AN ELECTRON SPIN RESONANCE STUDY OF NITROGEN
HETEROCYCLIC ANIONS AND ION PAIRS

by

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Abstract.

The purpose of this investigation has been to make a comparison of the experimental and theoretically calculated electron spin resonance spectra of nitrogen heterocyclic radical ions. Because of the recent nature of the field, and because of recent advances in theoretical aspects, the theory of ESR and of the calculation of spin density distributions is reviewed in some detail in Chapter I.

In Chapter III the ESR spectra of methyl substituted pyrazine and pyridine anions prepared by chemical reduction with alkali metals are described. Hückel and McLachlan calculations have been performed using various theoretical models and it has been found that presently used simple theories of spin density distributions give a reasonably good explanation of the ESR spectra of these aromatic radical ions.

The modified ESR spectra of the ion-pairs of methyl substituted pyrazine, pyridine, and benzene anions with alkali metal cations are examined in Chapter IV. Factors influencing the stability of the ion-pairs are discussed and the theory of alkali metal hyperfine interaction is
considered in some detail. It is found likely that in future work attention will have to be directed at the estimation of the energy of excitation from the anion to the cation.

Finally, the ESR spectra of some aromatic heterocyclic N-oxide anions generated electrolytically are examined in Chapter V and the results of Hückel and McLachlan calculations of the spin density distributions in the ions are discussed. Because of the perturbed nature of the molecules agreement with the experimental distributions is found to be not quite as satisfactory as with the pyrazine anions. The mechanism of the nitrogen hyperfine interaction in N-oxide anions is investigated and it is suggested that this interaction is overwhelmingly due to the spin density on the nitrogen itself. This last aspect of the ESR spectra of N-oxide anions awaits more complete experimental confirmation.
Acknowledgement.

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CHAPTER I. THEORETICAL REVIEW.

A. Electron Spin Resonance.

(1) Introduction:

Since it was first discovered by Zavoiskii (1,2) the phenomenon of electron spin resonance (ESR) has undergone intensive investigation and development. As a result, the field has grown too broad to be treated in a condensed manner and it will be necessary to restrict this discussion specifically to those aspects of ESR which pertain to the study of free radical species in solution. The theory of spin resonance and its application to the elucidation of the electronic structure of chemical species has been reviewed in detail by various authors (3-15).

Electron spin resonance is concerned exclusively with species in which a certain number of electrons is "unpaired". The energy of such electrons is influenced by factors such as the coulomb field of atomic nuclei in molecules or the electric fields associated with certain crystal lattices. After all these effects have been taken into account, however, there remains an additional degeneracy of the electronic energy levels (16) which is lifted only by the application of an external magnetic field. This degeneracy is due to the existence of an intrinsic angular momentum and magnetic moment associated with the electron.
Interaction of the electron magnetic moment with an external magnetic field will separate the degenerate levels and transitions between them can be induced through the application of an oscillating magnetic field of appropriate frequency, provided the transition probabilities do not vanish.

The observation of transitions between energy levels influenced by electronic interactions alone can give substantial information about, for example, the structure of paramagnetic complex ions (7,9). Of particular interest, however, is the fact that many species containing unpaired electrons also contain nuclei with non-zero magnetic moments, such as the proton or the nitrogen-14 nucleus. Interaction of the electrons with these nuclei can further modify the electronic energy levels in an experimentally detectable fashion. This aspect of ESR, called hyperfine interaction, has proved to be very helpful in elucidating the distribution of electrons in molecules, and has given additional impetus to theoretical work on the electronic structure of molecules.

(2) Simplifying Assumptions:

The discussion which follows will be restricted to only a certain narrow class of species containing unpaired
electrons. Some aspects of the complete theory may have a limited importance in special cases, however, and these will be mentioned when applicable.

The species considered are planar aromatic radical-ions in non-viscous liquid solutions, containing one unpaired electron which is distributed in a $\pi$-orbital above and below the plane of the ion. If, for the moment, solvent effects are neglected then only interactions within the isolated ions need be taken into account, since solutions containing the ions can always be diluted sufficiently for inter-ionic effects to become negligible.

In $\pi$-electron radical ions orbital angular momentum is almost totally quenched so that coupling interactions involving this type of angular momentum are neglected. A further term in the expression for the energy of the electron which can be ignored is the coupling of nuclear magnetic moments with the external magnetic field. This interaction does not influence the ESR transitions to first approximation, although it may be important in solids (17).

The interaction of the electron spin angular momentum $S$ with the external field $H$ and a non-zero nuclear spin angular momentum $I$ can then be written (7)
in Hamiltonian form as

\[ \mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} \]

where \( \beta \) is the absolute value of the Bohr magneton, \( \mathbf{g} \) is the spectroscopic splitting factor, and \( \mathbf{A} \) the hyperfine interaction constant. Both \( \mathbf{g} \) and \( \mathbf{A} \) are, in general, tensorial quantities.

Two further simplifications are now possible. In solution, free radicals are constantly changing their orientation with respect to the static magnetic field, at a rate rapid compared with the electronic transition frequency, with the result (18) that the anisotropy in \( \mathbf{g} \) and \( \mathbf{A} \) is averaged out. Because of the quenching of the orbital angular momentum, the isotropic value for the g-factor is close to that of the free electron, \( g = 2.0023 \), for most free radicals in solution (4,19,20). The second simplification arises because, in the strong magnetic fields employed in ESR, the sharp component of a spin angular momentum is that along the direction of the field. If \( \mathbf{H} \) is directed along the z-axis then the Hamiltonian takes the form

\[ \mathcal{H} = g \beta \mathbf{H} S_z + g \beta \alpha S_z I_z \]
\( \alpha \) is the hyperfine coupling constant and can be written (21-23) in the form

\[
\alpha = \frac{2\pi}{3} \frac{g_I}{\beta} \left( \sum_k S_{3k} \right) \delta(\mathbf{r}) \]

where \( g_I \) and \( \beta \) are the nuclear \( g \)-factor and nuclear magneton, respectively. \( \delta(\mathbf{r}) \) is the Dirac delta function (24) for the vector distance \( \mathbf{r} \) between electron and nucleus, and the sum is over all electrons \( k \). In what follows, attention will be directed at the second term in equation 2) since it provides most of the experimental information.

(3) Hyperfine Interaction:

(a) Applicability to \( \pi \)-electron Radicals:

Equation 3) indicates that the isotropic interaction is a contact interaction which will vanish unless the distance between electron and nucleus is zero. Now in the usual one-electron approximation for \( \pi \)-electron radicals the bonding \( \sigma \)-electrons are treated independently of the bonding and unpaired \( \pi \)-electrons, so that in this approximation the unpaired electron orbital has a node at the position of the nuclei in the plane of the molecule and the contact term is zero.
The experimental evidence shows that this picture is inadequate. Since a complete treatment of all $\sigma$- and $\pi$-electrons is impracticable for most radicals it is necessary to consider interaction between the $\sigma$- and $\pi$-electrons as a perturbation on the states where these electrons are rigorously separated (25,26).

The physical picture being considered is then the following. The unpaired electron moves in a $\pi$-orbital above and below the plane of the aromatic ring. Electronic interactions $\frac{e^2}{r_{ij}}$ cause a mixing of the ground state of the radical with excited states in which electrons in $\sigma$-orbitals become unpaired. The expectation value of the contact term of equation 3) will then be finite and lead to a finite value of the hyperfine splitting.

A number of authors have treated this problem and it has been reviewed severally (6,13,14). McConnell and Chesnut (27) have given an early calculation of the hyperfine interaction for protons attached to aromatic ring carbon atoms. More recent treatments of the aromatic C-H bond have been those of Aono (28), of Ben Jemia and Lefebvre (29), and of Higuchi (30). McLachlan (31) and Chesnut (32) have extended this to methyl groups attached to centers where unpaired electrons are located.
Much of the recent work has been concerned with hyperfine splitting due to nuclei in the aromatic ring itself. Most calculations have been done for carbon-13 nuclei (33-36) and these have been extended to nitrogen-14 nuclei in heterocyclic radicals (37,38).

The treatment which will be given below is one first proposed by McConnell (39) and subsequently developed by others (33,38,40,41). The notation of Henning (38) is followed.

(b) **Theoretical Treatment**: 

For a radical ion with $2n + 1$ electrons let $\sigma_i$, $\bar{\sigma}_i$ stand for the bonding $\sigma$-orbitals occupied by electrons with $\alpha$ and $\beta$ spin, respectively, and $\pi_j$, $\bar{\pi}_j$ for the bonding $\pi$-orbitals. Let $\pi_{n+1}$ denote the $\pi$-orbital occupied by the unpaired electron. Then, to a first approximation, the ground state of the ion can be expressed as a single determinant (42,43) of the form

$$\Psi_0 = | \sigma_i \bar{\sigma}_i \ldots \sigma_m \bar{\sigma}_m \pi_{n+1} \ldots \pi_n \bar{\pi}_n |$$

For the reasons mentioned above excited configurations must now be taken into account in which an electron from a bonding orbital $\sigma_i$ is promoted to an antibonding orbital $\sigma_i^*$. In first approximation, only singly-excited
configurations need be considered and from these two doublet states $\psi_1$, $\psi_2$ can be constructed (44) which may mix with the ground state.

$$\psi_1 = \frac{1}{\sqrt{2}} \left[ | \sigma_1 \ldots \sigma_c \bar{\sigma}_p^* \ldots \pi_{n_1} | - | \sigma_1 \ldots \bar{\sigma}_c \sigma_p^* \ldots \pi_{n_1} | \right]$$

$$\psi_2 = \frac{1}{\sqrt{6}} \left[ 2 | \sigma_1 \ldots \sigma_c \sigma_p^* \ldots \pi_{n_1} | - | \sigma_1 \ldots \sigma_c \sigma_p^* \ldots \pi_{n_1} | - | \sigma_1 \ldots \bar{\sigma}_c \sigma_p^* \ldots \pi_{n_1} | \right]$$

It will be useful to define a spin-density operator (39) whose expectation value $\varphi(\tau)$ in an eigenstate $\psi$ of $S_3$ with eigenvalue $m_s$ gives the density of spin angular momentum at a point $\tau$ in the radical ion.

$$\varphi(\tau) = m_s^{-1} \langle \psi | \sum_k S_3(k) \delta(\tau) | \psi \rangle$$

If $\psi$ is expressed in a complete set of molecular orbitals $\{\phi_i\}$ then 7) can be rewritten as

$$\varphi(\tau) = m_s^{-1} \sum_{i,j} \langle \psi | \phi_i \rangle \varphi_{ij} \langle \phi_j | \psi \rangle$$

$$= m_s^{-1} \sum_{\tau,s} \langle \psi | \chi_\tau \rangle \varphi_{\tau s} \langle \chi_s | \psi \rangle$$

if the $\phi_i$ are further expanded in atomic orbitals $\chi_\tau$. $\varphi_{ij}$ is the matrix element of the spin-density operator.
between \( \Phi_i \) and \( \Phi_j \), and \( \Phi_{+s} \) that between \( \chi^+ \) and \( \chi_s \). The molecular orbital spin-density matrix \( \varphi' \) and the atomic orbital matrix \( \varphi \) are related by

\[
\varphi_{+s} = \sum_{i,j} \langle \chi^+ | \Phi_i \rangle \varphi'_{ij} \langle \Phi_j | \chi_s \rangle
\]  \hspace{1cm} (9)

If \( \varphi(r) \) is evaluated for the state \( \psi_0 \), equation \( 4 \), then using the orthogonality of the molecular orbitals

\[
\varphi(r) = | \pi_{n\iota}(r) |^2
\]  \hspace{1cm} (10)

The molecular orbital spin-density matrix \( \varphi' \) has then only one non-zero element

\[
\varphi'_{n\iota, n\iota} = 1
\]  \hspace{1cm} (11)

If \( \pi_{n\iota} \) is expanded in the \( 2p \) orbitals \( p_\iota \) of the atoms making up the aromatic ring

\[
\pi_i = \sum_p c_{+,i} p_\iota
\]  \hspace{1cm} (12)

then equation \( 9 \) gives for the atomic orbital spin-density matrix \( \varphi \)

\[
\varphi_{+s} = c_{s,n\iota}^* c_{+,n\iota}
\]  \hspace{1cm} (13)

To first approximation there will be no contribution to the spin density from \( \psi_i \), equation \( 5 \), and the perturbed
ground state is then written to first order as
\[ \mathcal{Y} = \mathcal{Y}_0 + \frac{\langle \mathcal{Y}_0 | \mathcal{H} | \mathcal{Y}_2 \rangle}{E_0 - E_2} \mathcal{Y}_2 \]  \hspace{1cm} (14)

where \( \mathcal{Y}_2 \) must be summed over the orbitals \( \sigma_i \) and \( \sigma_p^* \). \( \mathcal{H} \) is the total electronic Hamiltonian and \( E_0, E_2 \) are the expectation values of \( \mathcal{H} \) in \( \mathcal{Y}_0, \mathcal{Y}_2 \) respectively.

Since \( \mathcal{Y}_0 \) gives no contribution to the spin density in the plane of the aromatic ring the first order contribution is now
\[ \varphi(t) = 2 \frac{\langle \mathcal{Y}_0 | \mathcal{H} | \mathcal{Y}_2 \rangle}{E_0 - E_2} \langle \mathcal{Y}_2 | m_s^z \sum_k S_j(k) \delta(t) | \mathcal{Y}_0 \rangle \]  \hspace{1cm} (15)

The matrix elements between \( \mathcal{Y}_0 \) and \( \mathcal{Y}_2 \) are
\[ \langle \mathcal{Y}_2 | m_s^z \sum_k S_j(k) \delta(t) | \mathcal{Y}_0 \rangle = \frac{2}{\sqrt{6}} \sigma_i(t) \cdot \sigma_p^*(t) \]  \hspace{1cm} (16)

and
\[ \langle \mathcal{Y}_0 | \mathcal{H} | \mathcal{Y}_2 \rangle = -\sqrt{\frac{3}{2}} \langle \sigma_i \pi_{n_i} \frac{e^2}{\hbar c} \pi_{n_i} \sigma_p^* \rangle \]
\[ = -\sqrt{\frac{3}{2}} \sum_{\tau s} c_{\tau i \tau} c_{s \pi i} \langle \sigma_i \pi_{\tau} \frac{e^2}{\hbar c} \pi_{\tau} \sigma_p^* \rangle \]  \hspace{1cm} (17)

where the coefficients \( c_{\tau i \tau} \) are now taken as real. If the hyperfine coupling matrix \( Q^i \) for nucleus \( i \) is defined by its elements
\[ Q_{\tau s}^i = -\frac{16\pi}{3} \beta_i \sum_{\tau p} \frac{\langle \sigma_i \pi_{\tau} \frac{e^2}{\hbar c} \pi_{\tau} \sigma_p^* \rangle}{E(\tau) - E(\pi)} \sigma_i^*(\tau) \cdot \sigma_p^*(\pi) \]  \hspace{1cm} (18)
then using equation (13) the final expression for the hyperfine coupling (or splitting) constant for nucleus \( i \) is

\[
\alpha_i = \text{Tr} \left( Q^t \varphi \right) = \sum_{s,t} Q^t_{ss} \varphi_{sr} \tag{19}
\]

Equation 19) thus indicates a direct relation between the spin density and the hyperfine splitting.

(c) **Special Cases:**

(i) **Aromatic Ring Protons:**

Figure 1a shows the geometry of the CHC\(_2\) fragment which illustrates the case of a proton attached to a carbon atom in an aromatic ring. The proton does not bear a p-orbital so that \( Q^H_{mm} \) vanishes. If the assumption is made that off-diagonal elements and elements arising from the spin density on non-contiguous carbon atoms can be neglected then only \( Q^H_{cc} \) will be important and equation 19) becomes

\[
\alpha_H = Q^H_{cc} \varphi_{cc} \tag{20}
\]

This is the relation originally proposed by McConnell (46). For the benzene negative ion, where \( \varphi_{cc} = 1/6 \) for all carbon atoms, the experimental value (47) of the hyperfine coupling constant is
(G stands for Gauss throughout this thesis). The most recent calculation (29) gives a value of -23.61 G for this constant. The negative sign has been confirmed experimentally (48). Since the hyperfine splitting in the hydrogen atom is 508.6 G (49), a unit spin density on a ring carbon thus induces a negative spin density, i.e. a spin density of polarization opposite to that on the carbon atom, of approximately 0.05 on the adjacent proton.

Experimentally it is found that $Q_{cc}^n$ is not a constant for all aromatic free radicals. In particular (50), it has become clear that $|Q_{cc}^n|$ is considerably larger than 22.5 G for polynuclear hydrocarbon radicals. Nor is $Q_{cc}^n$ the same for both the positive and negative ions of a particular alternant hydrocarbon, although the pairing properties of the molecular orbitals of these compounds (51) suggest that this should be so. Discrepancies of a different kind are found when $|Q_{cc}^n|$ seems too large because of the presence of negative spin densities (52,53).

The problem has been treated with an extension of the present theory. Colpa and Bolton (41) have taken as perturbed ground state for the radical species the function
Figure 1: Models for configuration interaction.

a) The CHC$_2$ fragment.
b) The CNC fragment.
c) The CNO$_2$ fragment.
\[ \mathcal{V}' = (1 + \lambda^2 + \mu^2)^{-\frac{1}{2}} \{ \mathcal{V}_0 + \lambda \mathcal{V}_1 + \mu \mathcal{V}_2 \} \]

where \( \lambda, \mu \ll 1 \) and the \( \mathcal{V}_i \) were defined in equations 4 to 6. By a consideration of the one-particle reduced density matrix (54) constructed from \( \mathcal{V}' \) they have concluded that, to second order, \( \mathcal{V}_2 \) influences mainly the spin density and \( \mathcal{V}_1 \) the charge density. They have derived and tested an equation of the form

\[ \alpha_H = \varphi_{cc} (Q + K \varepsilon_{cc}) \]

where \( \varphi_{cc} \) and \( \varepsilon_{cc} \) are the spin and excess charge densities, respectively. \( Q \) and \( K \) have been determined empirically to be \( Q = -31.2 \, \text{G}, \, K = -17 \, \text{G} \).

Giacometti, et al. (55) have proposed and tested a superficially similar relation. They include the first off-diagonal elements of both \( \varphi^H \) and \( \varphi \) to give

\[ \alpha_H = Q_{cc} \varphi_{cc} - 2 Q_{cc}^H (\varphi_{cc'} + \varphi_{cc''}) \]

with \( |Q_{cc'}^H| = 31.5 \, \text{G}, \, |Q_{cc''}^H| = 3.5 \, \text{G} \) if overlap is neglected in the calculation of spin densities. For positive ions the sign in equation 24) is changed. It is to be noted that in all these treatments only excitations of the form \( \sigma_{\text{ee}} \rightarrow \sigma_{\text{ee}}^* \) are considered since \( \sigma_{\text{ee'}}(\tau_\text{ee}) \) and \( \sigma_{\text{ee'}}^*(\tau_\text{ee}) \) are very small at the position of the proton.
A second problem that has arisen is that $Q_{cc}^n$ changes when the angle $C'CC''$ in figure 1a changes from 120°. For example, the $Q_{cc}^n$ found experimentally for cyclopentadienyl radical (56), benzene negative ion (47), cycloheptatrienyl radical (57, 58), and cyclooctatetraene negative ion (59) are -28.0, -22.5, -25.6 to -27.6, and -25.7 G, respectively.

Bernal, et al. (60) have attempted to calculate the dependence of $Q_{cc}^n$ on bond angle, but their results do not agree with the experimental findings. More recently Higuchi (30), who also considered the effect of charge density, has found little dependence of the calculated constant on bond angle. Berthier, et al. (61) have suggested the possibility of bent bonds between the carbons (62), assuming that the hybridization at the carbon does not change appreciably with bond angle, and have arrived at good agreement with experimental values for $Q_{cc}^n$ when they used the theory of Bernal, et al. (60).

(i1) Carbon-13 in the Ring:

If the CHC$_2$ fragment is again taken as model for a ring carbon atom attached to two other carbons and a proton (figure 1a) then equation 19) gives for the carbon-13 splitting $\alpha_c$
\[
\alpha_c = Q_{cc} \varphi_{cc} + (Q_{cc} + Q_{c'c}) (\varphi_{c'c} + \varphi_{c''c}) \\
+ Q_{c'c'} (\varphi_{c'c'} + \varphi_{c''c''}) + 2 Q_{c'c''} \varphi_{c''c'}
\]

If the reasonable assumptions are made that \( Q_{c''c} \) is negligible for the non-neighbours \( C' \) and \( C'' \), and that off-diagonal elements of \( Q^c \) are small then equation 25) reduces to that derived by Karplus and Fraenkel and by others (33,34,36)

\[
\alpha_c = Q_{cc} \varphi_{cc} + Q_{c'c'} (\varphi_{c'c'} + \varphi_{c''c''})
\]

It should be noted that the \( Q \)'s in equation 26) include summations over all significant \( \sigma_i \rightarrow \sigma_p^* \) excitations, and also an excitation \( \sigma_i \rightarrow \sigma_q^* \) where \( \sigma_i \) represents a carbon 1s orbital. In Fraenkel's notation (36)

\[
Q_{cc} \equiv (Q^c + Q_{ch}^c + 2 Q_{c'c'}) = 35.6 \text{ G}
\]

\[
Q_{c'c'} \equiv (Q_{c'c'}) = -13.9 \text{ G}
\]

The symbols in equation 27) enclosed by brackets are those defined by Fraenkel and are not to be confused with the elements of \( Q^c \).

For a tertiary carbon such as the one in position 9 of naphthalene the proton is replaced by a carbon \( C'' \) and
equation 26) becomes
\[ \alpha_c = 30.5 \phi_{e} - 13.9 (\phi_{e'c'} + \phi_{e''c''} + \phi_{e''c''} ) \]  

These equations have been tested and found to agree quite well with experimental results (35,36).

(iii) Nitrogen-14 in Heterocyclic Anions:

For the hyperfine splitting due to a nitrogen-14 nucleus in an aromatic heterocyclic such as pyridine the model taken is that of the CNC fragment, figure 1b. Evaluating equation 19) for this model gives

\[ \alpha_n = Q_{NN} \phi_{NN} + (Q_{NC}^N + Q_{CN}^N)(\phi_{NC}^N + \phi_{NC}^N) + Q_{CC}^N (\phi_{CC} + \phi_{CC}) \]  

where the non-neighbour term \( Q_{CC}^N \) has been dropped, as before.

In the present case the effect of the non-bonding electron pair \( n_N \) must also be considered. In equation 4) the first two \( \sigma^- \) orbitals then stand for \( \sigma_1 = (1s)_N \), \( \sigma_2 = n_N \). Other terms that are taken into account (38) are the higher nitrogen \( s \) orbitals \( \sigma_i = (i s)_N \). Additional excitations are then of the type \((1s)_N \rightarrow \sigma_{NC}^*\), \((1s)_N \rightarrow (i s)_N \) \((i=3,...7)\), \( n_N \rightarrow \sigma_{NC}^* \).
Henning (38) has done a complete calculation for this case and his results are summarised in the hyperfine coupling matrix $Q^N$ (unit: Gauss)

$$Q^N = \begin{pmatrix}
N & C' & C'' \\
N & +24.4 & +7.0 & +7.0 \\
C' & -3.5 & +8.2 & 0 \\
C'' & -3.5 & 0 & +8.2 \\
\end{pmatrix} \quad (30)$$

so that equation 29) becomes

$$\alpha_N = 24.4 \varphi_{NN} + 8.2 (\varphi_{CC} + \varphi_{CC'}) + 3.5 (\varphi_{NC'} + \varphi_{NC''}) \quad (31)$$

Considerable experimental material on nitrogen heterocyclic anions has been collected in recent years. Comparing Hückel spin densities (see part B) with nitrogen splittings in a number of diazine negative ions Carrington, et al. (63), and McDowell, et al. (64), concluded that only $Q_{NN}^N$ was of significant magnitude, $Q_{NN}^N = 25.3$ G (63). Other authors have considered also the effect of the neighbouring carbon atoms (37,38,65-69). Stone and Makl (37) have evaluated some of the constants in equation 29) semi-empirically and have concluded that

$$\alpha_N = (30.9 \pm 2) \varphi_{NN} - (2 \pm 2) (\varphi_{CC} + \varphi_{CC'}) \quad (32)$$
By empirical methods Atherton and co-workers (68) have found
\[ Q_{nn}^N = 28.4 \, \text{G} , \quad Q_{cc}^N = -3.9 \, \text{G} \]
while Ward (67) gives
\[ Q_{nn}^N = 20.9 \, \text{G} , \quad Q_{cc}^N = 7.0 \, \text{G} \]. Neglecting off-diagonal elements Henning and de Waard (38,69) have done a detailed least-squares fit of experimental data to a 2-parameter equation and have derived

\[ a_N = 19.1 \varphi_{nn} + 9.1 (\varphi_{cc} + \varphi_{cc}^n) \]

This agrees quite well with the calculated values (equation 31), and also with the results of Ward (67).

(iv) Nitrogen-14 in Nitrogroups:

For N-14 in nitrogroups attached to aromatic rings the model of a CNO2 fragment, figure 1c, is considered. Using equation 19) with the previous assumptions and with neglect of off-diagonal elements the hyperfine splitting due to the nitrogen nucleus becomes

\[ a_N = Q_{nn}^N \varphi_{nn} + Q_{cc}^N \varphi_{cc} + Q_{oo}^N (\varphi_{oo} + \varphi_{oo}') \]

Rieger and Fraenkel (70) have fitted experimental splitting constants to equation 34), using McLachlan spin densities (see part B). They obtain the values

\[ Q_{nn}^N = \pm (99 \pm 10.2) \, \text{G} , \quad Q_{oo}^N = \pm (35.8 \pm 5.9) \, \text{G} , \quad Q_{cc}^N = 0 \]

giving reasonable agreement with experiment. Fischer (71) has done the same with Hückel spin densities, and found that
\[ Q'_{\text{nn}} = 172 \text{ G} \] for nitrobenzenes and \[ Q'_{\text{nn}} = 185 \text{ G} \] for nitronaphthalenes, \[ Q'_{\text{oo}} = -74.6 \text{ G} \] and \[ Q'_{\text{cc}} = 8.06 \text{ G} \] give again reasonable agreement between calculated and experimental values for \( \alpha_n \).

(v) Methyl Protons:

Hyperfine splitting due to methyl protons is common, as, for example, in the methyl-substituted benzo-semiquinones (72), methyl-substituted benzene negative ions (73), or aliphatic free radicals in solution (74). The exact mechanism of the interaction has been the subject of controversy and will be discussed further in Chapter 3. The splitting can be given as

\[ \alpha_n(\text{CH}_3) = Q'_{\text{cc}}(\text{CH}_3) \phi_{c'c} \]  \(35\)

where \( C' \) is the carbon adjacent to the methyl group. \( Q'_{\text{cc}}(\text{CH}_3) \) has a positive sign, and this has been shown experimentally (75).

McLachlan (31), Chesnut (32), and Derbyshire (76) have calculated \( Q'_{\text{cc}}(\text{CH}_3) \) using the hyper-conjugative model (see Chapter III). They arrive at values of the order of 20 to 25 G for this constant. This compares with a value of 26.87 G for the methyl-proton splitting in the ethyl radical in solution (74). De Waard and Henning
(77,78) have recently studied a number of dimethylnaphthalene anions and have concluded that a value of 19.0 G best fits their results. Splitting due to carbon-13 in methyl groups has also been found experimentally and analysed by theoretical means (79).

B. The Calculation of Spin Densities.

(1) Introduction:

As was pointed out in part A of this chapter, the most satisfactory way to treat the interaction between electronic and nuclear spin angular momenta would be to carry out a complete calculation and then evaluate the expectation value of the hyperfine interaction in the electronic state thus arrived at. Despite modern computing methods, however, this is impossible for practically all cases of interest. It is necessary then to make assumptions which will facilitate the calculations while still paying due attention to physical realities.

For simplicity of the calculations it must be assumed that a rigorous separation of $\sigma$- and $\pi$-electrons is possible (42). A further approximation that is implied is the separation of the vibrational and rotational motion of the nuclei and of the motion of the electrons (80). This approximation can break down, especially when species with nearly degenerate energy levels are involved, as was recently demonstrated for the anions of mono-alkylbenzenes (81).
In the molecular orbital approximation it is then assumed that each π-electron moves independently of all others in the average field of the nuclei and of the other electrons. Electrons of anti-parallel spin fill these orbitals pairwise. The total state of all π-electrons is then described by a simple product of molecular orbitals. Correlation between the electrons arising from their indistinguishability is taken into account by writing a sum of products in the form of a determinant, as in equation 4), or even a sum of determinants. As a further approximation the π-orbitals are expressed as linear combinations of atomic p-orbitals, as in equation 12).

Just as the interelectronic repulsion term $\frac{e^2}{r_{ij}}$ can cause excitations of the type $\sigma \rightarrow \sigma^{*}$ it can also cause $\pi \rightarrow \pi^{*}$ excitations so that the ground state of the molecule or radical must often be supplemented by the inclusion of excited configurations. The method of the self-consistent field (SCF)(82,83) includes the repulsion term in the total Hamiltonian and then finds eigenstates of this Hamiltonian by an iterative process. An alternative method is to pick a number of physically reasonable excited configurations and mix them with the ground state as has, for example, been done in the calculation of spin densities in the cycl(3,2,2) azine anion (84,85).
(2) The Hückel Method:

The simple Hückel molecular orbital method for conjugated molecules has been widely used because of its mathematical simplicity, and has been reviewed by many authors (42,44,86-88).

Let the $\pi$-electronic state of an aromatic molecule be described by the function

$$\Psi = |\pi_{(1)} \pi_{(2)} \cdots \pi_{(2i-1)} \pi_{(2i)} \cdots |$$  \hspace{1cm} (36)

in the previous notation. The $\pi_i$ can be expanded in terms of atomic $p$-orbitals as in equation (12). An effective one-electron Hamiltonian $\mathcal{H}^{\text{eff}}$ is defined for each $\pi$-electron, including interelectronic repulsions in an average fashion, so that the total Hamiltonian is

$$\mathcal{H}^{\pi_{(1,2,\ldots)}} = \sum_k \mathcal{H}^{\text{eff}}(k)$$  \hspace{1cm} (37)

The molecular orbitals $\pi_i$ are then solutions of

$$\mathcal{H}^{\text{eff}}(i) \pi_i(i) = \varepsilon_i \pi_i(i)$$  \hspace{1cm} (38)

where $\varepsilon_i$ are the orbital energies. Making use of the expansion of the $\pi_i$ in atomic orbitals, and employing the variational principle (44) the coefficients are then solutions of
\[ \sum_{\tau} c_{\tau,i} \left( H_{\tau\tau}^{\text{eff}} - \varepsilon_i S_{\tau\tau} \right) = 0 \quad s=1,2,\ldots \quad (39) \]

For non-trivial coefficients the \( \varepsilon_i \) must be solutions of the secular equations
\[ \det \left| H_{\tau\tau}^{\text{eff}} - \varepsilon S_{\tau\tau} \right| = 0 \quad (40) \]

where the matrix elements \( H_{\tau\tau}^{\text{eff}} \) and overlap integrals \( S_{\tau\tau} \) are defined by
\[ H_{\tau\tau}^{\text{eff}} = \langle p_{\tau}(\mu) \mid \mathcal{H}^{\text{eff}}(\nu) \mid p_{\tau}(\nu) \rangle ; \quad S_{\tau\tau} = \langle p_{\tau}(\mu) \mid p_{\tau}(\nu) \rangle \quad (41) \]

The simple Hückel method now assumes the following. The overlap integral is ignored completely,
\[ S_{\tau\tau} = S_{\tau\tau} \quad (42) \]

\( S_{\tau\tau} \) is of the order of .3 for neighbouring carbon atoms, but its neglect along with the further assumptions below still leads to acceptable results (88). The matrix elements \( H_{\tau\tau}^{\text{eff}} \) are taken to be empirical parameters
\[ H_{\alpha\alpha}^{\text{eff}} = \alpha_{\alpha} ; \quad H_{\alpha\beta}^{\text{eff}} = \beta_{\alpha\beta} ; \quad \beta_{\tau\tau} = 0 \quad \text{if} \quad \tau \neq \pm 1 \quad (43) \]
i.e. \( \beta_{\tau\tau} \) vanishes for non-bonded atoms. For alternant hydrocarbons (51,89) the coulomb-integrals \( \alpha_{\varepsilon} \) are taken equal for all carbon atoms, and similarly for the resonance
integrals $\beta_{cc}$. A semi-empirical value (90) for the resonance integral in benzene is $\beta_{cc} = -2.60$ e.v.

It is useful to define now a complete charge- and bond-order matrix $d_{ij}$ (91) whose elements are

$$d_{ij} = c_{i,i} c_{j,i}$$  \hspace{1cm} (44)

for real coefficients. The usual $\pi$-electron densities $q_i$ and bond-orders $p_{ij}$ (51,89) are then

$$q_i = 2 \sum q_i = 2 \sum d_{ii} ; p_{ij} = 2 \sum p_{ij} = 2 \sum d_{ij}$$  \hspace{1cm} (45)

where the sum is over the occupied $\pi$-orbitals. If $\pi_{n\sigma}$ denotes the $\pi$-orbital containing the unpaired electron in a free radical then the atomic orbital spin density in this approximation is

$$q_{rs} = d_{rs}^{n\sigma,n\sigma}$$  \hspace{1cm} (46)

The term unpaired electron density should really be used in this context but, in the present thesis, the distinction between unpaired electron densities and spin densities is not always made.

If the species in question also contains heteroatoms then this can be considered as a perturbation on the corresponding hydrocarbon. If this perturbation $V$ is
defined so that the difference between the matrix elements of the perturbed Hamiltonian $H^\text{eff}$ in the perturbed orbitals $\pi_i$ and of the original $H^\text{eff(o)}$ in the unperturbed $\pi_i^{(o)}$ is

$$V_{ts} = H^\text{eff}_{ts} - H^\text{eff(o)}_{ts}$$

then the charge-order in the new molecule is given (91) by

$$q^{ij}_r = d^{ij}_r = q^{ij(o)}_r + \sum_{s,t} V_{st} \pi^{jj(o)}_{ts,rs}$$

where the mutability matrix $\pi$ has elements

$$\pi^{ij}_{ts,ru} = \frac{d^{ik}_{ts} d^{kj}_{ru} + d^{ik}_{ru} d^{kj}_{ts}}{\varepsilon^{(o)}_i - \varepsilon^{(o)}_k}; \pi^{\text{tot}}_{ts,ru} = \sum_i \pi^{li}_{ts,ru}$$

In terms of the notation of Coulson and Longuet-Higgins (89) the atom-atom polarizabilities $\pi_{rs}$, the atom-bond polarizabilities $\pi_{st,r}$, and the bond-bond polarizabilities $\pi_{ts,ru}$ are

$$\pi_{rs} \equiv \pi_{rs,ss} = \pi_{s,t}; \quad \pi_{st,r} \equiv \pi_{st,ss} = \frac{1}{2} \pi_{s,t}$$

$$\pi_{ts,ru} = 2 \pi^{\text{tot}}_{ts,ru}$$

For calculational purposes the coulomb integral $\alpha_r$ of any hetero-atom $r$, and the resonance integral $\beta_{rs}$ of any bond $r-s$ in a molecule are written as

$$\alpha_r = \alpha_c + \hbar \beta_{cc}; \quad \beta_{rs} = \hbar \beta_{cc}$$
where $\alpha_e$ and $\beta_0c$ are the corresponding integrals in benzene.

It is well to keep in mind that serious approximations are involved in the Hückel theory applied to heteromolecules and that not too much validity should be ascribed to absolute values obtained from it. Although its empirical elements make it widely applicable the empirical parameters are often chosen in a cursory manner and usually do not carry over from one molecular property to another (87,88).

(3) **The McLachlan SCF Method:**

In the self-consistent field (SCF) method of molecular orbitals the total $\pi$ -electron Hamiltonian is written (82) as

$$\mathcal{H} = \mathcal{H}' + \frac{1}{2} \sum_{r+s} \frac{e^2}{r_s}$$

$$\quad = \left( -\frac{1}{2} \nabla^2 - \sum_{r} V_r \right) + \frac{1}{2} \sum_{r+s} \frac{e^2}{r_s}$$

where $V_r$ is the potential due to nucleus $r$ screened by its $\sigma$ -electrons. In this Hamiltonian the interaction between $\pi$ -electrons is now taken into account explicitly.

The $\pi$ -electron state given by equation 36) can be treated by the Hartree-Fock method (82,83,88,92) to derive equations for the coefficients $C_{ri}$ if the molecular
orbitals are expanded in atomic orbitals \( \psi_i \). Pople, et al. \((93,94)\) have taken the Hamiltonian of equation 52) and, assuming that overlap integrals \( S_{rs} \) vanish unless \( r = s \) and that two-electron integrals depending on the overlap of the charge distribution of different orbitals are zero, have then shown that the \( c_{ri} \) are solutions of

\[
\sum_s F_{rs} c_{si} = \epsilon_i c_{ri} \tag{53}
\]

with the \( \epsilon_i \) being solutions of the secular equations

\[
\text{det} |F_{rs} - \epsilon \mathcal{S}_{rs}| = 0 \tag{54}
\]

where

\[
F_{rs} = \alpha_r + \frac{1}{2} q_r \gamma_{rs} + \sum_{s \neq r} (q_r - 1) \gamma_{rs}
\]

\[
F_{rs} = \beta_{rs} - \frac{1}{2} p_{rs} \gamma_{rs} \quad (r \neq s) \tag{55}
\]

with the definitions

\[
\beta_{rs} = \langle p_r \psi_i \mathcal{A} \psi_j | p_s \psi_i \rangle \quad ; \quad \alpha_r = \beta_{rr}
\]

\[
\gamma_{rs} = \langle p_r \psi_i \psi_j | \mathcal{F}_i | p_s \psi_i \psi_j \rangle \tag{56}
\]

The \( q_r \) and \( p_{rs} \) were defined before. Equation 53) is nonlinear since the \( F_{rs} \) are functions of the coefficients to be evaluated. The SCF method then assumes a set of \( c_{ri} \), calculates \( F_{rs} \) and derives a new set of coefficients from equation 53). This iterative process is repeated until the starting and final coefficients within a cycle agree within desired limits.
Hoijtink (95) has treated correlation between the π -electrons in free radicals by the method of configuration interaction using a function of the type of equation 22), where the excited orbitals are now π -orbitals. Instead of this another possibility is to use a function of the type (96)

\[ \psi = | \pi_1, \pi'_1, ... \pi_n, \pi'_n, \pi_{n+1} | \]

where now electrons of α- and β- spin move in the orbitals \( \pi_i \) and \( \pi'_i \), respectively. Starting with an SCF function of the type

\[ \psi_{SCF} = | \pi_1, \pi'_1, ..., \pi_n, \pi'_n | \]

McLachlan (97) has solved equations 53) to construct the "alternant orbital" function of equation 57).

The exchange interaction \( \gamma_{rs} \) does not affect the odd electron orbital but causes the energetically lower electrons of α- and β-spin to move in spatially different orbitals, which fact then changes the spin density at a given atom. McLachlan (97) has treated this perturbation of the spin density by the methods indicated before (equation 48)) to derive the following expression for the altered spin density

\[ \phi_{rs} = \phi_{rs}^{(o)} - \frac{1}{2} \sum_{t,u} p_{tu}^{(o)} \gamma_{tu} \pi_{rs,tu} \]

59)
where \( \pi_{rs, tu} \) are the bond-bond polarizabilities of Coulson and Longuet-Higgins (89).

For alternant hydrocarbons the atom-bond polarizabilities \( \pi_{rs, tu} \) vanish unless \( r \) and \( u \) are in the same set \((51, 89)\) and McLachlan (97) has assumed that they can all be neglected. Making the further assumption that all integrals \( \gamma_{rs,tu} \) are equal to \( \gamma \) then the diagonal elements of the spin density are

\[
Q_{rr} = c_{r,m_{0}}^2 - \frac{1}{2} \sum_{t} c_{t,m_{0}}^2 \pi_{r,t} \tag{60}
\]

McLachlan concluded that Hückel orbitals were sufficiently good as starting orbitals. Taking the resonance integral \( \beta \) outside the expression for \( \pi_{r,t} \) equation \(60\) becomes

\[
Q_{rr} = c_{r,m_{0}}^2 - \lambda \sum_{t} c_{t,m_{0}}^2 \pi_{r,t}' \tag{61}
\]

\( \lambda = -\frac{\gamma}{2 \beta} \) has been calculated \((97)\) from the integrals of Pariser and Parr \((98)\) as \( \lambda = 1.2 \).

It can be shown that \(61\) is equivalent to

\[
Q_{rr} = c_{r,m_{0}}^2 + \sum_{i=1}^{n} \left( c_{r,i}^2 - c_{r,i}'^2 \right) \tag{62}
\]

where \( c_{r,m_{0}}, c_{r,i}' \ (i = 1, 2, \ldots, n) \) are the coefficients of the ordinary Hückel orbitals and \( c_{r,i} \ (i = 1, 2, \ldots, n) \) are the coefficients of Hückel orbitals with resonance integrals unchanged, but with coulomb integrals altered to
C. de Waard (78) has derived equation 59) with the method of configuration interaction. 

This theory has been applied with good results to alternant hydrocarbon neutral and ionic radicals (97), and to hetero-ions such as the nitro- (70) and cyano-aromatic anions (99). It has the advantage over the Hückel theory of being able to explain the occurrence of negative spin densities. In its application to heterocyclic radicals it should be noted that some of its assumptions which hold for alternant hydrocarbons break down for heteromolecules. Some of these difficulties, and those involved in the Hückel theory, have been discussed by Dewar (100).
CHAPTER II. EXPERIMENTAL PROCEDURES.

A. Introduction.

The preparation of the radical anions of aromatic molecules has been accomplished in several ways. One of the most common methods has been the reaction of alkali or alkaline earth metals with the neutral compounds in polyethers such as dimethoxyethane or tetrahydrofuran (101). It was recognised that initially only one atom of the metal reacted with one molecule of the substance to be reduced (102), and it was proposed that transfer of one electron to the $\pi$-system of the aromatic molecule took place (103). Magnetic (104) and electron spin resonance investigations (105) showed that the result of the reaction with active metals was indeed a $\pi$-electron radical anion. Species quite analogous to these anions were found in the aromatic radical cations (50) which resulted from the reaction of aromatic hydrocarbons with concentrated sulphuric acid.

A technique which has found some application recently has been the ultra-violet irradiation of aromatic molecules dissolved in polyethers (106,107). It appears that radical ions are formed, but the processes involved are not completely understood at present (107).
The second major method for the preparation of radical ions has been that of electrochemical reduction in solution. This technique was first employed in connection with ESR by Galkin and co-workers (108), the reduction being that of sodium ion to sodium in liquid ammonia. Maki and his co-workers (109,110) have applied the technique to aromatic radical ions and it is now widely used (see, for example, references (70) and (71)).

B. Chemical Reduction.

Chemical reduction in the present work was usually performed with potassium metal in 1,2-dimethoxyethane (DME). In some cases sodium or sodium-potassium alloy were used and occasionally DME was replaced by tetrahydrofuran (THF), 2-methyltetrahydrofuran (MeTHF), or 1,4-dioxane. Because of the reactivity of the radicals contact with water or air had to be avoided especially in the chemical reduction procedure where radicals are not continuously generated during the recording of ESR spectra. A further reason for removing oxygen is that spin-spin interactions with the paramagnetic oxygen molecules broadens the spectral lines of ESR transitions undesirably even at low concentrations of oxygen (111).
The reduction of heterocyclic molecules and the recording of ESR spectra was accomplished under vacuum in the simple glass apparatus shown in figure 2a. The tip of the cell could be placed in the cavity of the ESR spectrometer and was constructed of silica to minimise absorption of microwave energy by the glass and unbalancing of the cavity. A small amount of the compound to be reduced was placed into the tip of the cell, the amount being small enough to make the final concentration of radical ions about $10^{-3}$ M or less. The cell could be evacuated through A.

A small, clean piece of sodium or potassium metal (or a piece of each, if the alloy was desired) was placed in a side-arm attached at B and, after evacuation, the metal was sublimed several times along the side-arm into the bulb C. After the cell was sealed off at B the appropriate solvent was distilled from a storage vessel into the bulb C by cooling C with liquid nitrogen or with a dry-ice-acetone mixture. After repeated warming-up and pumping of the solvent the cell was finally sealed off at A. The solvent was now unfrozen, the compound dissolved in it and poured back into the bulb C where the reaction took place. The reaction was left to proceed for some time to allow for complete reduction of the starting compound and the
Figure 2: Reaction Vessels,

a) for polyethers
b) for liquid ammonia
solution was then poured into the silica tip of the cell for the recording of its ESR spectrum. The concentration of anions in the tip could be changed by distilling over more solvent from the bulb.

The solvent in the storage vessel was kept under vacuum constantly, in contact with sodium-potassium alloy (112) and anthracene. This was accomplished in the following way. A small amount of anthracene was placed into a 500 ml bulb fitted with a side-arm and the bulb was attached to the vacuum system. Into the side-arm were placed about a gram each of clean sodium and potassium metal and the bulb was evacuated. The two metals were now heated together, and a globule of the liquid alloy rolled into the bulb, after which the side-arm was removed. Solvent, pre-dried with calcium chloride and under vacuum, was now distilled onto the anthracene and alloy by cooling the bulb in a dry-ice-acetone mixture. After staying in contact with the alloy for some time all the water and other chemicals containing active hydrogen had reacted with the metal, and the solution took on the permanent colour of the anthracene ions. The solvent was now ready for use. It was judged to be pure enough when a characteristic blue colour developed on contact of the solvent with potassium metal at low temperature (113). In some cases it was found
best to first reflux the solvent with sodium and anthracene until it developed a permanent colour and then to distill it onto the alloy in the storage bulb on the vacuum system.

Although the recording of most spectra took place at room temperature it was necessary in some cases to use lower temperatures. In such cases the silica part of the apparatus fitted into the dewar of the Varian V-45147 variable temperature system which uses a stream of pre-cooled nitrogen gas to lower the temperature of the sample. The temperature could be measured with a thermocouple one of whose junctions was placed inside the dewar near the sample.

In some instances, to be described later, liquid ammonia was employed as a solvent. Figure 2b shows the modified sample tube used with this solvent. The procedure in this case was analogous to that described above. The reaction was performed at the temperature of a dry-ice-acetone bath while the spectra were recorded at about -50°C. Before storage in gaseous form on the vacuum system the ammonia, obtained from a tank, was purified by liquefying it in contact with sodium metal.
C. Electrolytic Reduction.

The details of the electrochemical method of producing radical ions, used in some experiments to be described in Chapter V, have already been given by Fischer (71). Only a few additional comments need be made here.

The solvents used in the reductions were mostly mixtures of dimethoxyethane and acetonitrile. These solvents were stored on the vacuum system in contact with anhydrous calcium chloride. Since in this method the radicals are being formed continuously, the presence of traces of water or other reactive chemicals is not as critical as in the previous method. The concentration of the supporting electrolyte, tetra-n-propylammonium perchlorate, was 0.05 M in all cases, and the concentration of reducible material was approximately $5 \times 10^{-4}$ M to $10^{-3}$ M.

No polarography was performed, but in some cases approximate reduction potentials were obtained by measuring the increase in current through the electrolytic cell at the onset of electrolysis with a galvanometer. The potential of the reducing cathode could be measured with respect to that of the saturated calomel electrode (S.C.E.) by means of an observation cell to which the calomel electrode was attached via a salt bridge and sintered glass disc (71).
D. Recording of the ESR Spectra.

The ESR spectra were recorded on a standard Varian V-4500 spectrometer with some slight modifications. The spectrometer was operated at a frequency of about 9.4 kMcs. The 12-inch magnet provided a field of approximately 3,400 G and the magnetic field was modulated at 100 kcs. The magnetic field could be measured by means of a proton resonance magnetometer (4). The magnetometer oscillator supplied a variable frequency of about 14 Mcs to a glycerol probe near the cavity, and this frequency was made to beat with a 10 Mcs frequency from a signal generator. The beat frequency was measured with a Hewlett-Packard frequency counter.

The 100 kcs detection system used had been built in this department from the circuits of the Varian V-4560 100 kcs system, except that the transmitter and receiver were separated and shielded by copper plates. A further modification made late in the experimental stage of this work was that the klystron filament voltage was stabilised with a Kepco transistorised DC power supply, since the voltage derived from the line was found to fluctuate considerably.

Because of the possibility of saturation of the electronic energy levels of the radical ions by microwave
energy it was found best to use low power-levels for routine experiments. In the present work a power level of 5 milliwatts, measured with a bolometer, was used consistently. Since, further, the spectra consisted of many closely spaced lines it was necessary to use low amplitudes of the 100 kcs modulation. Whenever the intensity of the ESR absorption allowed the modulation was kept below 25 milligauss. To reduce contributions to the linewidth due to interactions on neighbouring radicals concentrations of radicals as low as \( \sim 10^{-5} \) M to \( 5 \times 10^{-5} \) M had to be used in some cases, and the spectrometer had to be operated under conditions of highest sensitivity.

E. Chemicals.

(1) Solvents:

Acetonitrile (Eastman 488) was used without special treatment, but was stored under vacuum in contact with anhydrous calcium chloride. Tetrahydrofuran (Anachemia 8914), 1,2-dimethoxyethane (Eastman 4639), 2-methyltetrahydrofuran (Eastman 5971) and 1,4-dioxane (Matheson, Coleman, and Bell 2347) were treated with sodium or sodium-potassium alloy and anthracene as described above. The DME preparate was stored under vacuum. THF, MeTHF, and dioxane, which were used only infrequently, were stored under a nitrogen atmosphere and evacuated when necessary.
(2) **Reagents:**

Anthracene (Eastman 480) was used without further purification. Tetra-n-propylammonium perchlorate, used as supporting electrolyte in electrochemical reductions, had been prepared by Fischer (71) and a sufficient stock was available. The mercury metal employed had been freshly distilled.

Sodium (Fischer S-206) and potassium (B and A 2080) metals were stored under paraffin oil. When needed the metals were washed with petroleum ether dried over sodium, and sublimed under vacuum.

(3) **Compounds Investigated:**

Pyrazine (K and K 28180 F), 2-methylpyrazine (Wyandotte 19905 D), 2,5-dimethylpyrazine (Wyandotte 19643), 2,6-dimethylpyrazine (Aldrich), tetramethylpyrazine (Aldrich T 2360), and 3,5-dimethylpyridine (Aldrich L 420) are all very volatile, colourless liquids or solids, and were sublimed under vacuum without heating.

4-nitropyridine was prepared from 4-aminopyridine (Aldrich A7840) by reaction with 30% hydrogen peroxide in concentrated sulphuric acid (114). The compound was re-crystallised from an ethanol-water mixture: ocher crystals, m.pt. 49-50°, reported m.pt. 50°.
4-nitropyridine-1-oxide was prepared from pyridine-1-oxide (Eastman P8282) by nitration with concentrated nitric acid in fuming sulphuric acid (115) and sublimed under vacuum: light brown crystals, m.pt. 159°, reported 159°.

4-chloropyridine-1-oxide was obtained from 4-nitropyridine-1-oxide by treatment with acetyl chloride (115) and recrystallised from acetone: colourless crystals, m.pt. 169-170°, reported 169.5°.

Pyrazine-1,4-dioxide, prepared from pyrazine with 30% hydrogen peroxide in glacial acetic acid (peracetic acid) (116), was recrystallised from ethanol: light brown plates. Elemental analysis: found C=43.03, N=23.18, H=3.85; calculated C=42.86, N=25.00, H=3.60.

2,5-dimethylpyrazine-1,4-dioxide was prepared from 2,5-dimethylpyrazine with peracetic acid (117) and recrystallised from ethanol: colourless crystals. Elemental analysis: found C=51.06, N=19.91, H=5.85; calculated C=51.42, N=19.99, H=5.75.

Quinoxaline-1,4-dioxide was obtained from quinoxaline (K and K 16374) with peracetic acid (116) and recrystallised from ethanol: orange needles. Elemental
analysis: found C=59.13, N=16.11, H=3.71; calculated C=59.25, N=17.28, H=3.73.

Phenazine-9,10-dioxide was prepared from phenazine (K and K 13874) with peracetic acid (116) and recrystallised from ethanol: red needles. Elemental analysis: found C=68.13, N=12.97, H=3.93; calculated C=67.92, N=13.20, H=3.80.

The preparation of the N,N'-dioxides with peracetic acid is straightforward. Since they all decompose at high temperatures melting points cannot be used for identification and the elemental analyses were used as a guide to their identity.
CHAPTER III. SUBSTITUTED PYRAZINES: ANION RADICALS.

A. Analysis of the ESR Spectra.

(a) Pyrazine:

Figure 3 gives the structural formulae for the compounds to be described in this chapter and also shows the numbering system employed in discussing the ESR spectra of their radical anions. All substituted pyrazine anion radicals were produced with potassium in DME, except for pyrazine anion radical itself which was prepared in liquid ammonia. All spectra except those in liquid NH₃ were recorded at room temperature, under the experimental conditions pointed out in Chapter II.

The pyrazine negative ion has been investigated previously in DME (38,63,64). When testing the suitability of liquid NH₃ as a solvent it was found that pyrazine negative ion could be prepared and observed easily in this medium. Figure 4 shows the ESR spectrum observed at -54°C in liquid NH₃. The lines are quite broad because of the high concentration of radicals. Nevertheless all 25 lines arising from 2 equivalent nitrogens with total nuclear spin \(\sum I_i = 2\) and from 4 equivalent protons with \(\sum I_i = 2\) can be observed. The least well-resolved lines have been indicated by arrows in figure 4.
FIGURE 3: STRUCTURAL FORMULAE.
Figure 4: ESR spectrum of pyrazine anion in NH₃ at -54°C.
The marked change in polarity of the solvent from DME to NH$_3$ does not affect the splitting constants appreciably. The experiments in liquid NH$_3$ give

\[ \alpha_n = 7.15 \, \text{G}, \quad \alpha_M = 2.65 \, \text{G}, \quad \text{total splitting } \Delta H_T = 39.24 \, \text{G} \]

in good agreement with previous values (64).

(b) 2,6-dimethylpyrazine:

The full spectrum of the radical anion of 2,6-dimethylpyrazine in DME is shown in figure 5. Figure 6 shows the low-field half of the same spectrum on an expanded scale. As is seen from figure 3, the two nitrogen atoms are now no longer equivalent and will have different coupling constants. There will be two additional coupling constants due to the two ring protons (\( \Sigma I_i = 1 \)) and the 6 methyl protons (\( \Sigma I_i = 3 \)). The single ESR line for a free electron will therefore be split by interaction with these nuclei into \( (2 \cdot 1+1)(2 \cdot 1+1)(2 \cdot 1+1)(2 \cdot 1+3) = 189 \) lines.

The coupling constants derived from the spectrum are

\[ \alpha_n = 2.85 \, \text{G}, \quad \alpha_n (\text{CH}_3) = 2.04 \, \text{G}, \quad \alpha_{N_1} = 6.16 \, \text{G}, \]

\[ \alpha_{N_4} = 7.35 \, \text{G}, \quad \Delta H_T = 44.40 \, \text{G}. \]
Figure 5: ESR spectrum of 2,6-dimethylpyrazine anion in DME.
Figure 6: ESR spectrum of 2,6-dimethylpyrazine anion in DME.
From the spectrum itself it cannot be decided which of the two nitrogen constants belongs to which ring position. This could be confirmed only by substitution of one of the ring nitrogens with nitrogen-15 which has a different nuclear spin. The assignment above had been made on the basis of the calculations to be described in succeeding sections.

The analysis of the experimental spectrum can be checked by reconstructing the spectrum from the above splitting constants. A number \( n \) of equivalent protons will give rise to \( 2\left(\frac{n}{2}\right) + 1 \) lines of binomial intensity distribution. One nitrogen gives rise to \( 2I + 1 = 3 \) lines of equal intensity and 2 equivalent nitrogens give 5 lines of intensity ratio 1:2:3:2:1. In this way the reconstructed spectrum shown in figure 7 is arrived at. Comparing the two half-spectra in figures 6 and 7 it is seen that agreement between them is quite good so that the analysis is very probably correct.

Not all the possible 189 lines are shown in the reconstructed spectrum since, on this scale, some of the lines are too close together to be drawn separately. It is also noticed that many lines occur in groups of 2 or 3 closely spaced lines which cannot be resolved with the present
Figure 7: Reconstructed spectrum of 2,6-dimethylpyrazine anion.
experimental set-up. However, the agreement between observed and reconstructed spectra is sufficiently good not to require any further experimental refinement. The reconstructed width is 44.96 G, somewhat larger than the experimental total width. This will, of course, contain the uncertainties in the individual splitting constants. The uncertainty is expected to be larger for the nitrogen coupling constants since they have to be measured near the center of the spectrum where the resolution of the lines is not as good as in the wings. The coupling constants reported in this thesis are generally accurate to at least .05 G, and better in many cases.

(c) 2,5-dimethylpyrazine:

The 2,5-dimethylpyrazine radical anion prepared with potassium in DME gives the ESR spectrum shown in full in figure 8 and in part in figure 9.

2,5-dimethylpyrazine, as is clear from figure 3, has a center of symmetry, and hence the two nitrogen nuclei will be equivalent. Similarly, there are two equivalent ring protons and 6 equivalent methyl protons. There will therefore be \((2\cdot2+1)(2\cdot1+1)(2\cdot3+1) = 105\) hyperfine lines in the ESR spectrum of the anion, and all of these have been observed experimentally. The spectrum is analysed without ambiguity to give the coupling constants.
\[ \alpha_H = 3.64 \text{ G}, \quad \alpha_{H(CH_3)} = 1.13 \text{ G}, \]
\[ \alpha_N = 6.67 \text{ G}, \quad \Delta H_T = 40.60 \text{ G}. \]

As outlined for 2,6-dimethylpyrazine, a reconstructed spectrum can be drawn up with the above splitting constants, for comparison with the experimental spectrum. The reconstruction is displayed in figure 10. The agreement between this and the experimental spectrum in figure 9 is very good, so that there can be no doubt about the analysis. The reconstructed total width is 40.74 G, close to the measured width.

(d) 2-methylpyrazine:

The ESR spectrum of the anion radical of 2-methylpyrazine has so far eluded all attempts to analyse it completely. The full spectrum and the low-field half of it are reproduced in figures 11 and 12, respectively. Resolution in all cases was not sufficient, and the line-shapes were somewhat odd. From figure 3 it is seen that all ring positions are different. There should be 6 different coupling constants and \[ (2 \cdot \frac{1}{2} + 1)^3(2 \cdot 1 + 1)^2(2 \cdot \frac{3}{2} + 1) = 288 \]
possible lines. From the wings of the spectra it is possible to derive the following coupling constants, with ring positions assigned according to the calculations which follow,
Figure 8: ESR spectrum of 2,5-dimethylpyrazine anion in DME.
Figure 9: ESR Spectrum of 2,5-Dimethylpyrazine Anion in DME.
Figure 10: Reconstructed spectrum of 2,5-dimethylpyrazine anion.
\[ \alpha_{N(\text{CH}_3)} = 1.57 \text{ G}, \quad \alpha_{N_2} = 3.83 \text{ G}, \quad \alpha_{N_5} = 2.14 \text{ G}, \]
\[ \alpha_{N_6} = 3.02 \text{ G}, \quad \alpha_{N_7}, \alpha_{N_9} = ? \quad \Delta H_T = 40.85 \text{ G}. \]

The value for \( \alpha_{N_5} \) is tentative only.

Using the above values, and the values for the nitrogen coupling constants calculated by the Hückel theory (see below), i.e. \( \alpha_{N_5} = 6.54 \text{ G}, \quad \alpha_{N_7} = 7.02 \text{ G} \), the "reconstructed" spectrum shown in figure 13 can be drawn up. To account for the poor resolution in the experimental spectrum lines closer than about .15 G in the reconstruction have been added together. As can be seen there is some measure of agreement, more so in the wings of the spectrum, but the agreement is certainly not good. The reconstructed width is 40.82 G, almost exactly the experimental value, but this is very likely to be fortuitous.

(e) **Tetramethylpyrazine:**

Figures 14 and 15 show the ESR spectrum of the tetramethylpyrazine radical anion, prepared with potassium in dimethoxyethane. Reference to figure 3 indicates that there should be a total of \( (2 \cdot 2 + 1)(2 \cdot 6 + 1) = 65 \) lines possible, while the spectrum obviously shows more lines. It is clear that there must be additional hyperfine structure due to the potassium-39 nucleus which has spin \( \frac{3}{2} \) and will
**Figure II:** ESR spectrum of 2-methylpyrazine anion in DME.
Figure 12: ESR Spectrum of 2-Methylpyrazine Anion in DME.
Figure 13: Reconstructed spectrum of 2-methylpyrazine anion.
split each of the 65 lines into an additional 4 lines of equal intensity. Since this aspect of the hyperfine spectra of the substituted pyrazines is discussed more fully in Chapter IV no further reference will be made to it here.

The spectrum can be analysed in terms of two splitting constants

\[ \alpha_n = 6.18 \text{ G} \quad \alpha_{\text{CH}_3} = 1.73 \text{ G} \quad \Delta H_T = 45.69 \text{ G} \]

neglecting the potassium hyperfine structure for the moment. A reconstructed spectrum drawn on this basis and shown in figure 16 compares well with the experimental one. The reconstructed total width is 45.48 G.

In the reconstructed spectrum the intensities of the weakest lines have been exaggerated somewhat in order to display them. Because of the binomial intensity distribution of the 13 lines due to the 12 methyl protons, the ratio of the intensities of the weakest and the strongest line will be 1:2,772 so that many of the weaker lines are not detected.

(f) 3,5-dimethylpyridine:

The anion radical of this compound has been studied by Atherton, et al. (68). Figure 3 shows that there should
Figure 14: ESR spectrum of (tetramethylpyrazine)\(^-\) (K)\(^+\) in DME.
Figure 15: ESR spectrum of (tetramethylpyrazine)$^-$ (K)$^+$ in DME.
be one nitrogen, 2 ring proton, and one methyl proton hyperfine coupling constants to give \((2 \cdot 1 + 1)^2 \cdot (2 \cdot \frac{1}{2} + 1)
\((2 \cdot 3 + 1) = 126\) components in the ESR spectrum. Because of serious discrepancies between Hückel calculations (see below) and the coupling constants found by Atherton and his co-workers (68), and because their spectrum was poorly resolved, it was felt desirable to re-investigate this compound.

No better resolution could be achieved, however, because of the rather large linewidths in the spectrum. It was found, on going to extreme dilutions, that this broadening was due to unresolved potassium-39 hyperfine structure. Up to almost 200 lines of this structure have been observed. This additional splitting due to K-39 will be discussed in Chapter IV. From this complex spectrum the following coupling constants could be derived

\[
\alpha_N = 6.12 \text{ G} \quad , \quad \alpha_{H_2} = 3.72 \text{ G} \quad , \quad \alpha_{H_3} = 8.70 \text{ G} \quad , \\
\alpha_{H(CH_3)} = 0.92 \text{ G} \quad , \quad \Delta H_T = 33.01 \text{ G} 
\]

These are somewhat lower than the previous values (68), except for the methyl splitting. The reconstructed width is 33.00 G in both cases, in exact agreement with the measured width.

It might be noted in this connection that no paramagnetic ions could be produced from 4-methylpyridine or
FIGURE 16: RECONSTRUCTED SPECTRUM OF TETRAMETHYLPYRAZINE ANION.
2,4,6-trimethylpyridine with potassium in DME at room temperature.

In table I a list of all splitting constants obtained in this chapter is given for later reference. The numbering of the compounds and positions refers to figure 3.

Table I. Experimental Coupling Constants for Methylated Nitrogen Heterocyclic Anions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Position</th>
<th></th>
<th></th>
<th></th>
<th></th>
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<td>5</td>
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<td>3.64</td>
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<td>1.57</td>
<td>(3.83)</td>
<td>?</td>
<td>2.14</td>
<td>3.02</td>
<td>40.85</td>
</tr>
<tr>
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<td>1.73</td>
<td></td>
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<td></td>
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<td>45.69</td>
</tr>
<tr>
<td>f</td>
<td>6.12</td>
<td>3.27</td>
<td>.92</td>
<td>8.70</td>
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<td></td>
<td>33.01</td>
</tr>
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</table>

B. Molecular Orbital and Hyperfine Coupling Parameters.

As indicated in Chapter I, the influence of heteroatoms in simple Hückel molecular orbital calculations is taken into account by letting the coulomb and resonance integrals of the heteroatom X and the bond X-Y be
\[ \alpha_x = \alpha_c + k \beta_{ee}, \beta_{14} = k \beta_{ee}, \] respectively. A considerable range of the parameters \( k \) and \( k \) has been used with nitrogen heterocyclics for various applications (87). In the following calculations it seemed best to use values of the integrals which had found previous application to ESR. In consequence, the values chosen were those of Carrington and dos Santos-Veiga (63), namely \( k = 0.75 \), \( k = 1 \).

The introduction of methyl groups instead of ring protons presents a different problem since methyl groups are devoid of \( p \)-orbitals. Several models have been employed to treat their effect on distributions of spin and charge densities in the ring, and these are discussed below.

The simplest model (87,118) considers the methyl group as just an inductive substituent whose only influence is to make the adjacent ring carbon atom slightly more electropositive than in the unsubstituted molecule. This model has been used by Bolton and Carrington (73) to explain the ESR spectra of methyl benzene anions. In the following calculations the parameters of Polansky (119) are used. With the numbering of figure 17a, \( \alpha_2 = \alpha_c - 0.15 \beta_{ee} \), while the resonance integrals \( \beta_{12} \) and \( \beta_{23} \) remain unchanged.
The second approach (118) uses the heteroatom model, which actually derives from the hyperconjugative model (see below and ref. (120)). Here the methyl group is taken as a single "heteroatom" attached to the ring and it is supposed that this heteroatom bears a \( \pi \) -type orbital containing 2 electrons and conjugated to the ring. The parameters used in the present calculation are those of Streitwieser (87,118). With the numbering of figure 17b

\[
\alpha_4 = \alpha_e + 2\beta_{ee}, \quad \beta_{2,4} = 0.7\beta_{ee}, \quad \text{with the other integrals unchanged.}
\]

In the inductive model any hyperfine splitting due to methyl protons would have to arise from spin polarization in the \( C'-C \) and \( C-H \) bonds. The third model to be discussed is the hyperconjugative one which assumes that the \( \pi \) -electrons of the ring are actually delocalised onto the methyl group. It is possible (86) to form linear combinations of the 3 hydrogen \( 1s \) orbitals of the methyl protons to give three new orbitals of \( \sigma^-, \pi_\sigma^- \) and \( \pi_\pi^- \) symmetry. Formally, the bonds between the protons of the methyl group and the methyl carbon are now similar to the carbon-carbon triple bond in acetylene. The \( \pi_\pi^- \) orbital of the methyl group can conjugate to the \( \pi^- \) orbitals of the ring, and delocalization of ring electrons into the \( \pi_\pi^- \) orbital can take place.
FIGURE 17: MODELS FOR METHYL GROUP

a) INDUCTIVE

b) HETEROATOM

c) HYPERCONJUGATIVE
Coulson and Crawford (121) have treated the theory in detail with the inclusion of overlap. In the following calculations overlap is neglected and the slightly modified (87,118) parameters of Coulson and Crawford are used. Referring to figure 17c for the numbering these are \( \alpha_n = \alpha_e - 0.1 \beta_{ee}, \quad \alpha_s = \alpha_e - 0.4 \beta_{ee}, \quad \beta_{2,4} = 0.8 \beta_{ee}, \quad \beta_{4,5} = 2.8 \beta_{ee} \).

There has been considerable discussion about the validity of the model, particularly as to its effects on the reactivities of methyl-substituted compounds (122). Bouman and Hoijtink (123) have shown that the simple molecular orbital theory predicts quite comparable effects on the charge distribution in substituted aromatic rings with both the inductive and the hyperconjugative model. The same can be said for the spin density distributions in, for example, methyl-substituted benzene anion radicals (73).

Recently, however, there has been more substantial evidence for the hyperconjugative effect. Bolton, et al. (120) found that the methyl proton splitting in methyl-substituted anthracene ions is about twice as large for the positive as for the negative ions. Colpa and de Boer (124,125) found the same effect for the CH₂ proton splitting in pyracene cations and anions. Colpa and de Boer have done explicit calculations and found that \( Q_{\text{c.c}}^n (\text{CH}_2) = -1.1 \, \text{G} \).
(see equation 35)) if spin polarization only were responsible for the hyperfine splitting. This is much too small and does not explain the difference between positive and negative ions. On the other hand, they have found very good agreement between calculated and experimental splitting constants when they assumed that hyperconjugative effects produce spin density at the methyl protons. These authors again point out that the effect of hyperconjugation on spin densities at the ring carbon atoms is by far not as large as that which produces spin density at the methyl protons.

For the calculation of spin densities by McLachlan's method the value $\lambda = 1.2$ was employed (97). This value was estimated by McLachlan for alternant hydrocarbon ions and it is doubtful whether it can be used for heterocyclics without modification. However, such modifications would involve dropping the assumption that all exchange integrals $\gamma_{tt}$ are equal and would complicate the theory considerably. In view of the fact that the $\gamma_{tt}$ for carbon and nitrogen are not vastly different, $\gamma_{cc}/\gamma_{nn} = .86$ (98), the value $\lambda = 1.2$ is retained for heteromolecules also (70,99).

C. Ring Proton and Methyl Proton Coupling Constants.

For comparison of the observed and calculated proton coupling constants a value must be chosen for the constants
Q in equations 20) and 35) were used. It seemed best to take the empirical value \( Q_{cc}^n = -22.5 \) G since theoretical estimates still differ appreciably. There should be little correction for bond-angle since the deviation from 120° of the N-C-C angle in pyrazine itself is only 2.5 degrees (126). For methyl proton hyperfine splittings the value \( Q_{cc}^n(CH_3) = +19.0 \) G of de Waard and Henning (77,78) was employed.

The spin densities calculated by the various methods discussed in the previous section are tabulated in Appendix A. Below only the splitting constants themselves are considered. Table II gives the calculated and experimental ring proton splitting constants. The numbering of the compounds and positions is that of figure 3. In the table, I refers to the inductive model, He to the heteroatom model, and Hy to the hyperconjugative model. The spin densities for pyrazine were taken from reference (63). McL in the table refers to the McLachlan method in which as starting orbitals those of the inductive model are employed.
Table II. Calculated Ring Proton Splitting Constants for Substituted Azines and Diazines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Position</th>
<th>Method</th>
<th>Exp't</th>
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<td></td>
<td></td>
<td>I</td>
<td>He</td>
</tr>
<tr>
<td>a</td>
<td>2</td>
<td>2.57</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>3</td>
<td>2.83</td>
<td>2.86</td>
</tr>
<tr>
<td>c</td>
<td>3</td>
<td>3.44</td>
<td>3.61</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.24</td>
<td>3.40</td>
</tr>
<tr>
<td>d</td>
<td>5</td>
<td>2.18</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.80</td>
<td>2.84</td>
</tr>
<tr>
<td>f</td>
<td>2</td>
<td>3.74</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.62</td>
<td>-</td>
</tr>
</tbody>
</table>

Table III lists the coupling constants for the methyl protons, with the same numbering as in tables I and II.

Table III. Calculated Methyl Proton Splitting Constants for Substituted Azines and Diazines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Model</th>
<th>Exp't</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>He</td>
</tr>
<tr>
<td>b</td>
<td>2.06</td>
<td>2.00</td>
</tr>
<tr>
<td>c</td>
<td>1.59</td>
<td>1.44</td>
</tr>
<tr>
<td>d</td>
<td>1.87</td>
<td>1.79</td>
</tr>
<tr>
<td>e</td>
<td>2.29</td>
<td>2.24</td>
</tr>
<tr>
<td>f</td>
<td>.86</td>
<td>-</td>
</tr>
</tbody>
</table>
Some comments can be made at this point about the applicability of the various theoretical models to the set of compounds discussed here. From table II it appears that the simple inductive approach best reproduces the proton hyperfine splitting in all compounds except 3,5-dimethylpyridine. Surprisingly, very similar results are obtained with the heteroatom model while the hyperconjugative model gives much poorer agreement. The hyperconjugative model, for presently unexplained reasons, gives practically equal ring proton and methyl proton splitting constants for the whole set of methylpyrazines. It is thus of little use in elucidating the ESR spectra of these compounds. It may be that the set of parameters chosen for the present set of compounds should be modified.

The methyl proton splitting constants are also explained nicely with the inductive and heteroatom models. Both models give thus a good picture of the distribution of the unpaired electron in the anions. In general the calculated methyl proton constants are too high. This is probably partly due to the fact that \( Q'_{\text{el}}(\text{CH}_3) \) was obtained from the ESR spectra of methyl substituted naphthalene anions (77, 78) and that this constant should be different for the methyl substituted benzene analogues.
If the experimental splitting constant is divided by the spin density calculated on the inductive model then an average value for $Q_{e'c'}^2(\text{CH}_3)$ for the four pyrazines is 13.4 G.

Quite good qualitative agreement of both ring and methyl proton splittings with calculated values is also obtained with McLachlan spin densities, and the method predicts the right relative order of the splitting constants. Quantitative agreement is not quite as good as with the inductive model.

The agreement of calculated and experimental values for 3,5-dimethylpyridine is not as good as for the other compounds. The McLachlan method correctly predicts a large value of the splitting due to the ring proton in the 4-position and predicts a negative spin density and hence a negative methyl proton splitting at position 3. The absolute value of the methyl splitting is still quite reasonably reproduced. It would be helpful if one could measure the sign of this splitting since Atherton, et al. (68) in their calculation of $Q_{NN}^n$ and $Q_{ee}^n$ from the ESR spectrum of this compound assumed that the spin density is everywhere positive. This may not be so, in view of the McLachlan calculation which does give a negative spin density.
It may be instructive to compare the pyrazines to other methyl substituted benzenes and benzene analogues. Bolton and Carrington (73) have studied the ESR spectra of the anions of toluene, m-xylene, and p-xylene which would correspond to the 2-methyl-, 2,6-, and 2,5-dimethylpyrazines. Venkataraman and Fraenkel (72), and Fairbourn and Lucken (127), have studied methyl substituted 1,4-benzosemiquinones, and Geske, et al. (128) have investigated methyl substituted 1,4-dinitrobenzene anions. Table IV lists the methyl proton splitting constants alongside the values for the pyrazines. The first row in the table gives the ring proton splitting constants for the unsubstituted ions.

The constants for toluene and p-xylene are not strictly comparable since in these anions the unpaired electron occupies an orbital of symmetry different from that in m-xylene, the 2,6-isomer of the table. In the p-dinitrobenzenes it is obvious from the small ring proton constant that most of the spin density is on the nitrogroups and hence the methyl splitting is small. Apart from these reservations the coupling constants are quite comparable for the pyrazines and p-benzosemiquinones and m-xylene, except that in the semiquinones there is less absolute variation in the constants than there is in the pyrazines.
Table IV. Comparison of Experimental Methyl Proton Splitting Constants.

<table>
<thead>
<tr>
<th>Substituted positions</th>
<th>Benzenes (a)</th>
<th>Pyrazines</th>
<th>1,4-benzosemiquinones (b)</th>
<th>1,4-dinitrobenzenes (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>unsubstituted</td>
<td>3.75</td>
<td>2.65</td>
<td>2.37</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>0.79</td>
<td>1.57</td>
<td>2.05</td>
<td>-</td>
</tr>
<tr>
<td>2,6</td>
<td>2.26</td>
<td>2.04</td>
<td>2.13</td>
<td>0.17</td>
</tr>
<tr>
<td>2,5</td>
<td>0.10</td>
<td>1.13</td>
<td>2.25</td>
<td>-</td>
</tr>
<tr>
<td>2,3,5,6</td>
<td>-</td>
<td>1.73</td>
<td>1.88</td>
<td>0</td>
</tr>
</tbody>
</table>

(a) ref. (73), (b) ref. (72,127), (c) ref. (128)

It is clear from the proton splitting in the unsubstituted compounds that the primary effect is a withdrawal of unpaired electron density onto the heteroatom and that methyl substitution further changes the spin densities in the ring slightly.

It should be noted that in the present discussion it was assumed for the inductive and McLachlan methods that the algebraic sum of the spin densities in the ring itself is unity, which implies that the methyl proton hyperfine interaction arises through spin polarization. Hyperconjugative delocalization of electrons onto the methyl groups, which appears to be the determining factor (125), would of course alter the spin densities in the ring. It might thus
turn out that a McLachlan-type extension of the hyperconjugative model would give better results than were obtained without the extension. However, it is doubtful whether the effort would be justified.

D. Nitrogen Splitting Constants.

To compare calculated and experimental nitrogen hyperfine coupling constants two approaches will be used. The first is to assume that only \( Q_{nn} \) is of importance, with \( Q_{nn} = 25.3 \, \text{G} \) (63). The second approach uses the two constants of Henning and de Waard (38,69), namely \( Q_{nn}^N = 19.1 \, \text{G} \) and \( Q_{ce}^{C\text{n}} = 9.1 \, \text{G} \) (38).

Table V gives a list of the calculated and experimental nitrogen splitting constants. The table gives only values derived from inductive and McLachlan spin densities. The heteroatom model gives values similar to those of the inductive model, while the hyperconjugative approach gives constants which are in most cases too high and do not differ sufficiently for the different compounds. The numbering of compounds and positions is again that of figure 3.

Table V shows that the inductive model gives a quite good quantitative correspondence between calculated and experimental splitting constants whether one or two constants
Table V. Calculated Nitrogen Hyperfine Coupling Constants for Substituted Azines and Diazines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Position</th>
<th>Inductive Model</th>
<th>McLachlan Method</th>
<th>Exp't</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>a</td>
<td>1</td>
<td>6.88</td>
<td>7.28</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>1</td>
<td>6.22</td>
<td>6.7</td>
<td>7.26</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.23</td>
<td>7.75</td>
<td>8.64</td>
</tr>
<tr>
<td>c</td>
<td>1</td>
<td>6.67</td>
<td>7.19</td>
<td>8.00</td>
</tr>
<tr>
<td>d</td>
<td>1</td>
<td>6.54</td>
<td>6.97</td>
<td>7.72</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>7.02</td>
<td>7.49</td>
<td>8.63</td>
</tr>
<tr>
<td>e</td>
<td>1</td>
<td>6.55</td>
<td>7.14</td>
<td>7.18</td>
</tr>
<tr>
<td>f</td>
<td>1</td>
<td>7.16</td>
<td>8.42</td>
<td>7.95</td>
</tr>
</tbody>
</table>

A: $Q_{nn}^n = 25.3 \, \text{G}$  B: $Q_{nn}^n = 19.1 \, \text{G}, Q_{c't'}^n = 9.1 \, \text{G}$

Q are used. It is thus not possible to decide from the present set of data which approach is the correct one (compare with the footnote in (79) where Lemaire, et al. compare the results of Carrington and dos Santos-Veiga (63) and of Ward (67)). Intuitively, and from the calculations of Henning (38), it would seem reasonable that $Q_{c't'}^n$ should not be negligible, but a point in question is whether the spin densities calculated in the present work
are good enough to allow any quantitative statements to be made.

Splitting constants calculated by the McLachlan method are invariably too high. Spin correlation causes the spin density on the nitrogens to be higher than in the inductive model. Since the single constant \( Q_{\text{HH}}^n \) was evaluated with Hückel spin densities it would seem that it is not appropriate for McLachlan densities. Making use of the data 2,6- and 2,5-dimethylpyrazine, tetramethylpyrazine, and 3,5-dimethylpyrididine a single constant \( Q_{\text{MN}}^n \) for McLachlan spin densities can be evaluated with the value \( Q_{\text{MN}}^n = 21.2 \pm .9 \) G. The two-constant approach with McLachlan densities gives somewhat better results than the one-constant approach, but again it seems that the two constants should be lower than Henning and de Waard's values.

At this point some experimental evidence may be mentioned which indicates that the sign of the nitrogen coupling constant in heterocyclic anions is actually positive. In a number of the spectra obtained in the present work it is seen that lines arising from transitions of the kind

\[
(S_3 = -\frac{1}{2}, I_N^3, I_{H_3} = 0) \rightarrow (S_3 = +\frac{1}{2}, I_N^3, I_{H_3} = 0)
\]

are sharper, and hence more intense, on the low-field side than on the high-field side of the spectrum. This is in
line with observations on other nitrogen heterocyclics \((38, 69)\) and in the present case is especially evident for 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, and tetramethylpyrazine (figures 5, 8, and 14).

It was assumed in Chapter I that both the hyperfine interaction tensor and the \(g\) -tensor are isotropic. However, small anisotropies may be present in general. Kivelson (129), and Stephen and Fraenkel (130) have taken such anisotropies into account and have shown that the width \(\Delta H\) of a line arising from a transition

\[
(s_3 = -\frac{1}{2}, I_{i_3}) \rightarrow (s_3 = +\frac{1}{2}, I_{i_3})
\]

is proportional to an expression in the nuclear quantum numbers \(I_{1z}\)

\[
\Delta H \propto K I_{i_3}^2 + LI_{i_3} + C \tag{64}
\]

where \(K, L,\) and \(C\) are constants. Carrington and Longuet-Higgins (131) and de Boer and Mackor (132) have shown that \(L\) may be taken as negative for an aromatic nitrogen atom.

The term in equation 64 which is linear in \(I_{1z}\) and arises from cross-terms between the \(g\) -tensor and hyperfine tensor anisotropies is of interest here. Since \(L < 0,\) lines of positive \(I_{1z}\) will be narrower and since narrower lines in the ESR spectra investigated occur at lower field, then the nitrogen hyperfine coupling constant must be positive.
E. General Comments.

From a comparison of the experimental and calculated splitting constants presented in this chapter it might be tempting to suggest that any one method of calculation is better, in an absolute way, than any other. However, in any particular case, better agreement obtained with one method may just be due to a fortuitously better choice of empirical parameters. Nevertheless, the following points may be offered by way of conclusion.

(1) On the whole, the inductive model, despite the perturbed nature of the methyl-pyrazine ring compared to the benzene ring, seems to give the best agreement with the experimental results.

(2) The hyperconjugative model gives rather poor results, on the whole, and does not differentiate enough between the different compounds. Surprisingly, the hetero-atom model, which seems to be less well-founded theoretically than the hyperconjugative one (125), gives very good agreement.

(3) The qualitative agreement obtained with the McLachlan calculations is good, although not as good quantitatively as with the inductive model.
(4) No decision can be made from the present set of results about whether one or two constants $Q$ should be used for the nitrogen splitting, although the second approach is more reasonable. With McLachlan spin densities these constants must be modified to give reasonable agreement with experiment.

In the above comments it should be kept in mind that all methods of calculation used employ approximations of varying severity. There is a considerable leeway in choosing the empirical parameters involved and good agreement obtained with one particular set of parameters does not justify statements of an absolute nature in all cases.
CHAPTER IV. SUBSTITUTED PYRAZINES: THE ION PAIRS.

A. Introductory Review.

It has been realised for some time that in solvents of poor solvating power the type of anion radicals described in Chapter III cannot always be considered as free. In fact, the anions often occur as "contact" ion-pairs with metal cations (133). While an electron is completely transferred to the molecule during the reaction with alkali metals, there can be some perturbation of the electronic levels of the metal cation by the unpaired electron on the anion; if the two species are sufficiently close together.

The usefulness of the ESR technique in this context arises from the fact that alkali metals have non-zero nuclear spin angular momenta. If, therefore, there exists some unpaired spin density in an S-level of the cation then hyperfine interaction with the nuclear spin can take place and this can be detected experimentally if instruments of sufficient resolving power are available.

The details of this hyperfine interaction can give information about the configuration of the ion-pairs. Some examples are given below. In hydrocarbon anions such as those of naphthalene or azulene the alkali metal cation is thought to be situated in the \( \pi \) -electronic charge cloud.
above the plane of the aromatic rings (134-136). Specific association of the cation with oxygen atoms in the anion probably takes place in benzophenone ketyl (137,138) and in orthosemiquinone anions (139).

In most cases only a very small amount of spin density appears on the cation and the splitting constants of the anion are found to be essentially unchanged when cation or solvent are changed (135). In some special cases this is not so, however. An interesting example is that of the pyracene anion (140,141) where the cation can jump from one methylene bridge to the other and where the CH₂ protons in the two bridges become non-equivalent.

Another example which had proved puzzling for some time is that of the dinitrobenzene anions. Ward (142) found that the m-dinitrobenzene anion prepared with alkali metals in tetrahydrofuran (THF) or dimethoxyethane (DME) exhibited only one nitrogen hyperfine splitting constant. He suggested association between the cation and one nitro-group, so that the two nitrogens become non-equivalent and almost no splitting is produced from one of them. This contrasts with the anion prepared electrolytically in acetonitrile (70,71), where the spectrum obtained is that of the essentially free anion. Blandamer, et al. (143) have recently resolved the
apparent contradiction. The ESR spectra of unsymmetrical nitrobenzene anions are strongly solvent dependent \((70,71, 144,145)\). Blandamer, et al. \((143)\) were able to reproduce Ward's spectrum in DME exactly, but when they removed this solvent and added acetonitrile then the ESR spectrum of the electrolytically produced anion was obtained. The difference between the two cases thus arises from the fact that DME cannot solvate the ions individually so that a tight ion-pair exists, while \(\text{CH}_3\text{CN}\) separates the ions more easily.

\section*{B. Spectra and Splitting Constants.}

(1) \textbf{Pyrazine:}

Alkali metal hyperfine structure in the ESR spectrum of the pyrazine radical anion has been found previously by several authors \((63,64)\). In the report of Carrington and dos Santos-Veiga \((63)\) lithium, sodium, and caesium were all found to give a hyperfine splitting \(a_m = .7 \text{ G}\), but no potassium interaction was observed.

Figure 18 gives the spectrum of a solution of the pyrazine negative ion prepared with sodium in DME. The sodium-23 quartets are clearly distinguishable. The original hyperfine structure, unsplit by Na-23, is indicated below the experimental spectrum. The spectrum obtained from a
Figure 18: ESR spectrum of (pyrazine)\(^+\)(Na\(^+\)) in DME.
solution of pyrazine negative ion and potassium cation is given in figure 19. Figure 19a gives the low-field half of the spectrum along with a reconstruction in terms of nitrogen and proton coupling constants only. Figure 19b gives the first three lines to the low-field side of center at higher dilution and lower rate of scan of the magnetic field. Corresponding lines in the two spectra are marked. The splittings due to sodium-23 and potassium-39 are found to be

\[ \alpha_{Na} = 0.535 \text{ G}; \quad \alpha_{K} = 0.094 \text{ G} \]

in DME. The values of the nitrogen and proton coupling constants are the same as those in liquid ammonia, within experimental error.

(2) Methyl- and Dimethylpyrazines:

No indication of sodium or potassium hyperfine interaction has so far been found in 2-methylpyrazine, but the matter was not pursued further because of the complicated nature of the spectrum.

With 2,6-dimethylpyrazine in DME the lowest line-width (between points of maximum slope of the absorption line, i.e. between extrema of the derivative curve)
Figure 19: ESR spectrum of (pyrazine)$^-(K)^+$ in DME, with reconstruction (see text).
obtainable for any of the lines was .208 G. At this point the onset of resolution is just detectable but the lines are too weak to achieve further resolution. The width of the lines arises from the presence of unresolved K-39 hyperfine structure and hence, since 4 lines will arise from the interaction of the electron with the nuclear spin 3/2 of potassium, the splitting must be

\[ \alpha_K = \frac{.208}{3} \text{ G} = .069 \text{ G} \]

with this value being quite close to the actual splitting. The anion of 2,6-dimethylpyrazine gives a more complicated spectrum due to sodium interaction. The splitting is

\[ \alpha_{Na} = .357 \text{ G} \]

but this value is somewhat inaccurate because the spectrum could not be sufficiently well resolved.

The sodium hyperfine structure for the ion-pair 2,5-dimethylpyrazine-Na is easily resolvable to give

\[ \alpha_{Na} = .148 \text{ G} \]

With potassium the width of the lines for the 2,5-dimethylpyrazine anion in very dilute solution, just before the
spectrum becomes too weak to be observed, is .075 G. Hence the potassium splitting is

\[ \alpha_k \leq \frac{0.075}{3} G = 0.025 G \]

The actual splitting, if there is any, is probably smaller than this value, since no indication of it could be found in the spectrum.

The possibility arises that in this case the ion-pair may have dissociated completely at the concentrations employed, so that only the free 2,5-dimethylpyrazine anion is detected. However, in all the other cases the only spectrum observed, even at the lowest concentrations is that of the ion-pair only, with no detectable indication of the presence of free ions. Undoubtedly there will be an equilibrium between the ion-pair and the free ions, but in view of the ESR evidence this must lie far towards the ion-pair side; i.e. the equilibrium constant in mole/1 will be quite small. It may thus be supposed with reasonable confidence that the failure to detect splitting from K-39 in the 2,5-dimethylpyrazine spectrum is due to the small size of the interaction, and not its complete absence.
(3) Tetramethylpyrazine:

The spectrum exhibiting potassium hyperfine structure has already been shown in figures 14 and 15. The splitting is

\[ \alpha_K = 0.307 \text{ G} \]

in DME. The experiment was also performed with potassium in THF and MeTHF, and with sodium in DME and THF, to obtain the following coupling constants

\[ \alpha_K = 0.254 \text{ G in THF}, \quad \alpha_K = 0.212 \text{ G in MeTHF} \]
\[ \alpha_{Na} = 0.716 \text{ G in DME}, \quad \alpha_{Na} = 0.717 \text{ G in THF}, \]

The tetramethylpyrazine-sodium ion-pair is much less soluble in DME than the potassium complex. Unless extreme dilutions are employed some of the complex precipitates to give a strong, exchange-narrowed line with superposed structure due to the ion pair in solution. Figure 20 gives the central portion of the ESR spectrum of the sodium ion-pair in DME. The quadruplet structure due to Na-23 (I=\(\frac{3}{2}\)) is clearly distinguishable and has been marked by bars placed below the spectrum. The complex with sodium in THF is more easily soluble.
Figure 20: ESR spectrum of (tetramethylpyrazine)$^-(\text{Na})^+$ in DME.
An attempt was made to carry out the reduction with potassium in 1,4-dioxane, but reaction took place only on the surface of the potassium mirror and not enough of the ion-pair dissolved to give an ESR spectrum. Similarly, the sodium complex was not soluble enough in MeTHF to give a spectrum.

The spectrum of the potassium complex in DME was observed in two experiments from 25°C to -50°C. No consistent trend was observed in the variation of the potassium hyperfine splitting. The temperature dependence of the splitting must therefore be small, but more accurate measurements are necessary to give some quantitative idea of the temperature variation.

3,5-dimethylpyrazine:

The difficulty experienced previously (Chapter III and reference (68)) in resolving the ESR spectrum of the 3,5-dimethylpyridine anion was found to be due to the existence of unresolved potassium hyperfine structure. However, resolution of this structure does not improve the situation as far as getting an easier analysis of the spectrum is concerned, since the total number of hyperfine lines expected is now $126 \times 4 = 504$. Since the total
number of lines resolved in the present work is about 200, the ratio of resolved to total number of lines is still about .4, as found previously (68), so that no improvement is obtained in this regard.

Figure 21a gives the low-field half of the spectrum with potassium hyperfine structure in DME. Figure 21b gives the outermost lines at a lower rate of scan of the magnetic field. Corresponding lines in the two spectra are marked. The splitting due to potassium is

$$\alpha_K = .137 \text{ G}$$

The sodium splitting in DME was also measured and is

$$\alpha_{Na} = .388 \text{ G}$$

which compares well with the previously measured value of .35 G (68).

All the metal splitting constants collected in the present work are given once more in table VI for reference. The solvent in all cases was DME, except for the last two measurements given for tetramethylpyrazine.
Figure 21: ESR spectrum of \((3,5\text{-dimethylpyridine})^- (K)^+\) in DME.
Table VI. Experimental Alkali Metal Hyperfine Coupling Constants.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\alpha_K$</th>
<th>$\alpha_{Na}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methylpyrazine</td>
<td>$\leq .025$</td>
<td>.148</td>
</tr>
<tr>
<td>2,5-dimethylpyrazine</td>
<td>$\sim .069$</td>
<td>.357</td>
</tr>
<tr>
<td>2,6-dimethylpyrazine</td>
<td>.094</td>
<td>.535</td>
</tr>
<tr>
<td>pyrazine</td>
<td>.137</td>
<td>.388</td>
</tr>
<tr>
<td>3,5-dimethylpyridine</td>
<td>$\sim .23(a)$</td>
<td>-</td>
</tr>
<tr>
<td>m-xylene</td>
<td>.307 (DME)</td>
<td>.716 (DME)</td>
</tr>
<tr>
<td>tetramethylpyrazine</td>
<td>.254 (THF)</td>
<td>.717 (THF)</td>
</tr>
<tr>
<td></td>
<td>.212 (MeTHF)</td>
<td>- (MeTHF)</td>
</tr>
</tbody>
</table>

(a) ref. (73)

C. Discussion of Experimental Results.

(1) Preliminaries: Geometry of Anions and Ion-Pairs:

It may be hoped that some idea about the geometry of the cation-anion pairs can be derived from the relative magnitudes of the metal splitting constants in the series of heterocyclic molecules investigated. Several models have been put forward in recent years for such ion-pairs.

Atherton and Weissman (135) have proposed that in the sodium-naphthalene ion-pair the metal cation is situated
in a plane above the anion radical. In the sodium complex of the 2,2'-dipyridyl negative ion Zahlan, et al. (146) have suggested that the sodium ion is associated with the two nitrogen lone pairs in the plane of the molecule. McDowell, et al. (64) have proposed that in the pyrazine-sodium ion-pair the sodium ion may be situated above the plane of the pyrazine ring and above the center of the anion.

Recently, complexes of silver ion with neutral pyrazines have been prepared (147,148), but the geometry of these complexes has not so far been elucidated. It has been suggested that in these, and also in the transition metal complexes of the pyrazines (149), the pyrazine acts as a bidentate ligand through its lone pairs, although \( \pi \) -bonding has not been ruled out for the silver complexes. In silver complexes of aromatic hydrocarbons, where no association with lone-pair electrons is possible, the silver ion appears to be localised above one of the carbon-carbon bonds of the hydrocarbon (150).

The geometry of only the two symmetrical diazines, pyrazine and tetramethylpyrazine, appears to have been studied, to date. Wheatley (151), and others (126) have measured the bond distances and bond angles in crystalline
pyrazine and obtained the following values (151) for the planar molecule

\[
\tau_{\text{CN}} = 1.334 \text{ Å}, \quad \tau_{\text{CC}} = 1.378 \text{ Å}, \quad \tau_{\text{CH}} = 1.05 \text{ Å}
\]
\[
\angle \text{NCN} = 122.4^\circ, \quad \angle \text{CNC} = 115.1^\circ
\]

Cromer and co-workers (152) have measured the following distances for tetramethylpyrazine

\[
\tau_{\text{CC}} \text{ (ring)} = 1.44 \text{ Å}, \quad \tau_{\text{CN}} \text{ (ring)} = 1.31 \text{ Å},
\]
\[
\tau_{\text{CC}} \text{ (ring-methyl)} = 1.50 \text{ Å}
\]

This molecule is planar also and all bond angles are equal to \(120^\circ \pm 2^\circ\). Full substitution by methyl groups thus expands the ring to some extent.

It is known that in some cases interaction with metal cations destroys the symmetry of the free anion, as, for example, in the pyracene-sodium ion-pair mentioned above (140,141), or in the ion pair of m-dinitrobenzene with potassium (142). It is also known that the coupling constants of the anions can change slightly when different alkali metals are used in their preparation. This has been found for the negative ion of cycl\((3,2,2)\)azine (84,85) and for the benzophenone ketyls (137), and Carrington and dos Santos-Veiga have indicated (63) that this may be the case
for pyrazine when caesium is replaced by lithium. However, in general the small changes of this nature that might be expected have not been recorded.

No evidence has been found in the present work that interaction of the anions with alkali metal cations changed the symmetry of the unpaired electron distribution to any appreciable extent from that expected for the free ion. Any change should be particularly noticeable in the ESR spectra of the anions of pyrazine and tetramethylpyrazine, but no anomalies have been found. It is therefore assumed that the electron distribution in the anion of the ion-pair is essentially that of a free ion expected to have the same symmetry as the neutral molecule.

(2) **Energy of Interaction within the Ion-Pair:**

It is expected that the major contribution to the stability of the ion pair will be the electrostatic interaction between anion and cation. To get any idea of the magnitude of this interaction a model must be assumed for the pair. It seems justified to suppose that the metal ion will move above the plane of the anion radical, for two reasons. Firstly, all of the excess electronic charge in the anion is distributed in a $\pi$-type "cloud" above
and below the plane of the ring, so that the interaction should be largest out-of-plane. Secondly, if it is supposed that the magnitude of the splitting is in some way related to the distance of separation of the ions then one can reject the notion that the cation is associated with the lone pairs of the nitrogen atoms since the splitting is largest for tetramethylpyrazine where one would also suspect the separation to be largest because of steric interactions with the methyl groups. Moreover, the presence of a large $K-39$ splitting in m-xylene (73) and the absence of anomalies due to a change in symmetry of the electron distribution in the anion-cation pair speak for an out-of-plane interaction.

In what follows it is now taken for granted that the cation is situated in a plane above the plane of the anion. The effect of the electrostatic interaction between cations and anions on the energy levels of the anion, and hence on its electronic spectrum, has been considered in detail by McClelland (153) and by Hush and Rowlands (154). The energy $E_j^0$ of orbital $j$ is changed by the electrostatic interaction (153) to

$$E_j = E_j^0 - e^2 \sum_s \frac{q_j^s}{s} + \frac{e^4}{2} \sum_{s,t} \frac{\pi_{ss,tt}^j}{t_s t_t} + O(e^6) \quad (65)$$
where all symbols have been defined previously (Chapter IB) except \( r_s \) which is the distance from the center of the cation to a nucleus \( S \) in the anion. In the following treatment the second- and higher-order terms are neglected and, summing over all orbitals \( j \), the total electrostatic energy of interaction is written as just

\[
\mathcal{E} = - \varepsilon^2 \sum \frac{q_s}{r_s}
\]

where \( q_s \) is now the excess charge density on atom \( S \) in the anion, i.e. the total \( \pi \)-electron density minus unity. Excess charge densities for the anions, calculated with the inductive model, are tabulated in Appendix B.

The assumption of point charges is implicit in equations 65) and 66). Further simplifying assumptions are now made as follows: Steric effects due to the methyl groups are not taken into account for the present and all comments will refer only to the \( \pi \)-electronic charge distributions. It is assumed that the geometry of all rings is the same as that of pyrazine, with the dimensions given by Wheatley (151).

The results of calculations of the energy of electrostatic interaction with potassium ion are presented as figures 22 and 23. The cation is taken to be \((2.5 + r_0)\mathcal{R}\)
Figure 22: Electrostatic interaction for the ion-pairs of pyrazine, 2,5-dimethylpyrazine, and tetramethylpyrazine anions with potassium cation.
Figure 23: Electrostatic interaction for the ion-pairs of 2,6-dimethylpyrazine and 3,5-dimethylpyridine anions with potassium cation.
above the plane of the anion (154), where \( r_{n+} \) is the radius of the cation. For potassium it was assumed that this radius is equal to the crystal radius of \( K^+ \), 1.33 Å (155).

Figure 22 shows the electrostatic interaction energy \( \varepsilon \) as a function of distance for pyrazine, tetramethylpyrazine, and 2,5-dimethylpyrazine. With the axes shown on the figure, the full curve gives \( \varepsilon(Y) \) when the cation moves along the Y-axis, with \( X=0 \). The dotted curve shows \( \varepsilon(X) \), with \( Y=0 \). Considering the excess charge distribution given in Appendix B it is somewhat surprising that \( \varepsilon \) is practically the same for all three ion-pairs at all distances along the axes. The extent of the spread of \( \varepsilon \) is very small and is indicated by the short vertical bars in the full curve. For the curve with \( X=0 \) the positions of the atoms are indicated by the vertical broken lines.

The effect of small changes in the dimensions of the anion does not seem to be important. Taking the bond lengths for tetramethylpyrazine given by Cromer, et al. (152) the minimum in the curve for \( X=0 \) is raised from -3.528 e.v. for the pyrazine dimensions to -3.522 e.v. if the bond angles are the same as for pyrazine, and lowered to -3.537 e.v. if all bond angles are taken as 120°.
From figure 22 it is clear now that the most stable position for the cation, if it moves above the plane of the ring, will be above the center of the ring in the three anions above.

The variation of $\mathcal{E}$ with distance along the $Y$-axis for 2,6-dimethylpyrazine and 3,5-dimethylpyridine on purely electrostatic grounds is given in figures 23a and b, respectively. It is seen that for both cases the minimum is slightly shifted. In 2,6-dimethylpyrazine the most stable position is moved along the $Y$-axis toward the nitrogen in the 4-position by a few tenths of an Angstrom. In 3,5-dimethylpyridine the shift is larger and also along the $Y$-axis toward the nitrogen. The minimum in this case is also somewhat lower than in all other cases. It is to be noted that in these two cases any steric effect of the methyl groups will be in the same direction as the electrostatic effect.

(3) Theory of Alkali-Metal Hyperfine Interaction:

The hyperfine structure due to alkali metal nuclei can be discussed in a manner similar to that of Chapter IA. Atherton and Weissman (135) have made some comments on this point, and Aono and Ohashi (156) have done an explicit
calculation of the splitting due to Na-23 in the sodium-naphthalene ion-pair. In the present and following sections some of the factors that are expected to influence the hyperfine splitting due to the alkali metal are discussed, but no numerical calculations are performed. A general treatment of interactions of the type considered here has been given for molecular complexes of the charge-transfer type by Mulliken (157,158).

The electronic state for the ion-pair with potassium in which the unpaired electron is completely transferred to the \( \pi \) -orbital system of the molecule can be represented as

\[
\gamma_o = |\sigma_i \sigma_i \ldots \pi_i \pi_i \ldots \pi_n \pi_n \pi_{\mu\mu} (1s)(\bar{1}s) \ldots (3p)(\bar{3}p)| \tag{67}
\]

in the notation of Chapter IA, where \((1s), \text{etc.}, \text{represent now atomic orbitals on the potassium cation. It is now supposed that electronic interactions will mix in small amounts of excited configurations, the relevant excitations being those which produce unpaired spin density at the potassium nucleus. Excitations such as } \sigma_i \rightarrow \sigma^* \text{ are therefore not considered, nor are excitations of the type } \sigma_i \rightarrow (4s) \text{ since they are not expected to produce significant spin density at the potassium nucleus.} \]
The following excitations are then considered possible

(a) \( \pi_{n+1} \rightarrow (4s) \) \hspace{1cm} (b) \( \pi_i \rightarrow (4s) \) \hspace{1cm} i \leq n \n
(c) \( \pi_N \rightarrow (4s) \) \hspace{1cm} (d) \( (Ns) \rightarrow (4s) \) \hspace{1cm} N = 1, 2, 3 \n
Excitations of the type \((Np) \rightarrow (4S)\), \(N=2,3\), will not contribute since \((Np)\) vanishes at the position of the potassium nucleus.

Writing \[ \sum' \] for \( \sum_i S_i(t) S'_i(t) \), the hyperfine splitting from the potassium nucleus is then given by

\[ \alpha_k = \frac{16\pi}{3} g_k \beta \left\{ \left( \langle \psi_o | \sum' | \psi_o \rangle + 2 \sum_i \frac{\langle \psi_o | P_i | \psi_i \rangle}{E_o - E_i + \epsilon} \langle \psi_i | \sum' | \psi_o \rangle \right) \right. \]

\[ + \sum_i \left( \frac{\langle \psi_o | P_i | \psi_i \rangle}{E_o - E_i + \epsilon} \right)^2 \langle \psi_i | \sum' | \psi_i \rangle \right\} \]

where now \( \psi_i \) is the electronic state that arises from an excitation of the type \(68)\). For example, the excitation \( (3S) \rightarrow (4S) \) gives rise to two states, one of which does not contribute to \( \alpha_k \). The other is

\[ \psi_{d,3} = \frac{1}{\hbar c} \left\{ 2 \left| \pi_{n+1} \ldots (3s) \ldots (4s) \right| - \ldots \pi_{n+1} \ldots (3s) \ldots (4s) \right| \]

\[ - \left| \ldots \pi_{n+1} \ldots (3s) \ldots (4s) \right| \}

\[ \right\} \]

The integrals in equation \(69)\) can now be written down in terms of one- and 2-electron integrals \((45)\). Some of the terms that arise from the integrals containing the spin
density operator are the following

\[ i) \langle \gamma_0 | \sum' | \gamma_0 \rangle = \pi_{n+1}^\text{e} (\tau_\text{K}) \cdot \pi_{n+1}^\text{o} (\tau_\text{K}) \]
\[ ii) \langle \gamma_0 | \sum' | \gamma_0 \rangle = \pi_{n+1}^\text{e} (\tau_\text{K}) \cdot (4s^\text{e} (\tau_\text{K})) \]
\[ iii) \langle \gamma_0 | \sum' | \gamma_0 \rangle = (4s^\text{e} (\tau_\text{K})) \cdot (4s^\text{o} (\tau_\text{K})) \]

where \((N_\text{s} (\tau_\text{K}))\) is the value of the \((N_\text{s})\) orbital at the potassium nucleus. The other type of integral will be of the form

\[ i) \langle \gamma_0 | \mathcal{H} | \gamma_0 \rangle = \sum_t \left( \pi_{n+1} \psi_t \| \phi_{12} \| \psi_t (4s) - (4s) \psi_t \right) \]
\[ ii) \langle \gamma_0 | \mathcal{H} | \gamma_0 \rangle = -\sqrt{\frac{1}{2}} \left( \pi_{n+1}^\text{o} \psi_t \| \phi_{12}^\text{o} \| \pi_{n+1} (4s) \right) \]

and so on, where the sum over \(t\) in the first integral runs over all orbitals \(\psi_t\) except \(\pi_{n+1}\) and \((4s)\). The integrals in (71) and (72) are easily expressed in terms of atomic orbitals \(p_r\) and the spin density \(9_+\).

From equations (69), (71), and (72) it is clear that the three factors that can influence the contributions to the metal hyperfine splitting are the excitation energies, the overlap integrals evaluated at the metal nucleus, and the exchange integrals of equation (72). These factors are discussed in the following section.
(4) **Discussion:**

Because of the term \((E_0 - E_i + \varepsilon)^{-1}\) in the first and second order terms in \(a_k\) some of the excitations of equation 68) can be excluded on the basis that the excitation energy is too high. Thus the excitation energies for \((1s) \rightarrow (4s)\) in potassium and \((1s) \rightarrow (3s)\) in sodium are 3,620 e.v. and 1,075 e.v., respectively (159), while the excitation energies for \((2s) \rightarrow (4s), (3s) \rightarrow (4s)\) in potassium and \((2s) \rightarrow (3s)\) in sodium are 379 e.v., 36.5 e.v. and 65.6 e.v. (159) and these latter ones are small enough to be expected to contribute.

The energy of a \((2p)\) orbital on carbon is -10.7 e.v. (159), but this will change when the molecular orbitals \(\pi^*\) are formed. It is clear, however, that the excitation most favourable energetically will be \(\pi_{n+1} \rightarrow (4s)\). Since the exchange and overlap integrals will be similar for the other \(\pi\) -orbitals this excitation should therefore be the most important of the \(\pi_i \rightarrow (4s)\) excitations. To estimate the energy of this excitation the absolute energies of the \(\pi_{n+1}\) and the \((4s)\) orbitals would have to be known.

Although the energy of an excitation from the non-bonding orbital \(\pi_N\) on nitrogen would not seem to be too
large (159), a consideration of overlap integrals will lead one to exclude the excitation $n_n \rightarrow (4s)$ for the case where the metal cation moves above the plane of the anion since $n_n$ is expected to vanish at the potassium nucleus. As a general result, excitations of the type $(N\sigma) \rightarrow (4s)$ on the metal ion itself should be significant on the basis of overlap integrals alone. In this type of excitation the determining factors will be the excitation energies and exchange integrals. The largest overlap integrals will arise from the second order terms, but their contribution to $\alpha_K$ is reduced because of the squared term in the inverse excitation energies and in the exchange integrals. This term is expected to be small.

Overlap with the $\pi$ -orbitals should be quite small. It will depend on the vertical separation of cation and anion and should decrease with increasing methyl substitution because of the bulky nature of the methyl groups. This should be so for the zero-order term $\langle \psi_o | \Sigma' | \psi_o \rangle$ as well as for the higher order terms arising from excitations of the type (a) and (b) in equation 68). Any vibration of the cation parallel to the plane of the anion in the electrostatic potential described above will bring the cation closer to the $\pi$ -orbitals of the anion and should increase
the overlap. This effect might be expected to increase with temperature. Any spin density on the methyl groups themselves might possibly be a contributing factor. However, there is no correlation between the magnitudes of the potassium and the methyl proton splitting constants.

Estimating the magnitudes of the exchange integrals in equation 72) is not a simple matter, since they are all 2-, 3-, or 4-center integrals which are difficult to evaluate in any case. Nevertheless, one may perhaps expect those arising from excitations of type (a) and (d) to be more significant than the others.

Aono and Oohashi (156) have considered excitations of the type (a) in equation 68) only. They have, in fact, concluded that the only terms in $\alpha_n$ of significant magnitude are the second order ones. This is intuitively reasonable since the overlap integrals are large, and the excitation energies are expected to be relatively small for this type of excitation. For the naphthalene-sodium ion-pair the exchange integral is appreciable, of the order of .25 e.v. (156).

(5) Concluding Remarks:

There appears to be no obvious effect which would
explain the experimental results completely. The symmetry of the \( \pi_{n+1} \) orbital of the anion is the same for all compounds, and the spin density on the nitrogens, or on the corresponding carbon atoms in m-xylene and 3,5-dimethylpyridine, is in all cases between .25 and .30. As seen from the calculations of the electrostatic interaction the effect of the excess charge distribution on the anion is practically the same for all anions.

Considering the steric repulsion of the methyl groups only it would seem that both overlap and exchange integrals should be smallest for tetramethylpyrazine where the cation is expected to be farthest from the anion. The potassium and sodium splittings, however, are largest in this case. Another point that negates a direct steric effect is that the splitting for the pyrazine-metal ion-pair is intermediate, and not at the beginning of the series as it should be since in this case there is no steric effect.

It is interesting that the metal splitting increases in the series 2,6-dimethylpyrazine, 3,5-dimethylpyridine, and m-xylene, which have similar geometries and \( \pi \) -electron distributions. The absolute change is not as large for
sodium as it is for potassium. The electrostatic interaction energy $\mathcal{E}(\gamma)$ for m-xylene is almost the same as for 2,6-dimethylpyrazine, except that the sides of the potential well are slightly steeper. In m-xylene and 2,6-dimethylpyrazine the cation experiences only a slight shift from the center of the ring, while the shift is larger in 3,5-dimethylpyridine. On an intuitive basis, one might speculate that in this series the increase in the number of nitrogen atoms increase a kind of "effective core potential" of the $\pi$-orbitals, resulting in a lowering of the energies of the $\pi$-orbitals (i.e. an increase in excitation energies) and perhaps in a reduction of the overlap and exchange integrals if the cation remains at the same distance from the anion in all cases. However, this does not explain the large splitting for tetramethylpyrazine. It would be interesting to investigate the ion-pairs with 2,3,5,6-tetramethylpyridine and with durene where, on the basis of the present experimental results, one might predict large metal splittings. Nothing is known about the tetramethylpyridine, and the durene anion has so far eluded detection (159).

A very unexpected result is also that the values for the potassium splitting with tetramethylpyrazine in THF and
MeTHF are smaller than in DME. It is a general experience that little or no splitting is found in DME while larger values are obtained in THF and the largest in MeTHF (134, 135,141,161). An apparent exception is formed by the benzophenone ketyls, $^\varphi CO^-M^+$ where even potassium splitting is detected in DME, although published results for THF are not clear (137,138).

The dielectric constant for MeTHF is smaller than that for DME and THF (163). MeTHF will therefore stabilise the separation of charges in the ground state of the ion-pair less well than the other solvents, thus reducing the excitation energy to the excited state and hence increasing the metal splitting. This is, in fact, found in most cases, while in the present series the opposite happens and the metal splitting decreases as the dielectric constant decreases. The reason for this remains unexplained. 1,4-dioxane has an even smaller dielectric constant than MeTHF (162), but unfortunately the potassium splitting could not be measured in this solvent. It may be that the geometry of the solvent molecules would have to be considered in the explanation of the above results.

If the splitting constants of Table VI are divided by the atomic splittings for the metals, 317.2 G for Na-23
and 82.8 G for K-39 (163), then the spin densities at the metal nuclei are those given in Table VII.

Table VII. Spin Densities at the Alkali Metal Nucleus.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Potassium</th>
<th>Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,5-dimethylpyrazine</td>
<td>.0003</td>
<td>.0005</td>
</tr>
<tr>
<td>2,6-dimethylpyrazine</td>
<td>.0008</td>
<td>.0011</td>
</tr>
<tr>
<td>pyrazine</td>
<td>.0011</td>
<td>.0017</td>
</tr>
<tr>
<td>3,5-dimethylpyridine</td>
<td>.0017</td>
<td>.0012</td>
</tr>
<tr>
<td>m-xylene</td>
<td>.0028</td>
<td>-</td>
</tr>
<tr>
<td>tetramethylpyridine</td>
<td>.0037(DME)</td>
<td>.0023(DME)</td>
</tr>
<tr>
<td></td>
<td>.0028(THF)</td>
<td>.0023(THF)</td>
</tr>
<tr>
<td></td>
<td>.0026(MeTHF)</td>
<td>- (MeTHF)</td>
</tr>
</tbody>
</table>

The perturbation of the levels of the metal cation is thus quite small. The perturbation for sodium appears to be stronger for pyrazine and the dimethylpyrazines, but weaker for 3,5-dimethylpyridine and tetramethylpyrazine. The latter result is in agreement with the findings of Aten, et al. (161).

No fully satisfactory explanation of the magnitude of the potassium and sodium splittings in the series
investigated can be offered at present. It appears reasonably certain that electrostatic and steric effects are not the main contributary factors. It would be desirable to know how the energy of a given excitation varies through the series and a consideration of this may give a clue to the correct interpretation of the results. A fairly advanced calculation would, however, be necessary. In place of this a knowledge of the electron affinities of the neutral compounds would be very helpful, or a knowledge of the energy change when an electron is abstracted from the ion-pair to give back the neutral molecule and potassium ion. The present experimental results seem to point to an explanation in terms of the variation of the excitation energies through the series, but further work is required to evaluate the degree of this variation.
CHAPTER V. HETEROCYCLIC N-OXIDES.

A. Analysis of the Spectra.

(1) Preliminary Experiments:

In the course of investigating anion radicals derived from heterocyclic N-oxides the N-oxides of 4-nitropyridine and 4-chloropyridine and the N,N'-dioxides of pyrazine, 2,5-dimethylpyrazine, quinoxaline, and phenazine were prepared. The ESR spectra of the 4-nitropyridine anion, of the N-oxide anion of 4-nitropyridine, and the N,N'-dioxide anions of quinoxaline and phenazine are described in succeeding sections of this chapter.

Electrolysis of 4-chloropyridine-1-oxide in acetonitrile or mixtures of acetonitrile and dimethoxyethane yielded no coloured solution or detectable radical species up to -1.8 V vs. s.c.e. Reaction with potassium in DME gave a coloured solution but no detectable ESR spectrum at room temperature. Reaction with potassium in liquid ammonia gave a green solution, and at -62.5°C the ESR spectrum shown in figure 24 was detected. This spectrum is not very stable and appears to undergo changes during the recording. The total width is about 22G. From the
Figure 24: ESR spectrum of the product of reaction of potassium with 4-chloropyridine-1-oxide in NH₃ at -62.5 °C.
negative ion of 4-chloropyridine-1-oxide one would expect a total \((2 \cdot 1 + 1)^3 = 27\) lines, while the actual ESR spectrum contains many more lines than this. It seems that the molecule reacts in some fashion to produce a more complicated species. The nature of this reaction was not further investigated.

Pyrazine-1,4-dioxide is practically insoluble in pure dimethoxyethane, and no results were obtained from reaction with potassium in this solvent. With potassium in liquid ammonia a red solution formed but no ESR spectrum was detectable. When the compound was electrolysed in pure CH\(_3\)CN or in mixtures of CH\(_3\)CN and DME a strong reduction wave was found at \(-1.1\) v vs. s.c.e., with concomitant appearance of a strong red-brown colour, but no ESR signal. The reduction is probably a 2-electron step, producing a diamagnetic dinegative ion.

Exactly similar results were obtained when reductions in the different solvents were performed on 2,5-dimethylpyrazine-1,4-dioxide. The reduction wave and appearance of colour in a \(1/1\) mixture of CH\(_3\)CN and DME occurred at \(-1.3\) v vs. s.c.e., but again no ESR spectrum was observed and it appears again likely that the dinegative ion was formed.
(2) 4-nitropyridine:

The ESR spectra of the anions of 4-nitropyridine and its N-oxide have been studied independently by Itoh and co-workers (164) who used potassium in DME as reducing agent.

In the present work, 4-nitropyridine was reduced electrolytically at -.65 v vs. s.c.e. in mixtures of CH₃CN and DME, containing 20 to 50% CH₃CN. The full ESR spectrum in a mixture containing 30% CH₃CN, at room temperature, is shown in figure 25. Figure 26 gives the low-field side with better resolution, in a 20/80 mixture of CH₃CN and DME.

Reference to figure 27a shows that there should be 4 different coupling constants to give a total of \((2 \cdot 1 + 1)^4 = 81\) lines. The spectrum can be analysed in these terms to give the coupling constants

\[
\begin{align*}
\alpha_{N_1} &= 2.52 \text{ G}, \\
\alpha_{N_2} &= 7.83 \text{ G}, \\
\alpha_{N_3} &= 3.13 \text{ G}, \\
\Delta H_T &= 27.68 \text{ G}.
\end{align*}
\]

One would expect the nitrogen coupling constant of the nitrogroup to be larger than the ring nitrogen constant and this has been confirmed by Itoh, et al. (164)
Figure 26: ESR spectrum of 4-nitropyridine anion in 20% CH₃CN, 80% DME.
**Figure 27: Nitrocompounds and N-Oxides.**

a) 4-Nitopyridine

b) 4-Nitropyridine-1-oxide

c) Quinoxaline-1,4-dioxide

d) Phenazine-9,10-dioxide
by substitution with N-15 in the nitrogroup. The assignment of the ring proton coupling constants is made on the basis of calculations to be described below. For comparison, the coupling constants obtained by Itoh, et al. (164) in DME with potassium are

\[ \alpha_{N_1} = 2.55 \text{ G}, \quad \alpha_{N_7} = 8.72 \text{ G}, \]
\[ \alpha_{H_2} = 3.00 \text{ G}, \quad \alpha_{H_3} = 0.53 \text{ G}. \]

A small change of the spectrum at higher concentrations of CH₃CN was noticed, but this was not pursued.

From the splitting constants obtained in this work the spectrum can be reconstructed and this is shown in figure 28. The reconstruction compares well with the experimental spectrum and so does the reconstructed total width of 27.84 G.

(3) 4-nitropyridine-1-oxide:

4-nitropyridine-1-oxide was electrolysed at -.80 v vs. s.c.e. in mixtures of CH₃CN and DME and in pure CH₃CN. The full spectrum in a mixture containing 25% CH₃CN is given in figure 29. Figure 30a shows the low-field side of the same spectrum on an expanded scale. The low-field half of a spectrum in 100% CH₃CN is shown in figure 31.
Figure 28: reconstructed spectrum of 4-nitropyridine anion.
Figure 29: ESR spectrum of 4-nitropyridine-1-oxide anion in 25% CH$_3$CN, 75% DME.
Fig. 30: a) Experimental and b) reconstructed ESR spectra of 4-nitropyridine-1-oxide. 25% CH₃CN, 75% DME.
Figure 3: ESR spectrum of 4-nitropyridine-1-oxide anion in 100% CH₃CN.
Figure 27b shows that there are again 4 different positions in the anion with nuclei of non-zero spin and a spectrum of 81 lines is again expected. The following coupling constants are derived on that basis:

in 25% CH₃CN, 75% DME: \( \alpha_{N_1} = 4.71 \text{ G}, \quad \alpha_{N_8} = 6.35 \text{ G}, \)
\( \alpha_{H_2} = 1.25 \text{ G}, \quad \alpha_{H_3} = 3.33 \text{ G}, \quad \Delta H_T = 31.33 \text{ G}. \)

in 100% CH₃CN: \( \alpha_{N_1} = 4.63 \text{ G}, \quad \alpha_{N_8} = 6.66 \text{ G}, \)
\( \alpha_{H_2} = 1.26 \text{ G}, \quad \alpha_{H_3} = 3.40 \text{ G}, \quad \Delta H_T = 31.90 \text{ G}. \)

Assignment of the proton coupling constants is made on the basis of Hückel calculations, and similarly with the nitrogen coupling constants. The assignment of the nitrogen constants has been confirmed by Itoh, et al. (164) by substitution with nitrogen-15 in the nitrogroup.

Itoh and his co-workers (164) have obtained the following splitting constants for the ion prepared with potassium in DME:

\( \alpha_{N_1} = 4.58 \text{ G}, \quad \alpha_{N_8} = 7.49 \text{ G}, \)
\( \alpha_{H_2} = 3.58 \text{ G}, \quad \alpha_{H_3} = 1.58 \text{ G}. \)
With the coupling constants obtained in a mixture of 25% CH₃CN and 75% DME the line spectrum shown in figure 30b can be reconstructed. The observed and reconstructed spectra agree quite well, and some of the closely spaced lines are resolvable in less concentrated solution. The reconstructed total width is 31.26 G. Reconstructed and observed spectra also agree well in 100% CH₃CN, where the reconstructed width is 31.88 G.

The coupling constant of the nitrogroup nitrogen is quite solvent dependent while the other constants show much less variation. This point will be discussed below. No detailed, quantitative investigation of the solvent dependence was carried out. There appears to be also some temperature dependence of the coupling constant, but again the details of this dependence were not followed up.

It is noted that for both 4-nitropyridine and its N-oxide the more intense lines of the nitrogen triplets for both the ring and nitrogroup nitrogens occur at the low-field side of the spectrum. Hence, by the argument of Chapter 3, the coupling constant is positive for both nitrogens in the two compounds.
(4) **Quinoxaline-1,4-dioxide:**

Quinoxaline-1,4-dioxide was electrolysed at -.97 v vs. s.c.e. in mixtures of CH$_3$CN and DME. It was noticed that the spectrum decayed rapidly and that apparently diffusion into the tip of the electrolytic cell was not fast enough to replenish unreduced material. Because of this the intensities of the lines in the ESR spectrum decreased during the recording of a spectrum. A strong colour remains after the ESR spectrum becomes undetectable. It may be that the anion radical decays not back to the neutral compound but to some other species which does not reduce at the applied voltage.

A full spectrum of the anion radical of quinoxaline-1,4-dioxide in a mixture containing 50% CH$_3$CN is shown in figure 32, with the low-field half of a spectrum in the same solvent mixture appearing in figure 33. According to figure 27c there should be 4 pairs of equivalent nuclei to give an ESR spectrum of $(2 \cdot 2 + 1)(2 \cdot 1 + 1)^3 = 135$ lines. The spectrum is easily analysed in this way to give the following coupling constants, with the numbering of figure 27c,

$$
\alpha_N = 7.11 \text{ G}, \quad \alpha_{H_2} = 2.27 \text{ G}, \quad \alpha_{H_5} = 1.94 \text{ G},
$$

$$
\alpha_{H_6} = 1.43 \text{ G}, \quad \Delta H_T = 39.67 \text{ G}.
$$
Again the assignment of proton coupling constants is made on the basis of the Hückel theory. The reconstructed spectrum based on these splitting constants is given in figure 34. The reconstructed width is 39.72 G.

(5) Phenazine-9,10-dioxide:

This compound gives an ESR spectrum when reacted with potassium in DME, but the radical is short-lived at room temperature. Phenazine-9,10-dioxide was therefore electrolysed at -.86 v vs. s.c.e. in mixtures of CH\textsubscript{3}CN and DME. The same phenomenon was noticed as for the quinoxaline-1,4-dioxide anion, that the anion seems not to decay back to the neutral compound so that rather rapid scanning of the spectrum is required.

Figure 35 gives the full spectrum of the anion in a mixture containing 30\% CH\textsubscript{3}CN and figure 36 gives the low-field half of the spectrum in a mixture with 25\% CH\textsubscript{3}CN, with better resolution. Figure 27d indicates that there should now be only 3 different coupling constants giving rise to a spectrum of $(2\cdot 2 + 1)^3 = 125$ lines. The coupling constants are found to be

\[
\begin{align*}
\alpha_H &= 6.02 \, G, \quad \alpha_{H_1} = 1.76 \, G, \\
\alpha_{H_2} &= 1.40 \, G, \quad \Delta H_T = 36.86 \, G.
\end{align*}
\]
Figure 36: ESR spectrum of phenazine-9,10-dioxide anion in 25% CH₃CN, 75% DME.
The reconstructed spectrum shown in figure 37 agrees well with the experimental spectrum. The reconstructed width is 36.72 G.

No information can be obtained in the case of the N,N'-dioxides of quinoxaline and phenazine with regard to the relative intensity of the high- and low-field lines because the concentration of radical anions is not constant during the recording of a spectrum, as pointed out above. It seems reasonable from the other work reported in this thesis, and from the work on nitrobenzene anions (71), that the sign of the nitrogen coupling constant should be positive.

B. Discussion of the Spectra.

(1) Solvent Dependence:

Although part of the discrepancy between the coupling constants for 4-nitropyridine and its N-oxide found by Itoh, et al. (164) and those of the present work can be ascribed to better resolution achieved with the electrolytic method, no doubt most of it is due to variation of the coupling constant with solvent.

Solvent effects on the coupling constants are quite common, particularly in radicals containing groups
Figure 37: Reconstructed Spectrum of Phenazine-9,10-Dioxide Anion.
susceptible to direct interaction with solvent molecules through, for example, hydrogen bonds. This effect has been particularly noted with the nitrobenzenes (10,71,142,143,145,165) and it is likely that very similar effects account for the variation in coupling constants in the present case. In the case of semiquinone ions (166) and of nitric-oxide radicals and nitrobenzene anions (144) the variation of coupling constants has been correlated with changes in the Hückel spin densities caused by association of solvent molecules with the oxygen atoms of the radicals concerned.

(2) 4-nitropyridine and its N-oxide:

Spin densities were calculated by both the Hückel and McLachlan methods. The empirical parameters necessary in the Hückel calculations seem to be somewhat disputed at present. Throughout the calculations on the four compounds described in this chapter the Hückel parameters employed by Rieger and Fraenkel (70) were used. These are, for a nitrogroup attached to an aromatic ring,

\[
\alpha_N = \alpha_e + 2.2 \beta_{ee} \quad , \quad \alpha_o = \alpha_e + 1.4 \beta_{ee} \quad , \\
\beta_{NO} = 1.67 \beta_{ee} \quad , \quad \beta_{CN} = 1.2 \beta_{ee} 
\]
These authors derived the above parameters from a fit of calculated and experimental spin densities in nitrobenzene anion. Most of the parameters are reasonable, except that the N-O resonance integral is rather high.

Tables I and II of Appendix C give the spin densities for the 4-nitropyridine and 4-nitropyridine-1-oxide anions. The numbering of the positions is that of figure 27. For the ring nitrogen in 4-nitropyridine the value \( \alpha_N = \alpha_c + 0.75 \beta_{cc} \) was used. For the N-oxide group, in which the nitrogen has a formal positive charge as it has in the nitrogroup, the parameters given above for the nitrogroup were employed, except that the resonance integral for the ring nitrogen-to-carbon bond is left at \( \beta_{cn} = \beta_{cc} \).

The second column of table I, Appendix C, gives spin densities calculated with the parameters suggested by Streitwieser (87), for comparison. It is seen that the main effect of the changed parameters is to pull more of the unpaired electron onto the nitrogroup. The configuration interaction calculation of Itoh, et al. (164) is given in the last row of table I. In this calculation the order of the spin densities on the 2 and 3 positions of 4-nitropyridine is the opposite of the order given by the
other three calculations in table I. As a consequence, the assignment of ring proton coupling constants by Itoh, et al. (164) is the reverse of the assignment in the present work. The McLachlan calculations were performed using Hückel orbitals calculated with Rieger and Fraenkel's parameters and with $\lambda = 1.2$ (see Chapter IB).

In table VIII, below, the calculated and experimental splitting constants are compared. For the ring proton splitting the value $Q_{cc}^N = -22.5$ G was used (see Chapters IA and III). For the ring nitrogen in 4-nitropyridine $Q_{NN}^N = 25.3$ G (63) was employed with Hückel spin densities (Rieger and Fraenkel's parameters) and $Q_{NN}^N = 19.1$ G, $Q_{cc'}^N = 9.1$ G (38) with McLachlan spin densities. To calculate the nitrogen splitting constant for the nitro-group the coupling constants of Fischer (71) were employed with Hückel spin densities, and those of Rieger and Fraenkel (70) with McLachlan spin densities. The N-oxide nitrogen coupling constant will be discussed in a later section of this chapter.

In view of the uncertainty in the choice of empirical parameters and hence in the calculated spin densities the agreement between experimental and calculated coupling
Table VIII. Calculated and Experimental Coupling Constants in the Anions of 4-nitropyridine and its N-oxide.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>$\alpha_{N_1}$</th>
<th>$\alpha_{H_2}$</th>
<th>$\alpha_{H_3}$</th>
<th>$\alpha_{N(NO_2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitropyridine</td>
<td>Hückel</td>
<td>3.23</td>
<td>.79</td>
<td>2.03</td>
<td>5.89</td>
</tr>
<tr>
<td></td>
<td>McLachlan</td>
<td>3.04</td>
<td>.16</td>
<td>2.04</td>
<td>5.56</td>
</tr>
<tr>
<td></td>
<td>Exp't</td>
<td>2.52</td>
<td>.44</td>
<td>3.13</td>
<td>7.83</td>
</tr>
<tr>
<td>4-nitropyridine-1-oxide</td>
<td>Hückel</td>
<td>-</td>
<td>(-).53</td>
<td>1.89</td>
<td>6.03</td>
</tr>
<tr>
<td></td>
<td>McLachlan</td>
<td>-</td>
<td>(+).86</td>
<td>2.33</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td>Exp't</td>
<td>4.71</td>
<td>1.25</td>
<td>3.33</td>
<td>6.35</td>
</tr>
</tbody>
</table>

The calculations for the nitrogroup nitrogen splitting also give reasonable results, although the values

constants is quite good. The same relative order of the coupling constants is predicted by both the Hückel and McLachlan calculations although the absolute magnitudes do not agree as well. It should be noted that in 4-nitropyridine-1-oxide the constant $\alpha_{H_2}$ calculated by the Hückel method has a negative sign, as is found for the great majority of ring proton coupling constants in aromatic anions, while the McLachlan calculation predicts a positive sign for $\alpha_{H_2}$ because of the calculated negative spin density at position 2.
are too low for 4-nitropyridine. The predicted ring nitrogen coupling constant is somewhat high in this compound.

(3) **Quinoxaline and Phenazine N,N'-dioxides:**

In the molecular orbital calculations for the two N,N'-dioxides for which ESR data are available the NO₂\(^{-}\) group parameters of Rieger and Fraenkel (70) were employed, except that the carbon-nitrogen resonance integral was \( \beta_{CN} = \beta_{CC} \). The McLachlan parameter \( \lambda \) was again 1.2.

The spin densities calculated with these parameters are given in tables III and IV of Appendix C, where the numbering of the positions is that of figure 27. In table IV are also given spin densities for phenazine-9,10-dioxide, calculated with the parameters evaluated by Kubota (167, 168) for heterocyclic N-oxides and N,N'-dioxides. These are

\[
\alpha_N = \alpha_e + 1.6 \beta_{ee}, \quad \alpha_o = \alpha_e + .8 \beta_{ee}, \quad \beta_{NO} = \beta_{CN} = \beta_{ee}.
\]

In view of the difference between the two sets of parameters the similarity between the spin densities is surprising.

Using the spin densities given in these tables, the ring proton splitting constants in table IX are obtained
with \( Q_{ee} = -24.2 \) G, rather than the value of \(-22.5\) G used for monocyclic anions.

Table IX: Calculated Ring Proton Coupling Constants for the Quinoxaline and Phenazine N,N'-dioxides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Position</th>
<th>Hückel</th>
<th>McLachlan</th>
<th>Exp't</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinoxaline-2</td>
<td>2</td>
<td>2.05</td>
<td>1.76</td>
<td>2.27</td>
</tr>
<tr>
<td>1,4-dioxide</td>
<td>5</td>
<td>1.68</td>
<td>2.01</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>.91</td>
<td>.60</td>
<td>1.43</td>
</tr>
<tr>
<td>Phenazine-9,10</td>
<td>1</td>
<td>1.18</td>
<td>1.34</td>
<td>1.76</td>
</tr>
<tr>
<td>dioxide</td>
<td>2</td>
<td>.79</td>
<td>.53</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The Hückel calculations appear to reproduce the relative order of the proton constants reasonably well, while the McLachlan calculations are somewhat less successful. The absolute values are in both cases too low. This suggests either that the electronegativity of the N-oxide grouping was overestimated, or that \( Q_{ee} \) may be too low. It is well known (97) that larger constants are required for polynuclear hydrocarbon anions than for the benzene anion. It may thus be advisable to use a still
larger $|Q_{ee}|$ and also to use a different constant for the two compounds.

As before, the assignment of proton coupling constants had to be made on the basis of the Hückel theory. The relative order for the different positions is in agreement with the relative order in naphthalene and quinoxaline on the one hand, and anthracene and phenazine on the other. One may thus be reasonably certain of the assignment.

It will be instructive to examine the effect on the spin densities as one passes from the hydrocarbon through the diazine to the N,N'-dioxide. Table X gives a list of corresponding ring proton coupling constants in the anions.

Comparison with naphthalene is not really applicable since the symmetry of the molecule changes on passing to the heterocyclic compounds. Several points are noted in both series, however. Firstly, the relative order of the coupling constants does not change from one ion to the next within a series. Secondly, although the main effect is an overall withdrawal of the unpaired electron from the positions indicated, there is superimposed on this a smoothing-out of the distribution away from the heteroatom, so that the ratios of the coupling constants decrease.
Table X. Comparison of Experimental Ring Proton Coupling Constants in Hydrocarbon and Heterocyclic Anions.

<table>
<thead>
<tr>
<th>Position</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthalene (a)</td>
<td>4.90</td>
<td>1.83</td>
<td>4.90</td>
<td>1.83</td>
</tr>
<tr>
<td>quinoxaline (b)</td>
<td>3.33</td>
<td>2.38</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>quinoxaline-1,4-dioxide</td>
<td>2.27</td>
<td>1.94</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>anthracene (a)</td>
<td>2.74</td>
<td>1.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenazine (b)</td>
<td>1.80</td>
<td>1.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenazine-9,10-dioxide</td>
<td>1.76</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) from reference (169) (b) from reference (38)

(4) Coupling Constant of the N-oxide Nitrogen:

It would seem reasonable to expect, in accordance with the theory of hyperfine interaction reviewed in Chapter IA, that the nitrogen hyperfine coupling constant be given by

\[ a_N = Q_{NN}^N \rho_{NN} + Q_{00}^N \rho_{00} + Q_{cc}^N \sum \rho_{c_i c_i} \]  \hspace{1cm} (73)

if off-diagonal elements are excluded. The most desirable procedure would be to attempt to fit the experimental data to equation 73) by a least-squares method, making use of
the calculated spin densities of Appendix C. This was done for the Hückel spin densities and the constants obtained are $Q_{nn}^N = 42.8$ G, $Q_{oo}^N = .27$ G, $Q_{cc}^N = -4.9$ G. However, considering that only three experimental points are available, these constants may not have much general validity. $Q_{oo}^N$ especially seems unreasonably low when compared to the large negative value obtained for this constant in aromatic nitrocompounds (70,71).

When the experimental splitting constants are divided by the calculated spin densities the ratios given in table XI are obtained.

Table XI. Ratio of Nitrogen Splitting Constants and Calculated Spin Densities in N-oxide Anions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hückel</th>
<th>McLachlan</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitropyridine-1-oxide</td>
<td>40.8</td>
<td>25.1</td>
</tr>
<tr>
<td>quinoxaline-1,4-dioxide</td>
<td>45.1</td>
<td>40.3</td>
</tr>
<tr>
<td>phenazine-9,10-dioxide</td>
<td>41.2</td>
<td>35.7</td>
</tr>
</tbody>
</table>

The surprising result is that the ratios are reasonably constant for the three compounds. For McLachlan spin densities the ratio for 4-nitropyridine-1-oxide alone
seems to fall out of line. The average ratio for Hückel spin densities is 42.4 G, consistent with the value of obtained from the three-parameter equation 73).

Using Hückel spin densities and, firstly, the set of three constants obtained above, and secondly, the average ratio of 42.4 G the splitting constants of the N-oxide nitrogen can be recalculated. The results are given in table XII.

**Table XII. Calculated N-oxide Nitrogen Coupling Constants.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>3 constants</th>
<th>1 constant</th>
<th>Exp't</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitropyridine-1-oxide</td>
<td>4.74</td>
<td>4.89</td>
<td>4.71</td>
</tr>
<tr>
<td>quinoxaline-1,4-dioxide</td>
<td>6.32</td>
<td>6.68</td>
<td>7.11</td>
</tr>
<tr>
<td>phenazine-9,10-dioxide</td>
<td>6.13</td>
<td>6.20</td>
<td>6.02</td>
</tr>
</tbody>
</table>

From these results it would appear that much the main contribution to the nitrogen splitting comes from the spin density on the nitrogen itself, with only a small contribution from spin density on the neighbouring atoms. This statement is, of course, subject to reservations. Principally, there are unfortunately only three compounds available from which this result could be derived and little
generality could be claimed for it at present. A second reservation must be the uncertainties in the calculated spin densities, as pointed out above.

(5) **General Comments:**

It was originally hoped that the two N-oxides and four N,N'-dioxides available would be sufficient to give a clear picture of the nitrogen splitting constant in heterocyclic N-oxides. Since, however, only three of these gave interpretable ESR spectra the conclusions drawn about the nitrogen coupling constant must remain tentative. It would be desirable if other N-oxides could be investigated. It is not clear whether 4-nitropyridine-1-oxide should be included in the same category as the N,N'-dioxides (compare with the discrepancies between the calculations for 3,5-dimethylpyridine and those for the methyl pyrazines, Chapter III). The bond lengths and bond angles for the N-oxide grouping will probably not be the same for the three compounds investigated, and this should influence the validity of the conclusions arrived at.

The molecular orbital calculations performed in this chapter seem to be less reliable than those of Chapter III. This can be ascribed firstly to the somewhat arbitrary
nature of the parameters employed, and also to the fact that the simple theories would seem to become necessarily less reliable when the molecule is as heavily perturbed as, for example, 4-nitropyridine-1-oxide. One should thus be more careful about making statements of a quantitative nature in this case.
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Appendix A. Calculated Spin Densities for Methyl Substituted Azine and Diazine Anions.

Table I. 2,6-dimethylpyrazine.

<table>
<thead>
<tr>
<th>Position</th>
<th>Model</th>
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<th>He</th>
<th>Hy</th>
<th>McL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>.2458</td>
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<td>.2690</td>
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</tr>
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<td>2</td>
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<td>.1084</td>
<td>.1052</td>
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<tr>
<td>3</td>
<td></td>
<td>.1259</td>
<td>.1271</td>
<td>.1110</td>
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</tr>
<tr>
<td>4</td>
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<td>.2856</td>
<td>.2845</td>
<td>.2659</td>
<td>.3416</td>
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Table II. 2,5-dimethylpyrazine.

<table>
<thead>
<tr>
<th>Position</th>
<th>Model</th>
<th>I</th>
<th>He</th>
<th>Hy</th>
<th>McL</th>
</tr>
</thead>
<tbody>
<tr>
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<td>.2637</td>
<td>.2581</td>
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<td>.3161</td>
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<td>.0839</td>
<td>.0760</td>
<td>.1145</td>
<td>.0422</td>
</tr>
<tr>
<td>3</td>
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<td>.1528</td>
<td>.1603</td>
<td>.1087</td>
<td>.1467</td>
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Table III. 2-methylpyrazine.

<table>
<thead>
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<th>Position</th>
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<th>Hy</th>
<th>McL</th>
</tr>
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<td></td>
<td>.1243</td>
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<td>.1121</td>
<td>.1048</td>
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Table IV. Tetramethylpyrazine.

<table>
<thead>
<tr>
<th>Position</th>
<th>Model</th>
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<th>He</th>
<th>Hy</th>
<th>McL</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td></td>
<td>.2588</td>
<td>.2471</td>
<td>.2631</td>
<td>.2837</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>.1206</td>
<td>.1181</td>
<td>.1094</td>
<td>.1081</td>
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</tbody>
</table>
Table V. 3,5-dimethylpyridine.

<table>
<thead>
<tr>
<th>Position</th>
<th>Model 1</th>
<th>Model McL</th>
</tr>
</thead>
<tbody>
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<td>.3144</td>
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<tr>
<td>2</td>
<td>.1663</td>
<td>.1837</td>
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<tr>
<td>3</td>
<td>.0451</td>
<td>-.0348</td>
</tr>
<tr>
<td>4</td>
<td>.2942</td>
<td>.3878</td>
</tr>
</tbody>
</table>

Appendix B. Calculated Excess Charge Densities in Substituted Pyrazine, Pyridine and Benzene Anions (Inductive Model).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Position 1</th>
<th>Position 2</th>
<th>Position 3</th>
<th>Position 4</th>
<th>Position 5</th>
<th>Position 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-.4812</td>
<td>-.0094</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>-.5085</td>
<td>+.0604</td>
<td>-.0546</td>
<td>-.5029</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>-.5037</td>
<td>+.0694</td>
<td>-.0656</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>-.5000</td>
<td>+.0710</td>
<td>-.0550</td>
<td>-.4958</td>
<td>-.0042</td>
<td>-.0158</td>
</tr>
<tr>
<td>e</td>
<td>-.5200</td>
<td>+.0100</td>
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<td></td>
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<tr>
<td>f</td>
<td>-.5666</td>
<td>-.0924</td>
<td>+.0093</td>
<td>-.2670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>-.3505</td>
<td>-.0186</td>
<td>-.1312</td>
<td>-.3496</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Compound g is 2,6-dimethylbenzene (m-xylene), the other compounds being numbered as in figure 3. $\pi$-electron densities in the neutral molecules may be obtained from the table by adding unity to all positions and subtracting the spin densities of Appendix A calculated by the inductive model.

Appendix C. Calculated Spin Densities in Heterocyclic Nitro- and N-oxide Anions.

Table I. 4-nitropyridine.

<table>
<thead>
<tr>
<th>Position</th>
<th>Huckel (a)</th>
<th>Huckel (b)</th>
<th>McLachlan</th>
<th>Config. Int. (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.1277</td>
<td>.0554</td>
<td>.1522</td>
<td>.124</td>
</tr>
<tr>
<td>2</td>
<td>.0353</td>
<td>.0021</td>
<td>.0071</td>
<td>.052</td>
</tr>
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<td>3</td>
<td>.0904</td>
<td>.0634</td>
<td>.0907</td>
<td>.033</td>
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<td>.0776</td>
<td>.0021</td>
<td>.0581</td>
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<td>7</td>
<td>.1857</td>
<td>.2371</td>
<td>.1990</td>
<td>.261</td>
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<td>8</td>
<td>.1788</td>
<td>.2872</td>
<td>.1975</td>
<td>...</td>
</tr>
</tbody>
</table>

(a) Parameters of Rieger and Fraenkel (70)

(b) Parameters of Streitwieser (87): $\alpha_e = \alpha_c + \beta_{cc}$,

$\alpha_{N_7} = \alpha_e + 2.0\beta_{cc}$, $\beta_{c,N_7} = \beta_{ce}$, $\beta_{N_7} = .70\beta_{ce}$.

(c) Reference (164).
### Table II. 4-nitropyridine-1-oxide.

<table>
<thead>
<tr>
<th>Position</th>
<th>Hückel</th>
<th>McLachlan</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1154</td>
<td>0.1877</td>
</tr>
<tr>
<td>2</td>
<td>0.0236</td>
<td>-0.0381</td>
</tr>
<tr>
<td>3</td>
<td>0.0841</td>
<td>0.1036</td>
</tr>
<tr>
<td>4</td>
<td>0.0613</td>
<td>0.0292</td>
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<tr>
<td>7</td>
<td>0.1084</td>
<td>0.1464</td>
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<tr>
<td>8</td>
<td>0.1736</td>
<td>0.1789</td>
</tr>
<tr>
<td>9</td>
<td>0.1630</td>
<td>0.1634</td>
</tr>
</tbody>
</table>

### Table III. Quinoxaline-1,4-dioxide.

<table>
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<tr>
<th>Position</th>
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<th>McLachlan</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1575</td>
<td>0.1764</td>
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<tr>
<td>2</td>
<td>0.0848</td>
<td>0.0726</td>
</tr>
<tr>
<td>5</td>
<td>0.0694</td>
<td>0.0831</td>
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<tr>
<td>6</td>
<td>0.0374</td>
<td>0.0248</td>
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<tr>
<td>9</td>
<td>0.0096</td>
<td>-0.0186</td>
</tr>
<tr>
<td>11</td>
<td>0.1413</td>
<td>0.1618</td>
</tr>
</tbody>
</table>
Table IV. Phenazine-9,10-dioxide.

<table>
<thead>
<tr>
<th>Position</th>
<th>Hückel (a)</th>
<th>Hückel (b)</th>
<th>McLachlan</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.0554</td>
</tr>
<tr>
<td>2</td>
<td>0.0328</td>
<td>0.0330</td>
<td>0.0217</td>
</tr>
<tr>
<td>9</td>
<td>0.1462</td>
<td>0.1469</td>
<td>0.1688</td>
</tr>
<tr>
<td>11</td>
<td>0.1557</td>
<td>0.1541</td>
<td>0.1914</td>
</tr>
<tr>
<td>13</td>
<td>0.0177</td>
<td>0.0208</td>
<td>-0.0073</td>
</tr>
</tbody>
</table>

(a) Parameters of Rieger and Fraenkel (70).
(b) Parameters of Kubota (167,168).