THE UNIVERSITY OF CALGARY

ELECTRON SPIN RESONANCE STUDIES OF THIOCARBONYL

ANION RADICALS

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

CALGARY, ALBERTA

SEPTEMBER, 1971

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Electron Spin Resonance Studies of Thiocarbonyl Anion Radicals" submitted by Leon J. Aarons in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

The temperature dependence of the electron spin resonance (esr) spectra of a series of sodium reduced thiones is reported. The thioketyls thiobenzophenone, pp'-dimethoxythiobenzophenone, xanthene-9-thione, thioxanthene-9-thione, and their ketone analogues have been studied. Several show temperature dependent sodium hyperfine structure near room temperature, but dissociate at lower temperatures to give spectra of thioketyl anions with no sodium coupling but with markedly different g values. Ring proton hyperfine splittings are found to be independent of the ion pairing process, and independent of temperature. Models of ion pairing are discussed. Comparison is made to unrestricted Hartree-Fock self-consistent field molecular orbital (UHF-SCF-MO) calculations.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor and counsellor, Frank Adam, whose continued interest in my research and nebulous career has kept me out of trouble over the last couple of years. I would also like to extend my gratitude to the invaluable technical assistance of Glen Smith. Thanks are also due to my colleague Fred King for his advice and tolerance, if at times unwarranted.

I also wish to acknowledge the award of an Isaac Walton Killam Memorial Fellowship.

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".... the main object of physical science is not the provision of pictures, but it is the formulation of laws governing phenomena and the application of these laws to the discovery of new phenomena. If a picture exists so much the better; but whether a picture exists or not is a matter of only secondary importance."

P.A.M.Dirac

"The Principles of Quantum Mechanics", Oxford University Press, London, 4th Ed., 1958

CHAPTER I

INTRODUCTION

The technique of electron spin resonance (esr) spectroscopy has proved a valuable tool in the elucidation of molecular structure of aromatic radicals¹. The complex interactions between the magnetic nuclei in the molecule with the unpaired electron act as a probe to determine the distribution of the unpaired electron throughout the molecule.

Many methods for the production of radicals appear in the literature. These include electrolysis, irradiation by electromagnetic radiation, oxidation by concentrated acids such as sulphuric and perchloric, and the reduction by active metals such as those of the alkali and alkaline earth groups. Early investigators² using the technique of alkali metal reduction noted the presence of extra hyperfine structure in the spectra due to the magnetic moment of the alkali metal, which suggested that the radical anion and alkali cation were complexed in some way. This has become referred to as an 'ion pair'. Subsequent studies³ have revealed a large number of aromatic compounds that undergo ion pairing upon reduction by an alkali metal, mainly in ethereal solvents.

Although the presence of the alkali metal splitting in the esr spectra of a radical ion confirms the presence of an ion pair the exact nature of ion pairs is not known. Temperature studies

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of the ion pair systems have yielded additional information on their structure. Atherton and Weissman⁴ noted that the sodium splitting of the naphthalene ion pair in various ethereal solvents showed a positive temperature dependence, increasing with increasing temperature. Since the alkali metal splitting decreased towards zero as the temperature was lowered they concluded that at sufficiently low temperatures the metal sat above the molecular plane at the mid-position of the central 9,10 bond which happens to be a nodal plane of the molecular orbital containing the unpaired electron. As the temperature is raised the metal ion vibrates back and forth across this plane and hence interacts with the unpaired π electron. They consider that the metal ion may occupy a large number of thermally accessible vibrational levels such that the splitting observed at a particular temperature T is given by :-

$$\overline{a} = \sum_{n=0}^{\infty} \frac{a_n \exp(-E_n/kT)}{\sum_{n=0}^{\infty} \exp(-E_n/kT)}$$
(1.1)

This idea was later extended by Aono and Oohashi⁵, who gave a more formal mathematical treatment. The ground state of the system, (1.2),

$$\Psi_{0} = \Psi(Ar^{-}, Na^{+})$$
(1.2)

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is mixed with an excited non-bonding state, (1.3),

$$\Psi_1 = \Psi(\operatorname{Ar}, \operatorname{Na}) \tag{1.3}$$

to give a wave function, Ψ , for the system given approximately by (1.4).

$$\Psi = \Psi_0 + \lambda \Psi_1 \tag{1.4}$$

where λ is a mixing parameter given by :-

$$\lambda = -H_{10}/\Delta E_{10} \tag{1.5}$$

with

$$\Delta E_{10} = \langle \Psi_1 | \hat{H} | \Psi_1 \rangle - \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$
 (1.6)

and

$$H_{10} = \langle \Psi_1 | \hat{H} | \Psi_0 \rangle$$
 (1.7)

where \hat{H} is the electronic Hamiltonian. The unpaired electron density on the alkali metal may be then interpreted as λ_{i}^{2} with the alkali metal splitting given approximately by the relation⁶ :-

$$\mathbf{u}_{\mathbf{M}} = \mathbf{Q}_{\mathbf{M}} \mathbf{\rho}_{\mathbf{M}} \tag{1.8}$$

where Q_M is given by the atomic hyperfine splitting of the gaseous alkali metal. The motion of the alkali metal back and forth across the 9,10 bond can be approximated by a one-dimensional harmonic oscillator, in which case the expectation value of the square of the amplitude of the metal ion is given by⁵ :-

$$< x^{2} >> = (1/2a^{2}) \operatorname{coth}(\beta \hbar \omega/2)$$

where $\beta = 1/kT$, k is Boltzmann's constant and T is the absolute temperature;

$$u^2 = (m\alpha)^{\frac{1}{2}}/\hbar$$
; (1.10)

(1.9)

m is the mass of the metal ion, $\hbar = h/2\pi$, h being Plank's constant, and α is the quadrature of the potential in which the metal ion oscillates; and $\omega = \sqrt{\alpha/m}$.

Hence the temperature dependence is found by evaluating << x^2 >> for a particular temperature and then evaluating λ^2 and consequently an a_M for this configuration. Using this method Aono and Oohashi were able to obtain reasonable agreement with Atherton and Weissman's experimental findings.

An alternate model was proposed by Hirota^{7,8} and involves a rapid equilibrium among structurally different ion pairs which differ mainly in the amount of solvation of the metal ion. This idea is supported by evidence from conductivity experiments⁹. The two main types of ion pairs are termed the 'tight ion pair' with a large alkali metal splitting, and the 'loose ion pair' or 'solvent separated ion pair' with a small or zero alkali metal splitting. Thermodynamic equilibrium between the two forms results in the temperature dependence of the alkali metal splitting. If the two types of ion pairs are denoted as A and B and are in thermal equilibrium, one can write :-

$$A \xrightarrow[k_{-1}]{k_{-1}} B \qquad (1.11)$$

where k_1 is the rate constant for conversion of A to B and k_{-1} is the rate constant for the reverse step. If the probabilities of finding forms A and B are given by p_A and p_B respectively, and if these forms have alkali metal splittings α_A and α_B respectively, the equilibrium constant, K, is given by :-

$$K = \frac{p_B}{p_A} = \frac{k_1}{k_{-1}}$$
 (1.12)

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In the limit of rapid exchange the observed alkali metal splitting is given by :-

$$\overline{\alpha} = p_A \alpha_A + p_B \alpha_B = \frac{\alpha_A + K \alpha_B}{1 + K}$$
(1.13)

For sodium naphthalenide in tetrahydrofuran, $\alpha_A = 1.15$ Oe and $\alpha_B = 0.0$ Oe and plots of log K vs 1/T proved to be linear.

Aromatic ketones have proved particularly useful in the study of ion pairing¹⁰. This is due to their greater stability and their tendency to form contact ion pairs (as opposed to solvent-separated ion pairs) presumably because of the greater localization of negative charge in the carbonyl function. Thus ketyl solutions require up to 40 volume percent of the polar solvent dimethylformamide before the metal free anion is obtained¹¹. Further, experiments by Carter, McClelland and Warhurst¹² on the electronic spectra of aromatic ketyl ion pairs show general agreement with Beer's law indicating that there is no detectable dissociation of the monomeric ion pair to form separated ions. They concluded that the ion pairs most probably consist of the cation and anion in close contact, surrounded by a solvation shell.

The alkali metal splittings of the ion pairs of ketyl radicals also usually decrease with a decrease in temperature⁷. Canters and de Boer¹³ proposed that the alkali metal ion lies in the nodal

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plane of the π electrons at low temperatures but at higher temperatures spends a proportionately greater fraction of the time out of the nodal plane and in regions of higher electron density. This motion is similar in kind to that proposed by Atherton and Weissman for sodium naphthalenide. This idea is supported by a calculation done by McClelland¹⁴ who calculated the most stable position of the alkali metal ion to be in the vicinity of the carbonyl group using as a perturbation the electrostatic interaction between the ions. Thus the model of Hirota would seem less applicable in the case of aromatic ketyls than that proposed by Canters and de Boer.

Although an extensive study has been made of the aromatic ketyl systems¹⁰ little work has been done on their sulphur analogues, the thicketyls. The preparation and esr of a number of thicketyls has been recently reported¹⁵. These systems also exhibited ion pairing when reduced with alkali metals in ethereal solvents. No temperature studies were made, but several interesting features in their spectra suggested that a temperature study would be useful in the study of the ion pairing process. It was the purpose of this work to study several of the thicketyl systems in comparison to their carbonyl analogues in an effort to shed some light on the nature of ketyl (and thicketyl) ion pairs.

The experimental procedure followed and the experimental results so obtained are discussed in the first two sections. The molecular orbital calculations are expounded in the following section and

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finally the implications of the study are discussed in the last section. The formal theory of esr is not discussed here as it is well documented elsewhere¹⁶. The theory necessary for the understanding of certain results, as they arise, is given in the appendices.

CHAPTER II

EXPERIMENTAL

Table 1 lists the parent ketones that were studied and notes the commercial sources from which they were obtained. The thioketones were prepared from their oxygen analogues by heating the molten ketone with P_2S_5 neat, or by refluxing the ketone in toluene in the presence of excess $P_2S_5^{15b}$. Also included in Table 1 are the uncorrected melting points. Thiobenzophenone could not be obtained by recrystallisation due to its extreme sensitivity to air and moisture, being converted back to benzophenone. It could however be purified by vacuum sublimation and stored satisfactorily under vacuum. Preparations of these samples showed no carbonyl stretch in the IR spectrum, and no benzophenone ketyl could be detected in its esr spectrum using slight reduction with an alkali metal. The method was therefore deemed satisfactory for the present study.

The homodyne X-band spectrometer employed is a unit built up from precision components. It uses a Currie, McLaughlan and Len MOS-1 phase lock klystron stabilizer fed by an AFC circuit which operates at 6Kc. The field modulation was at a nominal 10 KHz, using a Princeton Applied Research HR-8 phase sensitive detector and amplifier. Detection was by a balanced pair of L128 Philco backward diodes. Field markers were obtained using a Harvey Wells F-10 gaussometer unit monitered by a Hewlett-Packard 5168-L counter. Klystron frequencies were determined using a combination of the Hewlett-Packard counter to determine the base frequency, and a

TABLE I

Compound	Symbol	Source	Melting Pt. (°C)	Reference
Benzophenone	В	Eastman	-	
Thiobenzophenone	BS	$P_{2}S_{5}$ neat	*	
Xanthone	X	Fluka 'purum'	-	
Xanthene-9-thione	XS	P_S_/ toluene	153-154	(17)
Thioxanthone	TX	K&K Labs.	>	
Thioxanthene-9-thione	TXS	P ₂ S ₅ / toluene	167	(18)
pp'-dimethoxy- benzophenone	DMB	K&K Labs.	-	
pp'-dimethoxy- thiobenzophenone	DMBS	P_S_/ toluene	113-115	(17)

Note:

* No melting point recorded as the compound decomposed on contact with air.

Hewlett-Packard wavemeter which gives sufficient resolution (±5MHz) to determine the particular harmonic of the crystal to which the klystron was locked. Several preliminary studies were carried out using a Varian 4502 spectrometer at the University of Sydney, Sydney, Australia.

The ethereal solvents used were distilled from lithium aluminium hydride and stored under vacuum over sodium-potassium alloy. All samples were prepared using standard high vacuum techniques¹⁹. Low temperature spectra were obtained by passing a stream of cold, dry nitrogen gas past the sample in a quartz dewar insert set in the cavity.

CHAPTER III

EXPERIMENTAL RESULTS

The hyperfine coupling constants and g values of the radicals studied are given in Table 2. The numbering system used is shown in Figure 1 and the notation is that of Table 1.



Figure 1

For benzophenone (B) and thiobenzophenone (BS) Z represents two hydrogen atoms and Y=O and S respectively. Xanthone (X) and xanthene-9-thione (XS) have Z=O and Y=O and S respectively, while thioxanthone (TX) and thioxanthene-9-thione (TXS) have Z=S and Y=O and S respectively. In most cases the coupling constants quoted in Table 2 were checked by comparison of the experimental spectrum with a computer simulated spectrum based on the measured coupling

TABLE 2

System ^(a)		<u>Coupl</u>	ing Co	nstant	(0e)	<u>g value</u>
	^a 1	^a 2	a ₃	a4	a _{metal}	
B-Na-DME ²⁴	2.60	0.88	3.45	0.88	1.16	2.0034
BS-Na-DME (23 [°])	2.41	0.94	2.85	0.94	3.62	2.0057
BS-Na-DME (-56°)	2.41	0.93	2.85	0.93	-	2.0067
X-Na-THP	3.88	0.91	3.88	<0.2	0.9	2.0034
XS-Na-DME (22°)	3.42	0.78	3.42	0.39	3.44	2.0055
XS-Na-DME (-50°)	3.42	0.78	3.42	0.39	-	2.0063
TX-Na-DME	3.57	0.97	3.57	0.34	1.0	2.0036
TXS-Na-THP	2.92	0.91	3,07	0.61	4.24	2.0055
DMB-Ca-DME ²⁴	2.86	0.97	0.29 ^b	0.97	-	2.0037
DMBS-Na-DME (23°)	2.58	0.98	0.28 ^b	0.98	3.85	2.0058
DMBS-Na-DME (-42°) ^C			<u></u>	<u></u>	a	2.0063

Note:

- (a) DME \equiv 1,2-dimethoxyethane; THP \equiv tetrahydropyran.
- (b) Methoxyl protons.

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(c) Spectra poorly resolved.

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constants and line widths, assuming Lorentzian line shapes. The spectra were plotted on a Calcomp 565 Digital Incremental Plotter. Representative spectra with their simulations are shown in appendix 1. The assignment of the coupling constants given in Table 2 were made in the case of the thicketyls by comparison to their oxygen analogues, and from the results of UHF-SCF-MO calculations to be described in the next chapter. The assignments given also conform to those obtained by Sevilla and Vincow²⁰ for xanthyl radicals deuterated in either the 2 or 3 positions.

The spectra of the thioketyls are qualitatively similar to the corresponding oxyketyls. They showed decreased proton hyperfine splittings at most ring positions compared to the corresponding oxyketyls. This indicates that less spin density is present in the rings and more is accumulated on the thiocarbonyl moiety than found in the corresponding carbonyl function. This is evident in all pairs of ketyls and thioketyls studied. Also, the ring proton splittings of the xanthylene derivatives are larger than the corresponding hyperfine couplings of the unbridged derivatives (i.e. B,BS,DMB, and DMBS). This can probably be attributed to the nonplanarity of the latter compounds which results from the steric repulsion between the ortho protons at positions 5 and 10²¹ whereas the xanthylene derivatives are constrained to be planar. As the phenyl groups are twisted out of the plane of the central carbonyl group the resonance integrals for the extracyclic 6-7 and 7-9 bonds

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decrease (i.e. the overlap between the $p\pi$ orbitals on centres 6 and 7 and on 7 and 9 decreases) with the result that spin density is withdrawn from the rings and augments that present in the carbonyl or thiocarbonyl group.

A look at Figure 1 will show that of the ortho sites 1, 5, 10 and 14, 1 is geometrically equivalent to 14 while 5 is geometrically equivalent to 10, but 1 is not equivalent to 5 or 10, nor is 14 equivalent to 5 or 10. Thus one would expect that the spin densities, and hence the proton hyperfine couplings, to show only pairwise equivalence. The same is also true for the meta sites 2, 6, 12 and 13. In general spectra of the unbridged species show all four ortho (and meta) sites to be equivalent. This results from rapid rotation of the phenyl rings at a frequency greater than the difference in hyperfine frequency between the inequivalent sites. However Takeshita and Hirota¹¹ have detected inequivalent ortho splittings in the spectra of B at low temperatures and they were able to estimate the barrier to rotation of the phenyl rings to be ~5 kcal mole⁻¹. No inequivalence of the four ortho (or four meta) protons was noticed in the spectra of the unbridged thicketyls BS and DMBS. The inherently greater linewidths (0.1 to 0.3 Oe) of these compounds and the more complex hyperfine spectrum of DMBS made a detailed study into this effect difficult.

The thicketyls exhibited relatively larger sodium coupling constants of about 4 Oe compared to the 1 Oe splittings commonly

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obtained for the oxyketyls²² and in general show a similar temperature dependence in that this splitting increases as the temperature is raised. Plots of this effect are given in Figures 2 and 3 for the various compound-solvent combinations studied. The alkali metal splittings show a considerable solvent sensitivity for any particular thicketyl. In most cases the variation in the coupling constant decreases at higher temperatures and is in fact essentially constant for Na-TXS in all solvents tested, and for Na-XS in tetrahydropyran (THP).

While the thicketyl and oxyketyl ion pairs show a similar temperature dependence, they do differ in one extremely important aspect. This behaviour is typified by Na-BS in 1,2-dimethoxyethane (DME) which shows a well resolved spectrum in the region +50°C to -10°C with the temperature dependent sodium splittings shown in Figure 2. Within the accuracy of our measurements the g value (2.0057) and the proton hyperfine splittings are independent of temperature within this range. Below -10°C, however, a complex and unsymmetrical spectrum was observed to evolve. It appears to be a superposition the above spectrum upon a second spectrum which accounts for of the entire absorption below -40°C. The low temperature spectrum itself has no metal splitting and a different g value (2.0067). No discernible change in the proton coupling constants from the high temperature form is observed. Both the proton splittings and g value appear unchanged as the temperature is lowered to the gell point of the solvent near

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Figure 3

-80°C. The suggestion may be made that the ion pairs observed at elevated temperatures can be considered to be more or less completely dissociated at the lower temperatures. This occurs with a jump, rather than a gradual shift, in the g value, a loss of, rather than a gradual decrease, in the alkali metal splitting, but at the same time with no change in the ring proton hyperfine splittings. The temperature at which the dissociation occurs is indicated in Figures 2 and 3 by the termination of the curves.

The proposition suggested above is further substantiated by an experiment in which the salt tetra-n-butyl ammonium perchlorate was added to the Na-BS system in DME. This salt has the effect of removing the sodium ion and replacing it by the tetra-n-butyl ammonium-ion. The spectrum of the free ion was obtained with splitting constants $a_0 = 2.43$ Oe, $a_m = 0.94$ Oe, and $a_p = 2.82$ Oe and g value 2.0072, in good agreement with the spectrum of the species obtained at low temperatures in the Na-BS/DME system.

It can been seen from the spectra in appendix 1 that the hyperfine lines corresponding to quantum numbers $M_{Na} = \pm 3/2$ and $M_{Na} = \pm 1/2$ have the same peak-to-peak heights. Since peak heights are proportional to line widths, no selective broadening occurs in these systems to indicate that the sodium ion oscillates rapidly between a bound and an unbound state ^{8†}. If such oscillations occur

[†]See Appendix 2.

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they must proceed at a frequency much lower than the alkali metal hyperfine linewidths, or less than $\sim 10^5$ sec⁻¹.

The larger g values of the thicketyls result from a heavy atom effect²³⁺ which can be mostly attributed to the sulphur atom since it has a spin-orbit coupling parameter $\xi_s = -382 \text{ cm}^{-1}$ compared to that of oxygen $\xi_o = -152 \text{ cm}^{-1}$, and of carbon $\xi_c = -28 \text{ cm}^{-1}$. Shifts of the g value away from the free electron value, $g_e = 2.0023$, can be related linearly to the spin density on the sulphur atom^{15a+}.

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† See Appendix 3.

CHAPTER IV

MOLECULAR ORBITAL CALCULATIONS

A. The Pariser-Parr-Pople (PPP) method

The electronic structures of the radical anions studied were calculated theoretically by the self-consistent field linear combination of atomic orbitals (SCF-LCAO) method using the approximations of Pariser, Parr, and Pople²⁵. This method is fully described elsewhere²⁵ and only a brief description need be given here.

The method relies on choosing polycentric orbitals, Ψ_i , which are approximated as a linear combination of atomic orbitals, Φ_{μ} , centred on the various atoms of the molecule.

$$\Psi_{i} = \sum_{\mu} \chi_{i\mu} \Phi_{\mu}$$
(4.1)

The orbitals are then adjusted to give a stationary value of the energy, $\langle \Psi_i | \hat{H} | \Psi_i \rangle$, where \hat{H} is the electronic Hamiltonian for the system. The set of equations that result²⁶ are called the Hartree-Fock equations and determine the coefficients $\chi_{i\mu}$.

$$\sum_{\nu} F_{\mu\nu} \chi_{i\nu} = E_{i} \sum_{\nu} \chi_{\mu\nu} \chi_{i\nu} \qquad (\mu=1,2...) \qquad (4.2)$$

where $F_{\mu\nu}$ is called the Fock matrix and is given by :-

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$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \{ \langle \mu \lambda | G | \nu \sigma \rangle - \frac{I_2}{2} \langle \mu \lambda | G | \sigma \nu \rangle \}$$
(4.3)

and

$$H_{\mu\nu} = \int \overline{\Phi}_{\mu} \{ -\frac{1}{2} \nabla^2 - \Sigma \nabla_{\alpha}(\vec{r}) \} \Phi_{\nu} d\vec{r}$$
(4.4)

$$<\mu\lambda|G|\nu\sigma> = \iint \overline{\Phi}_{\mu}(1)\overline{\Phi}_{\nu}(2)(1/r_{12})\Phi_{\lambda}(1)\Phi_{\sigma}(2)d\vec{r}_{1}d\vec{r}_{2} \qquad (4.5)$$

$$S_{\mu\nu} = \int \overline{\Phi}_{\mu} \Phi_{\nu} d\vec{r}$$
 (4.6)

$$Y_{\lambda\sigma} = \frac{2\sum \bar{X}_{i\lambda} X_{i\sigma}}{i \lambda^{2} i \lambda^{2} i \sigma}$$
(4.7)

 $V_{\alpha}(\mathbf{r})$ is the potential due to the nucleus α and $H_{\mu\nu}$ is the matrix element for motion in the field of the bare nuclei alone. 25b

The following approximations are then made .

a.) The σ -system is treated as a nonpolarizable core and its effect included in the H terms.

b.) The zero differential overlap (ZDO) approximation is invoked. In this approximation overlap integrals, $S_{\mu\nu}$, are neglected unless $\mu=\nu$.

c.) All two-electron integrals which depend on the overlapping of charge distributions of different orbitals are neglected. i.e. $\langle \mu \lambda | G | \nu \sigma \rangle = 0$ unless $\mu = \lambda$ and $\nu = \sigma$.

d.) The two-electron integrals $\langle \mu \nu | G | \mu \nu \rangle = \gamma_{\mu\nu}$ are approximated

by the point charge model^{25a} while the integrals $\langle \mu | V_{\alpha} | \mu \rangle$ are approximated by $-Z_{\alpha} R_{\mu\alpha}^{-1}$ where Z_{α} is the "effective charge" of the σ -core of atom α . The remaining integrals, $H_{\mu\nu}$, are parameterised empirically.

Finally if the unrestricted Hartree-Fock (UHF) procedure is invoked in which different orbitals for different spins are used 27 we get the set of equations 28 :-

$$\sum_{\nu} F^{\alpha}_{\mu\nu} \chi^{\alpha}_{i\nu} = E^{\alpha}_{i} \chi^{\alpha}_{i\mu}; \quad \sum_{\nu} F^{\beta}_{\mu\nu} \chi^{\beta}_{i\nu} = E^{\beta}_{i} \chi^{\beta}_{i\mu}$$
(4.8)

where

$$F_{\mu\mu}^{\alpha} = U + P_{\mu\mu}^{\beta} \gamma + \sum_{\sigma\sigma} (P_{\sigma\sigma} - Z_{\sigma}) \gamma_{\mu\sigma}$$
(4.9)

$$F^{\beta}_{\mu\mu} = U + P^{\alpha}_{\mu\mu}\gamma + \Sigma (P - Z)\gamma \qquad (4.10)$$

$$\mu\mu \qquad \mu\mu \qquad \mu\mu \qquad \sigma(\neq\mu) \qquad \sigma\sigma \qquad \sigma \qquad \mu\sigma$$

$$F^{\alpha}_{\mu\nu} = \beta_{\mu\nu} - P^{\alpha}_{\mu\nu}\gamma_{\mu\nu}, \quad (\mu \neq \nu)$$
 (4.11)

$$F_{\mu\nu}^{\beta} = \beta - P_{\mu\nu}^{\beta} \gamma , (\mu \neq \nu)$$
 (4.12)

$$P^{\alpha}_{\mu\nu} = \sum_{i}^{occ} \chi^{\alpha}_{i\mu} \chi^{\alpha}_{i\nu} , P^{\beta}_{\mu\nu} = \sum_{i}^{occ} \chi^{\beta}_{i\mu} \chi^{\beta}_{i\nu}$$
(4.13)

$$P_{\mu\nu} = P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta}$$
(4.14)

which can be solved iteratively²⁹.

In the PPP scheme the total π electron energy is then given by :-

$$E_{\pi} = \frac{1}{2} \{ \sum_{r,s} P_{rs}^{\alpha} (H_{rs} + F_{rs}^{\alpha}) + \sum_{r,s} P_{rs}^{\beta} (H_{rs} + F_{rs}^{\beta}) \}$$
(4.15)

B. Parametrization

The geometry of the xanthyl type radicals was assumed to be planar whereas the diphenyl type radicals (B⁻ and BS⁻) were taken as nonplanar as will be discussed in the next section. The numbering system is that of Figure 1. All aromatic C-C bonds were taken as 1.40 Å and extracyclic C-C bonds (6-7 and 7-9) as 1.48 Å. The C=O and C=S bonds (7-8) were taken as 1.23 Å and 1.71 Å respectively³⁰. C-O- and C-S- ether linkages (5-15 and 10-15) were estimated to be 1.37 Å and 1.7 Å respectively³⁰. Normal valence angles of 120 were also assumed.

The parameters not calculated explicitedly by the PPP method were taken from the literature and are listed in Table 3.

The calculated spin densities are given in Table 4. Experimental spin densities (ρ_i) were computed from the hyperfine coupling constants (a_i) using McConnell's relation³¹:-

$$\rho_{i} = a_{i}/Q_{H} \tag{4.16}$$

TABLE	3
-------	---

Symbol (a)	Position	<u>Value</u> (eV)	Reference
I _C	all	-11.22	25a
I _O	8	-11.1	37
	15	-33.9	38 ·
Is	8	-18.0	40
5	15	-20.0	39
^β cc	ring	-2.39	25a
	6-7,7-9	-2.10	(b)
^β co	7-8	-2.60	(b)
	5-10,5-15	-2.16	(b)
βcs	7-8	-2.39	41
	5-10,5-15	-1.60	39
^ү с	all	10.53	25a
Ϋ́o	8	14.93	(c)
-	15	20.0	42
Ϋ́s	8	17.93	(c)
-	15	10.84	39

Note:

(a) I_X - ionisation potential of atom X; β_{XY} - resonance integral between atoms x and y (all non-nearest neighbour terms neglected); γ_X - electron repulsion integral for atom X.

(b) Calculated using Mulliken's approximation⁴³.

(c) Calculated using Paoloni's formula, $\gamma_{\mu}=3.29Z_{\mu}^{37}$.

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Parent Compound			Positi	on					
	1,14	2,13*	3,12	4,11*	5,10	6,9	7	8	15
x	<u> </u>								
Calculated	0.1228	-0.0653	0.1498	-0.0435	0.0762	0.0002	0.1686	0.3358	0.0209
Experimental	0.144	0.034	0.144	0.007					
xs		-							
Calculated	0.0826	-0.0461	0.0990	-0.0272	0.0468	0.0032	0.0077	0.6645	0.0112
Experimental	0.127	0.030	0.127	0.014					
тх									
Calculated	0.1335	-0.0708	0.1551	-0.0345	0.0637	-0.0051	0.1572	0.3253	0.0334
Experimental	0.132	0.036	0.132	0.012					
TXS									
Calculated	0.0898	-0.0498	0.1014	-0.0211	0.0390	-0.0010	0.0055	0.6631	0.0150
Experimental	0.108	0.034	0.114	0.023					

* <u>Note</u>: Experimental results give only the magnitude, and not the sign, of the coupling constants.

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where Q was taken to be -27 Oe. These are also listed in Table 4 for comparison.

C. Conformational studies of benzophenone and thiobenzophenone

The radical anions of B and BS are expected to be nonplanar due to the strong steric repulsion between the ortho protons. However since only one ortho (and meta) proton coupling constant is observed at room temperature the phenyl rings must be rotating at a frequency greater than the difference in hyperfine frequency between the unequivalent ortho (or meta) sites. Adam and Falle²¹ have suggested that the phenyl rings in radicals of the diphenylmethyl type may undergo a concerted rotation in which the steric repulsion energy between the ortho groups results in only one ring being coplanar with the carbonyl group at any one time. This motion occurs with a minimum loss of π delocalisation energy.

The equilibrium conformations of B and BS were calculated as giving the lowest total energy, E_{T} , considering the changes in both the π electron energy, E_{π} , and the steric repulsion energy, E_{S} , which result when the phenyl rings are rotated.

$$E_{\rm T} = E_{\rm T} + E_{\rm S} \tag{4.17}$$

 E_{π} was calculated using equation (4.15). E_{S} was calculated

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using the formulae of Bartell³² which are given by equations (4.18), (4.19), and (4.20) for C-C, C-H, and H-H nonbonded repulsions respectively (in eV - r in Å).

$$V_{\rm CC}(\mathbf{r}) = 12,800r^{-12} - 1.41 \times 10^3 r^{-6}$$
 (4.18)

$$V_{CH}(r) = \{-5.42 + 1.94 \times 10^3 \exp(-r/0.490)\}r^{-6}$$
 (4.19)

$$V_{\rm HH}(r) = -2.14r^{-6} + 2.86 \times 10^3 \exp(-r/0.245)$$
 (4.20)

The total repulsion energy was obtained by summing over all pairs of interacting atoms.

Only conformations in which each ring was rotated through equal and opposite angles (0) were considered, as suggested by Adam and Falle²¹. The formulae failed to give reasonable results around $\theta=0^\circ$, but these regions are obviously energetically unfavourable due to ortho proton-proton repulsion and so these values were ignored. The conformational energy map for B⁻ is shown in Figure 4 and suggests a minimum at 30°. The map for BS⁻ was similar and also gave a minimum at 30°.

The angle of rotation in B⁻ is slightly reduced from that of B in the crystal³³ (33°) and that calculated by Hoffman³⁴ (38°) for the ground state of B. This is in accord with a suggestion of Rieger and Fraenkel³⁵ who noticed that the calculated bond order between the carbonyl carbon atom (7) and the phenyl rings increased from 0.323 in neutral B to 0.428 in the anion.





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The results of spin density calculations for the benzophenone and thiobenzophenone anions in the planar $(\theta=0^{\circ})$ and nonplanar $(\theta=30^{\circ})$ conformations are given in Table 5. It is evident from the table that the calculated ring spin densities are relatively insensitive to twist of the phenyl rings. Hence the comparison of calculated and observed splitting constants to determine the equilibrium conformation could prove erroneous for these compounds. The use of conformational energy maps would appear to be a more satisfactory technique.

The barrier to rotation of the phenyl rings was calculated as the energy difference between the low energy conformation described above and that in which one ring was planar and one perpendicular to the carbonyl group³⁶, this being the path of concerted rotation. The calculated difference, 7.8 kcal mole⁻¹, is in reasonable agreement with the value found experimentally by Takeshita and Hirota (~5 kcal mole⁻¹). A value of 9.0 kcal mole⁻¹ was obtained for BS⁻.

TABLE 5

Benzophenone

Position	Planar	<u>θ=30</u> °	Observed
1,14	0.0777	0.0734	0.0963
2,13	-0.0379	-0.0362	0.0326
3,12	0.1297	0.1239	0.1278
4,11	-0.0560	-0.0519	0.0326
5,10	0.1047	0.0966	0.0963
6,9	0.0504	0.0580	
7	0.1642	0.1887	
8	0.3490	0.3417	

Thiobenzophenone

Position	Planar	<u>0=30</u> °	Observed
1,14	0.0592	0.0611	0.0893
2,13	-0.0359	-0.0374	0.0348
3,12	0.0975	0.0952	0.1056
4,11	-0.0476	-0.0446	0.0348
5,10	0.0798	0.0735	0.0893
6,9	0.0196	0.0135	
7	0.0204	0.0422	
8	0.6540	0.6487	

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CHAPTER V

DISCUSSION

While no attempt was made to vary the empirical parameters in the MO calculations in order to obtain a better fit with experiment, it can be seen from Tables 4 and 5 that the agreement between experimental and calculated spin densities is in general quite reasonable. It can be further seen from these tables that the experimental trends mentioned in Chapter III concerning planarity and the substitution of sulphur for oxygen in the 8 position are borne out by the calculated values. Thus there is a systematic decrease in spin density in the phenyl rings in going from the oxyketyl to the thioketyl anion with a consequential build up of spin density on the thiocarbonyl group. Although no experimental check on the conformational studies on B⁻ and BS⁻ is possible, the calculated conformations appear reasonable and the decreased spin density in the rings compared to the xanthyl analogues is in agreement with the experimental findings.

The dissociation of the metal ion from the thioketyl anion at low temperatures appears to change only the spin density distribution in the thiocarbonyl group, while it remains the same in the phenyl rings. The jump in g value that does occur with dissociation shows that while the total spin density in the central group may be constant, the fraction found in sulphur orbitals is greater in the free ion than in the ion pair. This carries with it the implication that the sodium ion is closely associated with the sulphur atom in the ion pair, which is analogous to the conclusions of Gill and Gough⁴⁴, concerning the sodium-durosemiquinone system, who found the metal ion to lie close to the heteroatom.

Thus the temperature dependence of the sodium splittings of the thioketyls may be explained if one assumes that the sodium ion is executing vibrations about the π nodal plane - presumably in the vicinity of the thiocarbonyl group. No equilibrium between structurally different ion pairs such as that postulated by Hirota⁷ was observed in these systems. Quite to the contrary the species formed at low temperatures can be assumed to be the free ion as it has no detectable metal hyperfine splitting and has a significantly larger g value. If the sodium ion were to undergo a rapid exchange between the bound and unbound states as required by the equilibrium model, one would expect to obtain an averaged g value which would vary with temperature between the two limits represented by the contact ion pair and the solvent separated ion pair. The present experiments show that this is clearly not the case and exchange between the two forms is very slow on the time scale of the present measurements - approximately 10^5 sec⁻¹.

Finally no selective broadening of the $M_{Na}=\pm 3/2$ over the $M_{Na}=\pm 1/2$ lines was observed in any of these systems. Such broadening is expected⁸ when an exchange between different types of ion pairs occurs at frequencies comparable to that of the sodium hyperfine frequency.

The effect of the solvent in the dissociation process follows the qualitative trends outlined by Aten, Dieleman, and Hoijtink⁴⁵ in that the energy of solvation increases with increasing dielectric

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constant and decreasing radius of the metal ion. In accordance with the negative temperature coefficient of the dielectric constants of the particular solvents studied here, the solvation of the metal ions becomes stronger as the temperature is lowered, and as a result this brings about the ultimate dissociation. Of the solvents used, DME has the highest dielectric constant and the highest dissociation temperatures, while THP has the lowest dielectric constant and doesn't in fact induce dissociation of TXS-Na above its freezing point. It is also apparent that solvent effects do not simply facilitate dissociation, but also change the atomic parameters that determine these couplings.

Hirota⁷ observed that the carbonyl C^{13} splittings of oxyketyl radicals were temperature dependent and that there was a strong correlation between the C^{13} splitting and the alkali metal splitting. He was able to explain these observations by assuming rapid exchange of the sodium ion between the bound and unbound states. Because of the intrinsically broader lines no study of the thiocarbonyl C^{13} splittings was made. However it is possible to explain the C^{13} splittings under the model suggested above.

The equation given by Das and Fraenkel⁴⁶ for the C^{13} coupling constants is :-

$$a_{CO}^{C} = (S^{C} + 2Q_{CC'}^{C} + Q_{CO}^{C})\rho_{C}^{\pi} + Q_{C'C}^{C}(\rho_{C'}^{\pi} + \rho_{C''}^{\pi}) + Q_{OC}^{C}\rho_{O}^{\pi}$$
(5.1)

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While most of the carbon atom parameters have commonly accepted values there appears to be several sets of values for Q_{CO}^{C} and Q_{OC}^{C} . The original values given by Das and Fraenkel are 17.7 and -27.1 Oe respectively and are appropriate for the free benzosemiquinone anion. However Gough and Taylor⁴⁷ give the values 8.9 and 16.4 Oe for the protonated derivative. Insertion of this latter set of values in equation (5.1) gives :-

$$a_{\rm co}^{\rm C} = 25.0\rho_7 - 27.8\rho_6 + 16.4\rho_8$$
 (5.2)

Using the calculated spin densities for benzophenone given in Table 5, gives a C^{13} coupling of 9.5 Oe in good agreement with the value of 9.3 Oe obtained experimentally by Ascough and Wilson $\frac{48}{.}$ However if the values of Das and Fraenkel are used equation (5.3) results.

$$a_{CO}^{C} = 33.9\rho_7 - 27.8\rho_6 + 16.4\rho_8$$
 (5.3)

Using this equation, a C^{13} coupling of -3.67 Oe is obtained. If one assumes a parallel exists between metal ketyls and the analogous hydroxy radicals⁴⁹ then the ONa bond can be considered to rotate about the C-O bond, changing the π -bonding between the C and O as it does. Under these circumstances ρ_0^{π} would decrease and ρ_C^{π} would increase. As a result the C¹³ splitting would then become less negative and decrease in magnitude, which is in fact what is observed. Since it is precisely this rotational motion that gives rise to the temperature dependence of the metal couplings, it serves to explain the close correlation between the sodium and the C^{13} splittings observed by Hirota⁷.

As was mentioned previously the large g values of the thione anions result from the heavy atom effect of the sulphur. The use of the g value as a spin density probe has proved less effective than proton hyperfine couplings. Stone⁵⁰ has done a theoretical study correlating the g shift with the energy of the highest occupied molecular orbital. It was suggested by Heller^{15a} that the g value of thiobenzophenone varied linearly as the spin density on the $sulphur^{\dagger}$ (position 8). This is evident in TX which has a g value close to X although it contains a sulphur atom. However the spin density on the sulphur atom (~0.03) in position 15 is considerably smaller than that of the sulphur atom in position 8 of the thiones (~0.6). Thus the reduction of g value upon ion pairing may be correlated with a decrease of spin density on the sulphur atom. As the ring proton hyperfine couplings do not change on ion pairing and little spin density is transferred to the sodium ion (approximately 1%) the electronic structure of the thiocarbonyl group must change so that more spin density resides on the carbon atom. This perhaps suggests that a 'pseudo' bond is formed between the sulphur and sodium atoms such that the system

[†] See Appendix 3.

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resembles that of the hydroxyxanthyls alluded to previously.

To summarize, the large sodium splittings observed in these systems result from an increased spin density on the thiocarbonyl function, particularly on the sulphur atom. This is evident from the decrease in hyperfine splittings of the ring protons as compared to the analogous carbonyls. The MO calculations further bear this out. The greater diffuseness of sulphur orbitals coupled with the increased spin density on the thiocarbonyl function explains the increased sodium splitting in the thiocarbonyls over the carbonyls. The temperature dependence of the sodium splittings may then be explained if one assumes that the sodium ion is executing vibrations about the π modal plane in the vicinity of the thiocarbonyl group.

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BIBLIOGRAPHY

1.	P.B. Ayscough, "Electron Spin Resonance in Chemistry", Methuen & Co. Ltd., London, 1967, Ch. 8.
2.	F.C. Adam and S.I. Weissman, J. Am. Chem. Soc., <u>80</u> , 1518 (1958).
3.	M.C.R. Symons, J. Phys. Chem., <u>71</u> , 172 (1967).
4.	N.M. Atherton and S.I. Weissman, J. Am. Chem. Soc., <u>83</u> , 1330 (1961).
5.	S. Aono and K. Oohashi, Progr. Theor. Phys. (Kyoto), <u>30</u> , 162 (1963); ibid, <u>32</u> , 1 (1964).
6.	I.R. Goldberg and J.R. Bolton, J. Phys. Chem., <u>74</u> , 1965 (1970).
7.	N. Hirota, J. Am. Chem. Soc., <u>89</u> , 32 (1967).
8.	N. Hirota and R. Kreilick, ibid, <u>88</u> , 614 (1966).
9.	T.E. Hogen-Esch and J. Smid, ibid, <u>88</u> , 307, 318 (1966).
10.	N. Hirota, J. Phys. Chem., <u>71</u> , 127 (1967).
11.	T. Takeshita and N. Hirota, J. Chem. Phys., <u>51</u> , 2146 (1969).
12.	H.V. Carter, B.J. McClelland and E. Warhurst, Trans. Faraday Soc., <u>56</u> , 343, 455 (1960).
13.	G.W. Canters and E. de Boer, Mol. Phys., <u>13</u> , 395 (1967).
14.	B.J. McClelland, Trans Faraday Soc., <u>57</u> , 1458 (1961).
15.	(a) H.C. Heller, J. Am. Chem. Soc., <u>89</u> , 4288 (1967).
	(b) E.G. Janzen and C.M. Dubose Jr., J. Phys. Chem., <u>70</u> , 3372 (1966).
16.	(a) A. Carrington and A.D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, 1967.
	(b) P.B. Ayscough, "Electron Spin Resonance in Chemistry", Methuen & Co. Ltd., London, 1967.

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- 17. Beilstein <u>17</u>², 328.
- A. Schoenberg, O. Schutz, S. Nickel, H. Krull, W. Marschner and F. Kaplan, Ber., <u>61B</u>, 1375 (1928).
- D. Lipkin, D.E. Paul, J. Townsend and S.I. Weissman, Science, <u>117</u>, 534 (1953).
- 20. M.D. Sevilla and G. Vincow, J. Phys. Chem., 72, 3635 (1968).
- 21. F.C.Adam and H.R. Falle, Can. J. Chem., 44, 1387, 1397 (1966).
- 22. N. Hirota and S.I. Weissman, J. Am. Chem. Soc., <u>86</u>, 2537, 2538 (1964).
- 23. D.S. McClure, J. Chem. Phys., <u>17</u>, 905 (1949); ibid, <u>20</u>, 682 (1952).
- 24. C.R. Kepford, Ph.D. thesis, University of Calgary, Calgary, Alberta, 1968.
- (a) R. Pariser and R.G. Parr, J. Chem. Phys., <u>21</u>, 466,767 (1953).
 (b) J.A. Pople, Trans. Faraday Soc., 49, 1375 (1953).
- 26. C.C.J. Roothaan, Revs. Mod. Phys., 23, 69 (1951).
- 27. J.A. Pople and R.K. Nesbet, J. Chem. Phys., 22, 571 (1954).
- 28. A. Bristock and J.A. Pople, Trans. Faraday Soc., 50, 901 (1954).
- 29. A.T. Amos and L.C. Snyder, J. Chem. Phys., <u>42</u>, 3670 (1965).
- 30. Chem. Soc. Spec. Publ., 11, 1958.
- 31. H.M. McConnell, J. Chem. Phys., 24, 632 (1956).
- 32. L.S. Bartell, ibid, 32, 827 (1960).
- 33. E.B. Fleischer, N. Sung and S. Hawkinson, J. Phys. Chem., <u>72</u>, 4311 (1968).
- 34. R. Hoffmann and J. Swenson, ibid, 74, 415 (1970).
- 35. P.H. Rieger and G.K. Fraenkel, J. Chem. Phys., <u>37</u>, 2811 (1962).
- 36. R.B. Flewwelling, M.Sc. thesis, University of Calgary, Calgary, Alberta, 1969.

- R.D. Brown and M.L. Heffernan, Trans. Faraday Soc., <u>54</u>, 757 (1958).
- 38. M.J.S. Dewar and T. Morita, J. Am. Chem. Soc., 91, 796 (1969).
- J. Fabian, A. Mehlhorn and R. Zahradnik, J. Phys. Chem., <u>72</u>, 3975 (1968).
- 40. "Handbook of Chemistry and Physics", The Chemical Rubber Co., Cleveland, Ohio, 49th Ed., 1969.
- 41. H.C. Longuet-Higgins, Trans. Faraday Soc., 41, 173 (1949).
- 42. F.P. Billingsley and J.E. Bloor, Theoret. Chim. Acta, <u>11</u>, 325 (1968).
- 43. R.S. Mulliken, J. Chim. Phys., 46, 675 (1949).
- 44. P.S. Gill and T.E. Gough, Can. J. Chem., <u>45</u>, 2112 (1967).
- A.C. Aten, J. Dieleman and G.J. Hoijtink, Discussions Faraday Soc., <u>29</u>, 182 (1960).
- 46. M.R. Das and G.K. Fraenkel, J. Chem. Phys., 42, 1350 (1960).
- 47. T.E. Gough and G.A. Taylor, Can. J. Chem., <u>47</u>, 3717 (1969).
- 48. P.B. Ayscough and R. Wilson, J. Chem. Soc., 5412 (1963).
- 49. R. Wilson, J. Chem. Soc. B, 1581 (1968).
- 50. A.J. Stone, Mol. Phys., 6, 509 (1963).
- 51. J.A. Pople, W.G. Schneider and H.J.Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., New York, 1959, p.222.

52. Ref. 24(a) Ch. 9.

- 53. A.J. Stone, Proc. Roy. Soc. A, 271, 424 (1963).
- 54. H.M. McConnell and R.E. Robertson, J. Phys. Chem., <u>61</u>, 1018 (1957).

APPENDIX I

Representative Spectra

Several of the spectra obtained in this work and their computer simulations are shown in this Appendix. The scale of the spectra (in Oersteds) is indicated on each diagram.



(b) Computer simulated

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(b) Computer simulated





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APPENDIX 2

Line Width Alternation Effects

The shape and width of a resonance signal (both in esr and nmr) is dependent on time-dependent processes which occur at rates of the order of the 'natural' line width. For processes slow compared to the line width, spectra appear as superpositions of distinct parts corresponding to the individual species present. For rapid processes the spectra are determined by the time-average of the system.

The exchange of an alkali metal ion between an ion pair and the solvent is just such a time-dependent process. The contribution of the exchange process to the line width is given in the limit of rapid exchange by 51 :-

$$(1/T_2)_{ex} = p_A^2 p_B^2 (\omega_A - \omega_B)^2 (\tau_A + \tau_B)$$
(B.1)

where ω_A and ω_B are the resonant frequencies of the ion pairs A and B respectively, p_A and p_B are the fractional populations of A and B, and τ_A and τ_B are the mean lifetimes of A and B.

As the proton hyperfine couplings remain unchanged on exchange one can substitute $(\omega_A - \omega_B) = M_{Na} (\alpha_A - \alpha_B) \gamma$ into equation (B.1), where α_A and α_B are the alkali metal hyperfine couplings for A and B respectively, M_{Na} is the magnetic quantum number of the alkali metal nucleus, and γ is the gyromagnetic ratio. Thus $(1/T_2)_{ex}$ depends on the square of M_{Na} and so lines with M_{Na} =±3/2 are selectively broadened over those with M_{Na} =±1/2.

Such a broadening is to be expected for exchanges between different types of ion pairs provided that these exchanges occur at frequencies comparable with electron-nuclear hyperfine interaction frequencies. This effect has been noticed by Hirota¹⁰ in the system sodium-naphthalenide in the mixed solvent of tetrahydrofuran and diethylether.

APPENDIX 3

Theory of the g Tensor⁵²

The electronic Zeeman interaction may be represented by the Hamiltonian :-

$$\hat{H} = \beta \bar{H}.g.\bar{S}$$
 (C.1)

where β is the Bohr magneton, \overline{H} is the magnetic field vector, \overline{S} is the spin angular momentum vector, and <u>g</u> is the g tensor. If the electron possesses spin angular momentum only <u>g</u> is isotropic and has the free electron value, g_e, so that equation (C.1) reduces to :-

$$\hat{H} = \beta g_e \tilde{H} \cdot \tilde{S} \qquad (C.2)$$

If the electron possesses orbital angular momentum, \overline{L} , there is an additional interaction between \overline{H} and \overline{L} so that equation (C.2) becomes :-

 $\hat{H} = \beta \bar{H}.\bar{L} + g_{e}\beta \bar{H}.\bar{S}$ (C.3)

Equation (C.3) may be now cast in the form of equation (C.1) in which \overline{S} will now be the 'fictitious spin' and is given the symbol

s.

The only way that the odd electron can obtain orbital angular momentum is through the effect of spin-orbit coupling, which can be represented by the simplified form $\zeta \overline{L}.\overline{S}$, where ζ is a constant called the spin-orbit coupling constant. If the ground state wave functions are denoted $|\Psi_0 \alpha \rangle$ and $|\Psi_0 \beta \rangle$ for α and β spin respectively, the spin-orbit operator mixes these states with excited states to give modified wave functions which are given by first-order perturbation theory as :-

$$|+> = |\Psi_{0}\alpha> - \sum_{n} \frac{\langle n | \zeta \overline{L}.\overline{S} | \Psi_{0}\alpha>}{E_{n} - E_{0}} | n>$$
(C.4)
$$|-> = |\Psi_{0}\beta> - \sum_{n} \frac{\langle n | \zeta \overline{L}.\overline{S} | \Psi_{0}\beta>}{E_{n} - E_{0}} | n>$$
(C.5)

which can be simplified after expanding the $\overline{L}.\overline{S}$ operator to give :-

$$|+> = |\Psi_{0}\alpha\rangle - \frac{l_{2\zeta}}{2\zeta} \sum_{n} \frac{\langle \Psi_{n} | \mathbf{L}_{z} | \Psi_{0} \rangle}{\mathbf{E}_{n} - \mathbf{E}_{0}} |\Psi_{n}\alpha\rangle$$

$$|-> = |\Psi_{0}\beta\rangle + \frac{l_{2\zeta}}{2\zeta} \sum_{n} \frac{\langle \Psi_{n} | \mathbf{L}_{x} + i\mathbf{L}_{y} | \Psi_{0} \rangle}{\mathbf{E}_{n} - \mathbf{E}_{0}} |\Psi_{n}\beta\rangle$$

$$(C.6)$$

$$|-> = |\Psi_{0}\beta\rangle + \frac{l_{2\zeta}}{2\zeta} \sum_{n} \frac{\langle \Psi_{n} | \mathbf{L}_{z} | \Psi_{0} \rangle}{\mathbf{E}_{n} - \mathbf{E}_{0}} |\Psi_{n}\beta\rangle$$

$$- \frac{l_{2\zeta}}{2\zeta} \sum_{n} \frac{\langle \Psi_{n} | \mathbf{L}_{x} - i\mathbf{L}_{y} | \Psi_{0} \rangle}{\mathbf{E}_{n} - \mathbf{E}_{0}} |\Psi_{n}\alpha\rangle$$

$$(C.7)$$

Introducing 'fictitious' spin operators \hat{S}_x , \hat{S}_y , \hat{S}_z defined to act on the states |+> and |-> in the following manner :-

$$\hat{S}_{z}|+> = \frac{1}{2}|+> , \hat{S}_{x}|+> = \frac{1}{2}|->$$
 (C.8)

$$\hat{S}_{z}| \rightarrow = -\frac{1}{2}| \rightarrow , \quad \hat{S}_{y}| \rightarrow = \frac{1}{2}i| \rightarrow$$
 (C.9)

and for a magnetic field along the z axis the spin Hamiltonian, equation (C.1), becomes :-

$$\hat{H} = \beta H_z (g_{zx} \hat{s}_x + g_{zy} \hat{s}_y + g_{zz} \hat{s}_z)$$
 (C.10)

Comparing this form to the true Zeeman Hamiltonian, equation (C.3), one obtains after evaluation of matrix elements for the diagonal term g_{zz} :-

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$$g_{zz} = g_e - 2\zeta \sum_n \frac{\langle \Psi_o | L_z | \Psi_n \rangle \langle \Psi_n | L_z | \Psi_o \rangle}{E_n - E_o}$$
(C.11)

Finally this analysis can be extended to molecules by writing the spin-orbit Hamiltonian as :-

$$\hat{H}_{LS} = \sum_{k} \xi_{k}(\mathbf{r}_{k}) \overline{L}_{k}.\overline{S} \qquad (C.12)$$

where the sum is over atoms. It is then straightforward to show

that⁵³ :-

$$g_{zz} = 2.0023 - 2 \sum \sum \langle \Psi | \zeta_{k} L \delta_{k} | \Psi \rangle \langle \Psi | L_{zj} \delta_{j} | \Psi \rangle$$

$$n k, j = \frac{o k zk k}{E_{n} - E_{o}}$$
(C.13)

McConnell and Robertson⁵⁴ have developed a qualitative treatment for aromatic radicals. Consider a planar axially symmetric aromatic molecule where g_{\perp} and g_{\parallel} refer to field directions perpendicular and parallel to the plane of the aromatic ring respectively. McConnell and Robertson observed the following qualitative results. $\pi + \sigma^*$ excitations with average energy ΔE_1 reduce g_1 by $2\zeta/\Delta E_1$. $\sigma + \pi$ excitations of average energy ΔE_2 increase g_1 by $2\zeta/\Delta E_2$. g_{\parallel} is close to g_e as only highly energetic $\sigma + \sigma^*$ transitions contribute to g_{\parallel} . Thus $g_{av} \approx 1/3(g_e + 2g_{\perp})$ and since ΔE_1 is usually greater than ΔE_2 , $g_{av} > g_e$. Heteroatoms are further expected to increase g since: (a) they have large spin-orbit coupling constants; and (b) they have low energy $n + \pi$ transitions which reduce the effective ΔE_2 . Further, the shift in g value is proportional to the odd electron density on the heteroatom.