view of the large discrepancies among the theoretical predictions, and also in view of the primary importance held by the phenyl radical among the aryl radicals, a more definitive study of the esr spectrum of phenyl radical appeared desirable.

We report here the analysis of the esr spectrum of phenyl radicals generated by the photolysis of phenyl iodide in an argon matrix at 4°K. The assignment of the g tensor, and the accurate assessment of both the isotropic and anisotropic parts of the hyperfine coupling constants of all the protons, was accomplished by utilization of a spectrum simulation technique. A brief description of this technique is also given. It allows a simulation of an esr spectrum exhibited by an ensemble of randomly oriented radicals having an orthorhombic g tensor and highly anisotropic hyperfine coupling tensors whose principal axes need not coincide with those of the g tensor.

Experimental Section

The design of the dewar and esr spectrometer system which allows the trapping of reactive intermediates in rare gas matrices and the measurement of their esr spectra has been described previously.⁶ The matrix is formed on a flat, spatula-shaped sapphire rod which can be rotated about its long axis and moved vertically in and out of the esr cavity. For the present series of experiments, an appendage consisting of a glass tube, a thermocouple pressure gauge, a needle valve, and a sample reservoir was attached to the dewar to inject a controlled amount of aryl halide onto the sapphire rod. During the matrix deposition the sapphire rod was positioned at "45°" to this molecular beam and irradiated simultaneously with the uv light focused through a quartz window; see Figure 1. A high-pressure mercury lamp (G.E. AH-6) combined with a uv filter (Corning 7-54 filter) was used as the light source. An essentially identical result was obtained when the matrix was irradiated after deposition had been completed. The simultaneous irradiation, however, was found to produce spectra with a slightly higher resolution, and hence was adopted as the standard procedure for experiments involving a simple photolysis. The higher resolution obtained with the simultaneous irradiation may be attributed to a higher degree of annealing achieved by the matrix deposited under such conditions. No orientation effect⁷ was observed in these matrices where radicals were produced by photolysis.

Phenyl iodide obtained from Aldrich Chemicals was used after purification by preparative glpc followed by bulb-to-bulb distilla-

(1) G. Porter and B. Ward, *Proc. Roy. Soc.*, **A287**, 457 (1965).

(2) J. E. Bennett, B. Mile, and A. Thomas, *ibid.*, **A293**, 246 (1966).

(3) W. T. Dixon, *Mol. Phys.*, **9**, 201 (1965).

(4) G. A. Petersson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966).

(5) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968).

(6) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *J. Chem. Phys.*, **44**, 2581 (1966).

(7) P. H. Kasai, W. Weltner, Jr., and E. B. Whipple, *ibid.*, **42**, 1120 (1965); and also ref 6.

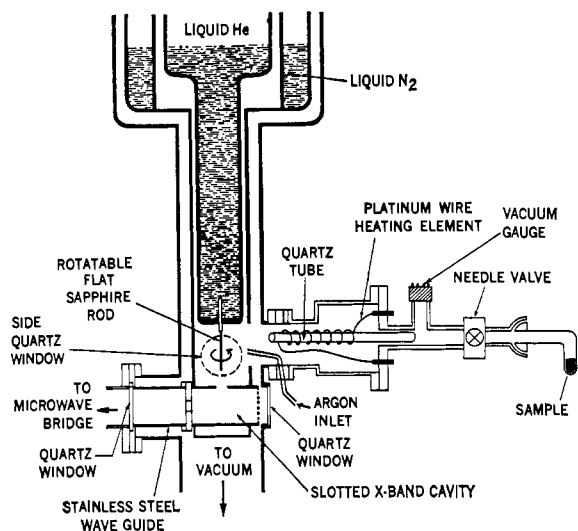
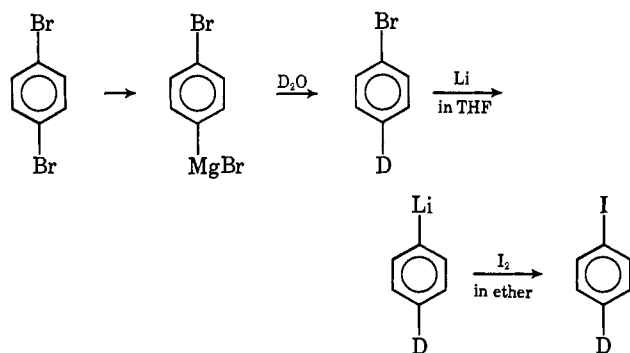


Figure 1. Cross section of the cryostat assembly consisting of a gaseous sample inlet, a sapphire rod at 4°K, and a microwave cavity into which the sapphire rod is lowered after the formation of matrix. Note the position of the side quartz window through which the photolysis was performed.

tion *in vacuo*. *para*-Deuterated phenyl iodide was prepared from *p*-dibromobenzene through the following scheme.



Details of the steps leading to the synthesis of *p*-deuteriobromobenzene and *p*-deuteriodobenzene follow.

***p*-Deuteriobromobenzene.** A solution (1 ml) of *p*-dibromobenzene (50.0 g in 100 ml of dry tetrahydrofuran) was added to a stirring mixture of magnesium turnings (4.0 g) in about 25 ml of dry tetrahydrofuran under nitrogen. The reaction was initiated with an iodine crystal, and then the remainder of the *p*-dibromobenzene solution was added dropwise with ice-bath cooling. At the completion of the addition the brown reaction mixture was stirred at room temperature for 30 min and then cooled with an ice bath. Deuterium oxide (10 ml) was then added dropwise with stirring. At the completion of the addition, the colorless reaction mixture was poured into 10% hydrochloric acid and extracted with methylene chloride. The methylene chloride solution was extracted with water and dried over magnesium sulfate. Distillation gave 11.3 g of product, bp 149–150°. The nmr and mass spectrum indicated that >99% *p*-deuterium was incorporated. The ir showed characteristic bands at 4.4 μ .

***p*-Deuteriodobenzene.** *p*-Deuteriobromobenzene (6.2 g in 30 ml of anhydrous ether) was added dropwise with stirring and under nitrogen to 0.9 g of lithium ribbon which was cut into small pieces. At the completion of the addition, 7 ml of anhydrous ether was added, and the mixture was stirred at room temperature for 2 hr. A saturated solution of iodine in dry ether was then added dropwise to the reaction mixture until a permanent iodine color remained. A 10% solution of sodium thiosulfate (20 ml) was added. After standing overnight the reaction mixture was filtered; the ether layer was separated (4.2 g) and dried over magnesium sulfate. The product was obtained by distillation *in vacuo*. Nmr, mass spectra, and glpc indicated >99% purity. A small portion of this product was further purified by preparative glpc followed by bulb-to-bulb distillation *in vacuo*, and this was used in the esr experiments.

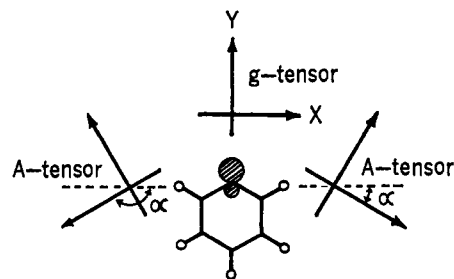


Figure 2. Principal axes of the g tensor and those of hyperfine coupling tensors of the *ortho* protons. The z axes are coincident for all the tensors and are perpendicular to the molecular plane.

Spectrum Simulation

The spectrum pattern, $S(H)$, exhibited by an ensemble of randomly oriented radicals is given by

$$S(H) = \sum_M \int_0^{2\pi} \int_0^\pi D[H - H_M(\theta, \varphi)] \sin \theta \, d\theta \, d\varphi \quad (1)$$

The angles θ and φ define the orientation of the principal axes of the g tensor of the radical relative to the external field, and the summation in M is to be performed over all the hyperfine components arising from the magnetic nuclei involved. $D[H - H_M(\theta, \varphi)]$ is the derivative of a line-shape function, and $H_M(\theta, \varphi)$ represents the resonance field of the M th hyperfine component. $H_M(\theta, \varphi)$ can be obtained from the well-known relation

$$h\nu = g\beta H_M(\theta, \varphi) + \sum_i A_i m_i \quad (2)$$

where m_i is the magnetic quantum number of the i th magnetic nucleus, and g and A_i are usually given by the eq 3 and 4, respectively.

$$g^2 = g_z^2 \cos^2 \theta + (g_x^2 \cos^2 \varphi + g_y^2 \sin^2 \varphi) \sin^2 \theta \quad (3)$$

$$A_i^2 = (g_z A_{iz}/g)^2 \cos^2 \theta + [(g_x A_{ix}/g)^2 \cos^2 \varphi + (g_y A_{iy}/g)^2 \sin^2 \varphi] \sin^2 \theta \quad (4)$$

The last expression (4), however, is applicable only when the directions of the principal axes of the hyperfine tensor coincide with those of the g tensor. Clearly this condition would not be met by the hyperfine tensors of the *ortho* and *meta* protons in the phenyl radical. Only the axis perpendicular to the molecular plane, say the z axis, is coincident with that of the g tensor. In this particular case, it can be shown easily that the following relations hold for each A_i .

$$A_i^2 = A_{i\parallel}^2 \cos^2 \theta + A_{i\perp}^2 \sin^2 \theta \quad (5)$$

where

$$A_{i\parallel}^2 = (g_z A'_{iz}/g)^2 \quad (6)$$

$$A_{i\perp}^2 = (g_x A'_{ix}/g)^2 \cos^2 \varphi + (g_y A'_{iy}/g)^2 \sin^2 \varphi + (g_x g_y / g^2) \cos \varphi \sin \varphi (A'_{ix}{}^2 - A'_{iy}{}^2) \tan 2\alpha \quad (7)$$

Here A'_{iz} , A'_{ix} , and A'_{iy} are the hyperfine coupling constants measured along the principal axes of the g tensor, and α defines the angle between the x axes of the principal A and the g tensors (see Figure 2). The A'_{iz} , A'_{ix} , and A'_{iy} are then related to the principal tensor elements A_z , A_x , and A_y by the equations $A'_{iz} = A_z$, $A'_{ix}{}^2 = A_x^2 \cos^2 \alpha + A_y^2 \sin^2 \alpha$, and $A'_{iy}{}^2 = A_x^2 \sin^2 \alpha + A_y^2 \cos^2 \alpha$. Inspection of the eq 5–7 reveals

Table I. Assessed Parameters of Phenyl Radical^a

Assign- ment	No. of protons	X	Y	Z	α , deg	A_{iso}
<i>g</i> tensor		2.0014 ± 0.0005	2.0023 ± 0.0005	2.0034 ± 0.0005		
<i>A</i> (<i>ortho</i>) ^b	2	21.9 ± 0.1	15.4 ± 0.1	14.9 ± 0.1	7.5 ± 1.0^c	17.4 ± 0.1
<i>A</i> (<i>meta</i>) ^b	2	6.6 ± 0.1	6.1 ± 0.1	5.0 ± 0.1	40 ± 3^c	5.9 ± 0.1
<i>A</i> (<i>para</i>) ^b	1	2.0 ± 0.1	2.5 ± 0.1	1.2 ± 0.1		1.9 ± 0.1

^a The axes *x*, *y*, and *z* are those defined in Figure 2. ^b Coupling constants are given in gauss. ^c The value of α is given for the proton in the right side of the molecule; see Figure 2.

that, as far as the apparent spectrum is concerned, the only term which causes a departure from the "normal" behavior is the last term in eq 7 involving $\tan 2\alpha$. Furthermore, for a pair of structurally equivalent protons situated symmetrically about the principal axes of the *g* tensor, e.g., the *ortho* or the *meta* protons in phenyl radical, this last term would be the same in magnitude but opposite in sign for each. Consequently, the resonance position of certain hyperfine components of phenyl radical, namely those in which both protons in each pair of equivalent protons have the same spin state, would not be affected very much by the last term in eq 7, if its magnitude is small compared to the sum of the first two terms. The latter condition is usually met when the magnitude of the isotropic coupling part is large compared to the anisotropic part of the hyperfine interaction. This would certainly be the case with all the protons in a phenyl radical if it were a σ radical. Hence, identification and analysis of the signals arising from these particular hyperfine components should lead to direct assessment of A'_x and A'_y as well as A'_z of these protons. In a spectrum whose anisotropy is governed more by the anisotropy of the hyperfine interactions than that of the *g* tensor, these signals can be easily recognized in the outer part of the spectrum. A computer simulation program based on eq 1-3 and 5-7 should then be able to reproduce the outer part of the spectrum with these parameters alone. The magnitude of the angle α can then be determined through a method of successive trials, since the program should produce correctly not only the outer region of the spectrum but also the central part when supplied with the proper value of α .

The theoretical spectra compared with the observed ones in the following section are simulated by a computer program which allows the rotation of the principal axes of the hyperfine tensors in the manner described above. The input data to the program are the elements of the principal *g* tensor, the diagonal elements of the hyperfine tensors of all the protons measured in the direction of the principal axes of the *g* tensor, and the angles, α , specifying respectively the orientation of each principal hyperfine tensor relative to the *g* tensor.

Results

Figure 3A shows the spectrum obtained at 4°K in an argon matrix in which phenyl iodide had been photolyzed. Although the spectrum is extremely complex, its reproducibility under various experimental conditions led us to conclude that, except for the weak quartet signal due to methyl radicals, the entire spectrum arises from the phenyl radical. Given in Table I are the elements of the principal *g* tensor, the hyperfine coupling terms, and the orientation angles of their

principal axes assessed from this spectrum by the method described in the preceding section. It should be emphasized that the hyperfine coupling terms given in the table are those measured along the principal axes of the *g* tensor. The isotropic coupling constants calculated by assuming positive signs for all the assessed coupling terms are also listed in the table. The validity of this assumption and the bases for the assignment of the assessed tensors to the respective

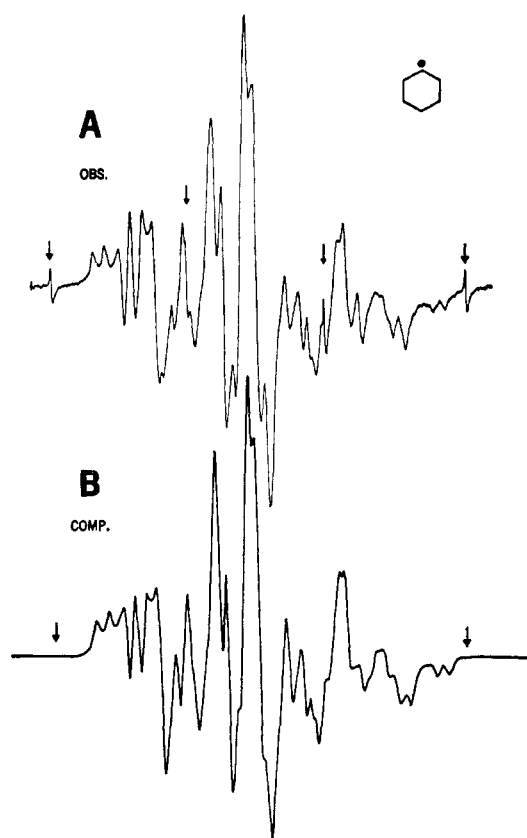


Figure 3. (A) ESR spectrum of phenyl radical in argon matrix at 4°K. The arrows indicate the quartet due to methyl radical. The microwave frequency was at 9.436 GHz. (B) Spectrum simulated based upon the assignment given in Table I.

protons are discussed in the following section. The computer-simulated spectrum (Figure 3B) based upon these assessments is in excellent agreement with the observed spectrum. Figure 4A shows the spectrum obtained from *para*-deuterated phenyl radical. Figure 4B is the spectrum simulated using the set of data in Table I taking appropriate account of the *para*-deuteron substitution. The excellent agreement between the observed and the simulated spectra strongly sub-

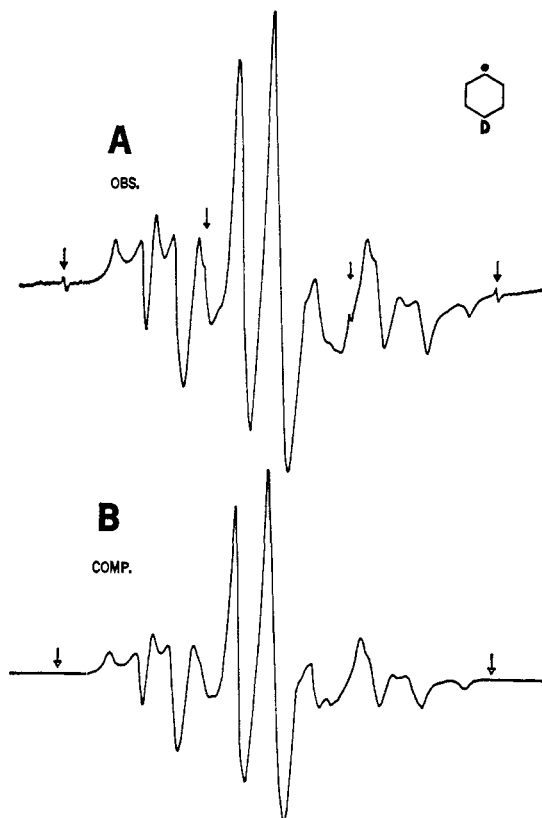


Figure 4. (A) ESR spectrum of *para*-deuterated phenyl radical in argon matrix at 4°K. The arrows indicate the quartet due to methyl radical. The microwave frequency was at 9.436 GHz. (B) Spectrum simulated based upon the assignment in Table I with the necessary adjustment for the isotopic substitution at the *para* position.

stantiates the accuracy of the assignment given in Table I. To illustrate the process through which the magnitude of the angle α has been determined, the computed spectra of *para*-deuterated phenyl radical based upon the set of g tensor and the coupling constants identical with those used in Figure 4B, but with different values of α for *ortho* protons, are shown in Figure 5.

Discussion

In an agreement with the conclusions reported earlier, the hyperfine interaction coupling constants given in Table I are most compatible with the assignment of phenyl radical to a σ radical. In particular, the large and very anisotropic coupling interaction with one pair of equivalent protons can be best understood if it were assigned to the interaction of the unpaired electron mostly localized in the nonbonding σ orbital centered at the 1 carbon with the *ortho* protons. As is well-known, a hyperfine interaction can be considered in two parts, the isotropic interaction, A_{iso} , and the orientation dependent part, A_{dip} .

$$A_{hfp} = A_{iso} + A_{dip} \quad (8)$$

where

$$A_{iso} = \frac{8\pi}{3} g_e \beta_e g_n \beta_n |\Phi(0)|^2$$

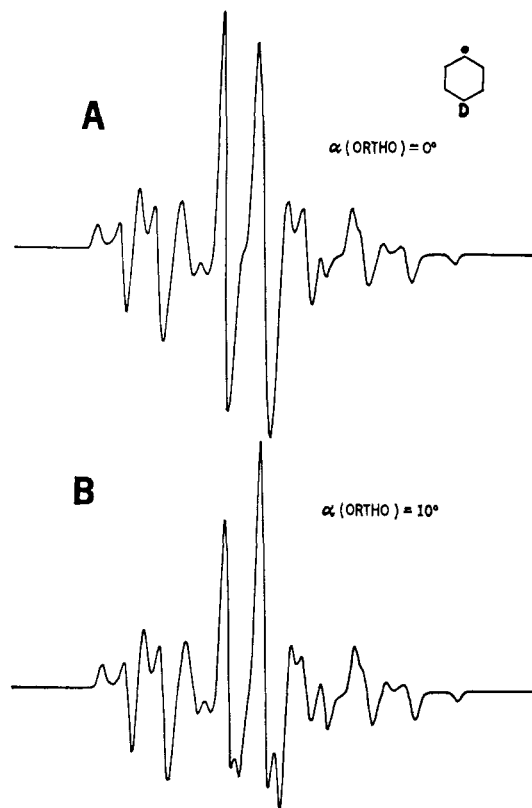


Figure 5. Computed spectra of *para*-deuterated phenyl radical using the set of parameters identical with that used for Figure 4B, except that (A) $\alpha(\text{ortho}) = 0^\circ$, and (B) $\alpha(\text{ortho}) = 10^\circ$.

and

$$A_{dip} = g_e \beta_e g_n \beta_n \left\langle \Phi \left| \frac{1 - 3 \cos^2 \eta}{r^3} \right| \Phi \right\rangle \cong |g_e \beta_e g_n \beta_n| \left\langle \frac{1}{r^3} \right\rangle (3 \cos^2 \theta - 1)$$

Here r is the distance between the unpaired electron and the magnetic nucleus concerned, and η is the angle between this line and the externally applied magnetic field. The latter approximation for A_{dip} applies when the unpaired electron can be considered localized at a point away from the nucleus; θ then defines the angle between the line connecting this point to the nucleus and the magnetic field. These equations then predict the following. If the signs of the isotropic coupling constants are positive for all the protons in phenyl radical, the smallest coupling constant should be observed for all the protons when the magnetic field is perpendicular to the molecular plane; the largest coupling constant should be observed for the *ortho* protons when the field is in the x direction (see Figure 2), and the largest coupling constant with the *para* proton when the field is in the y direction. It was from these considerations and the number of protons of each type that the final assignment of the observed coupling tensors to the respective protons, the assessment of the signs of the isotropic coupling constants, and the establishment of the orientation of the principal g -tensor axes relative to the molecular structure were made.

The result of our independent EHT molecular orbital calculation also shows that the phenyl radical is a σ radical. It places approximately 2 and 70% of the spin

density at the 2s and 2p_y orbitals of the 1 carbon, respectively, and 5% each at 2p_y orbitals of the carbon atoms at the *ortho* and *meta* positions. McConnell and Strathdee⁸ have developed an analytical expression for evaluating the dipolar term, A_{dip} , in eq 8. If one assumes the "benzene structure" for a phenyl radical, and the distribution of its unpaired electron given by this EHT molecular orbital calculation, usage of their expression gives the following "dipolar" coupling constants with the *ortho* protons. $A_{\text{dip},x} = +4.5$, $A_{\text{dip},y} = -1.5$, and $A_{\text{dip},z} = -3.0$ G. These are to be compared with the observed values of $A_{\text{dip},x} = +4.48$, $A_{\text{dip},y} = -1.99$, and $A_{\text{dip},z} = -2.49$ G. As for the magnitude of the isotropic coupling constants, the values determined by the present study are compared in Table II with those calculated by the method of hyper-

Table II. Comparison of the Observed Isotropic Coupling Constants with the Calculated Values

	Obsd	Calculated		
		Hypercon method	EHT method	SCF-INDO method
<i>A</i> (<i>ortho</i>)	+17.4	+23.3	+12.5	+18.7
<i>A</i> (<i>meta</i>)	+5.9	+4.2	+5.3	+6.1
<i>A</i> (<i>para</i>)	+1.9	+17.9	+11.0	+3.9
Reference	This study	3	4	5

conjugation,³ the EHT method,⁴ and an SCF method, respectively.⁵ It clearly reveals a danger of applying the result of a closed-shell calculation to an open-shell, σ -radical system. It is particularly interesting to note that the eigenfunction of the half-filled orbital of an SCF calculation⁹ is very similar to that obtained by the EHT method. The small coupling constant with the *para* proton is the result of the "spin polarization" of the lower filled orbitals.

It has been shown that, for a nondegenerate ground state, the deviation of the g value along a given principal axis, say " i ," from that of a free electron can be given by¹⁰

$$\Delta g_i = -2\lambda \sum_{n \neq 0} \frac{\langle 0 | L_i | n \rangle \langle n | L_i | 0 \rangle}{E_n - E_0} \quad (9)$$

Here λ is the spin orbit coupling constant of the relevant atom, L_i is the angular momentum operator

(8) H. M. McConnell and J. Strathdee, *Mol. Phys.*, **2**, 129 (1959).

(9) We are indebted to Dr. Patricia Clark for showing us the result of her SCF-INDO calculation of phenyl radical.

(10) M. H. L. Pryce, *Proc. Phys. Soc. (London)*, **A63**, 25 (1950).

along the i axis, and $E_n - E_0$ gives the energy separation between the ground state $|0\rangle$, and the other state, $|n\rangle$, into which the unpaired electron or "positive hole" may be promoted *via* a spin-orbit coupling interaction. For a hydrocarbon molecule where only the 1s orbitals of hydrogen atoms and 2s and 2p orbitals of the carbon atoms need to be considered in its molecular orbitals, evaluation of eq 9 in terms of the LCAO-MO scheme is straightforward.¹¹ When all the two-centered integrals are neglected, it yields

$$\Delta g_i = -2\lambda \sum_{n(\neq 0)}^{\text{MO's}} \frac{\sum_{\alpha}^{\text{C atoms}} (C_{\alpha k}^n C_{\alpha j}^n + C_{\alpha j}^n C_{\alpha k}^n)^2}{E_n - E_0} \quad (10)$$

The subscripts i , j , and k stand for the three principal axes of the g tensor, and $C_{\alpha k}^n$, for instance, is the coefficient of the 2p_k orbital of the α th carbon atom in the n th molecular orbital. A subroutine was written to the EHT program which would evaluate expression 10 from the eigenfunction and eigenvalue output of the main program. It gave, following the subscript notation given in Figure 2

$$\begin{aligned} \Delta g_x &= -0.458\lambda \\ \Delta g_y &= 0.0 \\ \Delta g_z &= +0.378\lambda \end{aligned} \quad (11)$$

The value of the spin-orbit coupling constant of carbon atom may be assessed from the known atomic energy levels of carbon.¹² Thus $\lambda_{\text{C-atom}} = 0.00188$ eV. Substitution of this value into the expressions given above yields $g_x = 2.0014$, $g_y = 2.0023$, and $g_z = 2.0030$ in a reasonable agreement with the observed values. The ground state of phenyl radical is 2A_1 , with a $\pi^6 n^1$ electronic configuration. Analysis of the calculation shows that the dominant contribution to the negative g shift in the x direction comes from the b_1 , antibonding π orbitals, and the largest contribution to the positive g shift in the z direction comes from the b_2 bonding σ orbitals.

Acknowledgment. The authors express their appreciation to Messrs. W. D. Bird and D. W. McNeil for their invaluable assistance in obtaining the experimental result.

(11) E. B. Whipple and P. H. Kasai, unpublished result. See also P. W. Watkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., Amsterdam, 1967.

(12) C. E. Moore, "Atomic Energy Levels," Vol. 1, National Bureau of Standards, Washington, D. C., 1949.