I. ANALYSIS OF THE SPECTRA

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ABSTRACT

Several ortho-substituted radicals of the benzhydryl type and a variety of diaryl ketyls have been studied through the nuclear hyperfine structure of their electron spin resonance spectra. A strong similarity is found between the spectra of a given ketyl and its hydrocarbon analogue. This suggests that when ketones are reduced, a very tight ion pair is formed between the ketyl anion and its cation. Although the coupling constants of the protons vary with different reducing agents, larger variations are observed when bulky groups are substituted into ortho positions. These larger changes are attributed to a forced internal rotation of the phenyl rings. The distortion results from the steric repulsion between the ortho groups. The effect of 'buttressing' of ortho methyl groups is also studied. Deuterium and ¹³C substitutions have been effected in some of the compounds.

INTRODUCTION

The underlying purpose of this study was to determine the effect that ortho substituents have on the proton hyperfine structure of the electron spin resonance (e.s.r.) spectra of various compounds with a benzhydryl skeleton. Molecular models of the parent compound, diphenylmethyl, show that two of the four ortho protons are in positions which should give rise to large steric repulsions when the two rings are held in a coplanar configuration. The other pair of ortho protons is not constrained in this way, and steric interactions should not occur unless the carbon-carbon bond angles are severely distorted from the normal sp² hybrid angles of 120°. For convenience in the following text, the sterically hindered pairs of ortho groups will be termed the "inner" groups and those at the sterically inactive positions the "outer" groups. This distinction is unique for the diarylmethyl radicals, because for triphenylmethyl derivatives both inner and outer groups are sterically involved, whereas for the benzyl radical neither of the ortho protons is particularly effective in introducing steric repulsions.

The e.s.r. spectrum of triphenylmethyl may be analyzed in terms of six equivalent or tho protons, six meta protons, and three para protons (1). The implied threefold axis of symmetry would result if the steric strain at the ortho sites were relieved by symmetrical rotation of the three phenyl rings about the central bonds, resulting in a propellor configuration. Nuclear magnetic resonance (n.m.r.) studies of the carbanion and carbonium ions of diphenyl and triphenylmethyl derivatives support this conclusion because similar shifts are found for equivalent protons in each ring of these compounds (2, 3). The optical spectra of the ions also suggest a symmetrical structure for both diphenyl and triphenyl derivatives. The inferences here are less clear-cut, and the suggestion has been made that the optical spectrum results from transitions which do not involve all of the phenyl rings (4). This conclusion is based mostly on the lack of a bathochromic shift due to extension of conjugation in proceeding from the monophenyl to the triphenyl ions of this series. It has been shown theoretically (5) that this behavior is to be expected, and calculations

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based on the transition intensities (6) appear to favor a structure in which all rings present contribute equally to the conjugation of the molecule.

It will therefore be assumed that the stable form of the radicals under consideration is of the form depicted in Fig. 1*a* rather than the unsymmetrical rotomer in Fig. 1*b*. Although this assumption leaves the question of the possible non-equivalence of the ortho substituents, the matter is not critical to the following discussion.



FIG. 1. Angular distortions of diphenylmethyl radicals. (a) Symmetrical, both rings rotated; (b) unsymmetrical, one of the four possible rotomers. The symbol X represents any sterically hindering group.

As can be seen from Fig. 1*a*, as the size of the ortho group, X, is increased, the additional steric strain may be partly relieved by rotation about the central carbon-carbon bonds. This will decrease the conjugation between the central carbon and each of the rings, with the result that the odd electron density will be confined more closely to the central position. In the extreme case of very large hindering groups, the phenyl rings would be held perpendicular to the plane of the central group. In all naivety it could be assumed that the unpaired electron would then be completely localized in the 2p orbital of the extracyclic carbon atom. According to the well-known formulation of McConnell (7), the coupling constant (a_i) of the *i*th aryl-type proton is given by the relationship

$$a_i = \rho_i Q(\mathbf{H})$$

where ρ_t is the spin density at the adjoining sp² hybridized carbon atom and Q(H) is a constant of the order of 25 Oe. For the localized electron considered above, $\rho = 1$, so the hyperfine splitting of the lone proton on this central carbon atom would be ~ 25 Oe. There would be no hyperfine splittings from the ring protons. Smaller hindering groups would give smaller internal rotations, and greater delocalization of the unpaired spin density. Thus the lone proton splittings would decrease, whereas the contributions of the ring protons to the hyperfine spectrum would increase as the coplanar configuration is approached.

Unfortunately, the hydrocarbon radicals corresponding to diphenylmethyl dimerize more or less completely, unless wholly substituted in the ortho positions by fairly bulky groups (8). To obtain spectra for compounds with smaller hindering groups, the study has been extended to include the ketyls of the analogous substituted benzophenones, with which similar effects might be expected to occur.

Kinetic studies on the racemization of optically active biphenyls (9) have indicated that the size of a hindering ortho group may be effectively increased by "buttressing" this

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group with bulky substituents in the meta position. As applied to the situation under consideration here, 'buttressed' ortho groups should lead to a decrease in the ring-splitting constants by increasing the internal angle of rotation. Accordingly, compounds of this sort have been included in the present study.

EXPERIMENTAL

A variety of methylated and methoxylated benzophenones has been prepared. These appear in Table I, along with the source, or method of preparation, and the shorthand notation which will be used in this paper. The hydrocarbon radicals were obtained from the corresponding ketones by reduction to the carbinol with lithium aluminium hydride in ether solution. This carbinol was treated with dry HCl gas in acetyl chloride. On completion of the reaction, the solvent was removed on a vacuum line and replaced by toluene, along with a small amount of triethylamine (10). The chloride was reduced with amalgamated silver.

In addition to the precursors listed in Table I, the isotopically labeled species 4,4'-dideutero-2,3,6.2',3',6'octamethylbenzophenone (i.e. dideutero diduryl ketone or DDK- d^2) and centrally substituted ¹³C diduryl ketone (DDK-¹³C) were prepared. Durene was dibrominated in chloroform at -10 °C and partially lithiated with *n*-butyl lithium in ether. Excess D₂O was added and the resulting monodeuterobromodurene isolated. The magnesium grignard of this material was then prepared in tetrahydrofuran. Half of it was carbonated with dry ice, hydrolyzed, and treated with thionyl chloride. To this product was added the remaining grignard, hydrolysis giving the desired ketone.

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Diphenyl ketones and precursors of the diphenylmethyl radicals

Compound	Symbol	Source	Melting point (uncorrected) (°C)
Benzophenone (diphenyl ketone)	DPK	Eastman	
(ditolyl ketone)	DTK	Eastman	
(dixylyl ketone)	DXK	Reference 8	127-129
(dimesityl ketone)	DMK	Reference 8	135–138
(diduryl ketone)	DDK	Reference 8	153-155
4,4'-Dimethoxybenzophenone (dianisyl ketone)	DAK	MCB*	
2,6,2',6'-Tetramethoxybenzophenone (tetramethoxydiphenyl ketone)	ТМК	Reference 12	204-205

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 13 C substitution was effected with gaseous 13 CO₂ from 55.9 atom % Ba 13 CO₃ (Isomet Corporation, Pallisades, N.J.) and concentrated sulfuric acid, using a vacuum-line preparation. The gas was frozen in a thickwalled pyrex cell containing normal duryImagnesium bromide in tetrahydrofuran. This cell was then sealed off from the vacuum line and heated for 2 days on a steam bath. Hydrolysis of the product gave tetramethyl benzoic acid-¹³C, which could then be treated as above to give DDK-¹³C.

The spectra of the radical species were obtained with a TE_{011} tunable cylindrical cavity in a modified Strand Labs X-band spectrometer and a Harvey Wells magnet (L-128) system. Field modulation was at 6.2 kc/s. The magnetic field sweep had a nonlinearity of about a half a percent so that after each spectrum was run, the field was retraced at fixed microwave frequency and the spectrum of peroxylamine disulfonate superimposed on the sample spectrum. The hyperfine constants were determined from the averaged values of the field standard values. Low temperature spectra were obtained in a similar manner by the standard technique of blowing cold nitrogen gas past the sample in a quartz dewar insert set in the cavity. The ketyl spectra reported were obtained at room temperature, in dimethyoxyethane, whereas the hydrocarbon radicals spectra were taken in toluene at -60 °C. Electrolytic reductions were done in acetonitrile solution, with tetra *n*-propylanimonium perchlorate as the supporting electrolyte and tungsten wire for the electrodes. The samples were prepared under vacuum. Three metals sodium, potassium, and calcium were also used as reductants. The first two were distilled into the system under vacuum by standard techniques (11), whereas calcium was cleaned as well as possible with emery paper and flamed thoroughly after introduction to the sample cell. The reductions with calcium were very slow and took several days at low temperatures, in some cases.

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RESULTS

The analyses of the hyperfine spectra result in the coupling constants appearing in Tables II and III. The notation which is used follows from the notation used for the kctones in Table I. For example, DMKK-e is taken to mean 'dimesitylketone ketylproduced electrolytically' and DMKK-Ca is the ketyl resulting from calcium metal reduction. DMM stands for dimesityl methyl, the neutral hydrocarbon species.

TABLE II	Π
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Coupling constants of the protons at various ring positions for the ketyls of the diphenyl ketone series of compounds

		Coupling con	stants (Oe)	
Compound	<i>a</i> _p	<i>a</i> _o	a_m	a _{metal}
DPKK-Ca DPKK-Na DPKK-e DTKK-Ca DTKK-Na DTKK-K DTKK-e DAKK-e TMKK-e DXKK-Ca DXKK-Ca	$\begin{array}{c} 3.46\\ 3.45\\ 3.44\\ 3.54\\ 3.53^*\\ 3.59^*\\ 3.60^*\\ 3.54^*\\ 0.29^{\prime}\\ 3.57\\ 2.52\\ 5.52\end{array}$	$\begin{array}{c} 2.77\\ 2.60\\ 2.55\\ 2.78\\ 2.80\\ 2.68\\ 2.67\\ 2.81\\ 2.86\\1\\ 1.49^*\\ 1.50^*\\ \end{array}$	$\begin{array}{c} 1.01\\ 0.88\\ 0.86\\ 0.95\\ 1.04\\ 0.98\\ 0.97\\ 1.03\\ 0.97\\ 0.82\\ 1.07\\ 0.95\end{array}$	1.16 0.24 0.25
DXKK-NA DXKK-e DMKK-Ca DMKK-Na DMKK-K DMKK-e DDKK-e	2.50 2.50 2.72 2.54* 2.62* 2.62* 2.89* 2.34	1.39^* 1.63^* 1.49^* 1.59^* 1.60^* 1.63^* 1.63^* 1.97^*	$\begin{array}{c} 0.93\\ 0.93\\ 0.85\\ 1.07\\ 1.02\\ 1.02\\ 0.93\\ 1.42* \end{array}$	

*Methyl protons. †Methoxyl protons.

TABLE III Splitting constants for methyl-substituted diphenyl methyl radicals

Compound	Coupling constants (Oe)			
		<i>a</i> _o	a_m	alp
DXM	3.27	2.18*	1.47	16.1
DMM DDM	3.38* 2.80	2.15^{*} 3.04^{*}	$1.45 \\ 2.16^*$	$15.7 \\ 15.9$

*Methyl protons.

The precise analysis of these compounds becomes very difficult and less certain as the number of ring substituents increases because of the proliferation of protons resulting from multiple methylations. To simplify the process the assumption has been made that if the substitution of methyl or methoxyl groups is made in sterically inactive positions, these substitutions do not materially change the spin distribution in the conjugated system, so that the magnitude of the splitting constants does not change from the order found in the parent ketyl of benzophenone. This latter spectrum is readily analyzed as being due to a triplet and two quintet splittings. The largest splitting is that of the triplet, and is due to the pair of para protons. This assignment is verified in the para-methylated and para-methoxylated derivatives of benzophenone, DTKK and DAKK, where the

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triplet has been replaced by septets in both cases. In the spectrum of DAKK, the methoxyl splittings are very small, whereas for DTKK the methyl proton splittings are only slightly larger than the ring protons that have been replaced. The remaining two quintet splittings are due to the ortho and meta protons and do not change markedly as a result of either of these substitutions. This fact lends support to the contention that the spin densities are not markedly changed by substitution at unhindered sites. Alternatively, these substitutions produce only small perturbations to the ground state wave functions. It also appears that freely rotating methyl groups give splitting constants a_i (Me) which follow the approximate relationship (13)

$$a_i(\mathrm{Me}) = \rho_i Q(\mathrm{Me}),$$

where Q(Me) is but slightly larger than the value for ring protons (25 Oe) and ρ_t is the unperturbed spin density at the substitution site. Although on somewhat doubtful theoretical ground (14) this formulation will be assumed to hold in the present work.

It remains to be decided which of the two quintet splittings of DPKK is due to the ortho protons. If the spectrum of TMKK is considered, a large triplet splitting is obtained. Each line is further split by a single quintet. The ortho protons have been replaced by methoxyl groups from which no splittings were found. Contributions from these protons were unresolved within the rather broad lines (~ 0.4 Oe) of the absorption spectrum. The triplet splitting is similar to that of the para protons in DPKK, and the remaining quintet splitting corresponds to the smaller of the quintet splittings in DPKK. This latter structure is therefore assigned as due to the meta protons, and the larger quintet splittings in DPKK as due to the ortho protons. Thus the magnitudes of the splittings fall in the order $a_p > a_o > a_m$ for DPKK and its derivatives. This order does not appear to change when the ortho positions are completely methylated. The 13 line progressions due to these protons are quite apparent in the spectra of the ketyls of both DMK and DXK. Since the spectrum of DXKK-Ca is fairly well resolved it is possible to locate the subsidiary triplet and quintet due to para and meta ring protons. In the case of DMKK-Ca, essentially the same meta quintet splitting is found, along with the expected para methyl proton septet. Again the methyl proton splitting is only slightly larger than that of a ring proton at the same position. As with DTKK (compared to DPKK), para methylation would not be expected to alter the spin distribution in the ring nor effect the 'steric size' of the ortho group.

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The spectrum of DDKK was not so amenable to the above cut-and-try method of analysis. The lines which appear in the spectrum may be interpreted in terms of two sets of 12 equivalent protons. The outer components of the triplet due to the para protons are of relatively lower intensity and appear to coincide with the progression of lines arising from the central component. As a result of this overlap a para proton coupling constant cannot be obtained except from a consideration of the relative intensities of the lines. Since the coincidences are probably not exact, this procedure would not give rise to an unequivocal assignment. On the other hand the ortho and meta methyl proton splitting constants must be considered anomalously large. This may result from the fact that these buttressed methyl groups interact very strongly; they may be interlocked in such a way as to allow only a concerted motion or may even be twisted out of the plane of the phenyl ring. In either case a different coupling constant from that obtained for freely rotating groups might be expected. For this reason, the para proton coupling constant would appear to be a more satisfactory index of the spin densities in the ring than would be the more readily available methyl splittings. Accordingly the para-deuterated DDKK was prepared.

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The spectrum of this derivative was considerably different than that of the normal ketyl. The envelope of the hyperfine lines was symmetrical and bell shaped in the former case, but serate in the latter. The 0.32 Oe spacing between adjacent lines was the same in both spectra. A number of possibilities exist. Firstly the deuterium splitting (1:2:3:2:1) may be very small compared to the linewidth. In this case one would expect the same symmetrical spectrum, or a 1:2:1 repetition of this symmetrical spectrum, for the normal derivative. Neither will give the characteristic spectrum observed. On the other hand, if the deuterium splitting corresponds to the 0.32 Oe interval (or a multiple of it), the symmetrical spectrum could result from the fivefold repetition of the basic 169 line pattern due to the ortho and meta methyl protons, with the coupling constants cited. Furthermore the proton coupling constant would be expected to be about $6\frac{1}{2}$ times the 0.32 Oe splitting, or an integral multiple of it. With this information it was possible to select the 'most likely' para proton coupling constant which appears in Table II. The ortho and meta coupling constants are assigned so that $a_o > a_m$ and correspond to the order found with the other compounds, but the reverse assignment may in fact be appropriate.

The spectra of the neutral hydrocarbon radicals are characterized by a large doublet splitting due to the lone central proton. However, the splitting is not so large as to prevent overlapping of the hyperfine components from the doublet states. This fact, along with a lack of symmetry between the high field and low field side of the spectrum, made the location of the central lines of the two halves of the spectrum rather uncertain. A striking similarity is to be observed between the intensity pattern of the ketyls and that of the corresponding neutral radicals. In fact the latter spectrum looks very much like the sum of two ketyl spectra displaced by the doublet separation. Comparison of the ketyl spectrum with that of the hydrocarbon radical leads to an assignment of the doublet splitting that is considerably more trustworthy than would have been obtained from the hydrocarbon data alone. The essential difference between the spectra of the two types of compound appears to be only in the doublet splitting and the fact that the coupling constants of the hydrocarbons are slightly larger than those of the ketyls. The assignments for the neutral radicals are set out in Table III. The same procedure was used in the case of DDM as was used for the corresponding ketyl; the para coupling constants were obtained from the comparison of the dideutero and the normal compound.

The lack of symmetry between the high and low field sides of the spectrum mentioned above was found in several of the cases studied. The situation with regard to the alteration of line intensities in these compounds is rather more difficult to cope with than in simpler spectra, where g value and residual dipolar anisotropies or intermolecular motional effects (15) serve to broaden the lines and so reduce the peak-to-peak amplitudes. The further complications arise because most of the lines observed result from the overlap of several transitions between different nuclear substates. The resulting line depends therefore not only on the width of the composite members but also on the degree of overlap. This complex matter is not considered further at present. However, to compare computed and observed spectra, an attempt was made to reduce intensity variation effects in the observed spectra by averaging the high and low field peak heights. This procedure will not yet give a true representation of the relative peak heights since these quantities will still be dependent upon the degree of superposition, and upon the intensities of the various components giving rise to the observed line. Plotted spectra corresponding to the suggested coupling constants have been drawn up for each of the compounds studied and have been compared to the averaged experimental intensities. Quite good agreement is found. While the computed intensities are generally somewhat higher than those observed, there is extremely

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good agreement between the intensity patterns. The same procedure has been carried out for other assignments which correspond to other possible molecular arrangements. For instance, spectra have been computed for the situations where there is coupling in one ring only, or in two rings unequally, or where different inner and outer group splittings are assumed. In no case was the fit with the experimental data nearly as good as given by the results cited, nor was such reasonable internal consistency of the results obtained.

One further observation may be made about the spectrum of DMM. The spectrum of this compound and its analysis agree with that reported by Chestnut and Sloan (16) and, apart from intensity alteration effects, agree very closely with the calculated values. The line widths in this spectrum are of the order of 0.08 Oe, and in none of the lines is there the slightest indication of a splitting of the ortho lines due to differences between the inner and outer groups. It is also apparent that the methyl groups in this compound rotate freely, even in the sterically restrictive sites occupied by the inner groups.

The ¹³C splitting for DDM-¹³C was found to be 24.8 Oe, which compares very closely with the value of 24.5 Oe obtained by Adam and Weissman (17) for DMM-¹³C. The spectrum of the corresponding diduryl ketyl was also taken, but although the resulting spectrum was different from the normal material, it proved impossible to analyze. However, from the increased width of the spectrum, an upper limit of some 15 Oe can be placed on the ¹³C coupling constant in this compound.

DISCUSSION

As was outlined in the Introduction, it should be possible to assess gross changes in the molecular structure of diphenylmethyl radicals by a study of the proton hyperfine structure. In particular, substitution into the ortho positions should result in an increase in spin density at the central position and a decrease in the total density in the rings as a result of the decreased electronic coupling between the central position and the rings. It is hoped that the substitutions themselves do not produce changes in spin distribution and electron-proton interactions which are sufficient to mask any effects which are due to the steric factors alone. Since the spin density at the central position would be the least affected by perturbations within the rings, the lone proton splittings, and, to a lesser extent, the ¹³C splittings, should therefore be the most reliable index of what is happening in the molecule as a result of chemical substitution. When the three compounds DXM, DMM, and DDM are compared on this basis, little change is observed in the lone proton splitting. The ¹³C coupling constants for DMM and DDM are also very similar. One is forced to conclude that neither p-methylation nor buttressing of the sterically hindered groups produces much change in the interannular orientation. The ring densities for DXM and DMM are also quite similar. On the other hand DDM has coupling constants which show that considerable changes have occurred; apparently the buttressed groups affect each other much more than they do the remainder of the molecule. Although the para coupling constant decreases, it is suggested in this case that this results from distortion of the phenyl ring rather than from any large change in the dihedral angles of the ring relative to the central position.

The hydrocarbon results cannot be directly compared to those obtained with the ketyls because of the presence of the oxygen function and its possible interaction with the outer groups. With the absence of the lone proton one has to rely on the coupling constants of the ring substituents to indicate the distribution of spin within the ketyl radical. If xanthone ketyl (XKK) is considered in addition to the remaining examples of Table II, then a series of compounds is obtained which vary considerably in the disposition of the

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two rings bonded to the ketone function. Xanthone ketyl (XKK-Ca) has splitting constants $a_o \approx a_p \approx 3.9$ Oe, and should be approximately planar by virtue of the oxygen bridge between the two rings. For DPKK-Ca, the value for a_p has dropped to 3.46 Oe, and for DXKK-Ca, to 2.52 Oe. The value of 2.34 Oe obtained for the buttressed form may or may not be real, since the coupling constant anomalies parallel those of its hydrocarbon analogue, which is also suspect. In any case this is the order predicted in the Introduction; as a result of steric repulsive forces, the odd electron population in the rings has decreased, planar > ortho hydrogens > ortho methyls. Whereas the meta coupling constants do not seem appreciably changed, the ortho values show a parallel decrease: XKK (3.9 Oe) > DPKK (2.77 Oe) > DXKK (1.49 Oe).

Attention must be drawn to the DAKK spectrum. The para coupling constant shows an increase over DPKK even though the ortho hydrogens have been replaced by methoxyl groups. It is not known whether this is due to a spin redistribution caused by the multiple substitution, or whether methoxyl has an intrinsically small steric effect in this particular situation where the methyl groups can get out of each other's way.

From the results in Table II, it can be seen that for each of the ketone samples for which the reducing agent is sodium, hyperfine coupling to that nucleus (I = 3/2) occurs. It is much smaller in the orthomethylated compounds than in the case of DPKK. The reverse situation would normally have been expected if the metal ion is associated with the oxygen atom which is, in turn, in a region of relatively higher spin density as a result of ortho methylation. This suggests that the ortho methyl groups interfere with the formation of a 'normal' bond between the metal and the oxygen atom. While the presence of metal nuclear coupling is strongly suggestive of a tight ion pair, there must be considerable difference in the structure of these complexes to give the order of magnitude variation which is observed. A further peculiarity may be observed in a comparison of the magnitudes of the splittings for various metals. Other recent work (18) reports lithium splittings for some of these compounds. For DPKK, $a_{Ll}/a_{Na} = 0.37$, whereas for DTKK, $a_{Ll}/a_{Na} =$ 0.36. The ratio of the nuclear moments $\mu_{L1}/\mu_{Na} = 1.47$. Similarly from Table II, $a_{\rm Na}/a_{\rm K} = 4.8$, whereas $\mu_{\rm Na}/\mu_{\rm K} = 5.68$ for the same compounds. Thus the more electropositive elements have relatively higher spin densities, all other factors constant. Arguments based on relative ionic character for the metal-oxygen bond, or the length of the bond, and so on, all appear to favor a higher spin density with the more electronegative metal atoms. Sodium also has a relatively larger coupling constant compared to magnesium (19).

A further trend may be noticed within the sequence of splitting constants observed for a particular ketone. The values in Table II may be arranged in the arbitrary order $N(iPr)_4^{1+}$, Ca^{2+} , Na^{1+} , K^{1+} (which probably corresponds to the ionization potentials). For the metal reductions, the ring proton coupling constant for a given ketone decreases, or at worst remains unchanged, in the above order. On the other hand if the substituent is a methyl proton, the coupling constants increase in the same sequence.

Finally, reference should be made to the observation that in the spectra studied no evidence has been found which would indicate that there is any difference between the coupling constants of the inner and outer groups. Furthermore no differences appear to exist between the protons of each methyl group in these sterically restricted situations. Whereas it is reasonable to suppose that these methyl groups are free to rotate about the carbon-carbon axis even in severely hindered environments, there is no simple explanation of the apparent equivalence of the different groups. They are not related by symmetry, and exist in very different spin localities. This is especially true of the ketyls, where any

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spin density on the oxygen atom would almost certainly be felt by the outer group. On the other hand the protons of the inner group are held close to the spin concentration of the adjacent ring. It is possible that these different sites may exchange places with sufficient rapidity to average out any field differences. The lack of high and low field symmetry may be a token of such an internal motion. The possibility of such an oscillation occurring at low energies of activation will be discussed in the second paper of this series.

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