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ELECTRON SPIN RESONANCE SPECTRA OF THE RADICAL ANIONS
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December 1966

Electron Spin Resonance Spectra of the Radical Anions of Pyridine and Related Nitrogen Heterocyclics.

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The ESR spectra of the radical anions of pyridine, 4-picoline, 3,5-lutidine, 2,6-lutidine, pyrazine, pyrimidine, pyridine N-oxide, 4-picoline N-oxide, and 2,6-lutidine N-oxide have been observed in liquid ammonia. The data for pyridine, pyrazine and pyrimidine can be combined to evaluate $Q_N^N = +27.3$, $Q_{NC}^N = -1.7$ and $Q_H = -24.5$ gauss independently of molecular orbital spin densities. Good agreement is found for the observed coupling constants for the N-heterocyclics and McLachlan theory with methyl group coupling consistent with both Levy's hyperconjugation equations and with $Q_{CH_3}^{eff} = 25.7$ gauss. The coupling constants for the N-oxides are in satisfactory agreement with an arbitrary set of molecular orbital parameters.

1. INTRODUCTION

There has been considerable interest in the electron spin resonance (ESR) spectra of radicals derived from nitrogen heterocyclics. The techniques used to produce these radicals include chemical reduction, electrolytic reduction, and photolysis. A recent article by Henning (1) reviews much of the theoretical and experimental work dealing with the N-heterocyclic radical anions. In spite of the large volume of data available, there are some significant gaps, particularly in the series of single ring compounds. It was to help fill these gaps and hopefully to clarify the question of hyperfine coupling dependence on spin density distribution that the present work was undertaken.

Many attempts have been made to observe the radical anion of pyridine by ESR. Kuwata (2) reports the evolution of gas and the appearance of a single broad line in the ESR when pyridine is treated with sodium in tetrahydrofuran (THF). Voevodskii and Solodovnikov (3, 4) obtained a multi-lined ESR spectrum by reducing pyridine with potassium in dimethoxyethane (DME), but they did not analyze the hyperfine splitting. Others including Ward (5a), Markau and Maier (6), and Carrington and dos Santos Veiga (7) have identified the ESR spectrum obtained upon reduction of pyridine with an alkali metal in THF or DME as that of the 4,4'-dipyridyl radical anion. Similarly a spectrum of greater width and complexity than would be predicted has been observed when pyrimidine is treated with alkali metal in THF or DME (5b, 7). The radical formed was not identified.

On the brighter side, Dodd and his co-workers (8) have reported the ultraviolet absorbtion (UV) spectra of the radical anions of pyridine, pyrimidine, pyrazine, pyridazine, and 4,4'-dipyridyl. These were formed by brief contact of a THF solution of the parent compound with a sodium mirror. Both the ESR (9) and UV (10) spectra of the 3,5-lutidine radical anion have been observed. In each case the parent compound was reduced by potassium or sodium in DME.

Using the technique developed by Levy and Myers (11) for production of radical anions by continuous electrolysis in liquid ammonia, we have obtained the ESR spectra of the radical anions of pyridine, pyrimidine, several methyl substituted pyridines, and the corresponding amine N-oxides.

2. EXPERIMENTAL

2.1 Chemicals

Reagent grade pyridine was refluxed over BaO, distilled at atmospheric pressure onto CaH_2, and transferred on a vacuum line, after degassing, to a capillary tube of appropriate volume (2 to 8 μl). This sample could then be distilled into the electrolytic cell.

All other compounds were purchased from the Aldrich Chemical Co. Pyrimidine and pyrazine were used without further purification. 4-picoline and 3,5-lutidine were stored over CaH_2, distilled once at atmospheric pressure and once on the vacuum line. Pyridine N-oxide arrived as a soupy solid and is about as hygroscopic as KOH pellets. It was dried for about a week over $CaCl_2$ in vacuo. No further purification

was attempted. 4-picoline N-oxide was recrystallized from benzene. The

2,6-lutidine N-oxide arrived as a brown highly viscous tar. It was

stored over BaO at about 100°C overnight. Distillation at atmospheric

pressure resulted in apparent decomposition, therefore the tar was placed

on the vacuum line and about 0.75 cc were collected in a liquid nitrogen

trap after 24 hours. This sample was a clear colorless liquid at room

temperature. Due to the low vapor pressure this compound was transferred

to the electrolytic cell with a microliter syringe.

2.2 General Procedure and Remarks

For each radical observed, an ammonia solution saturated with

tetramethylammonium iodide and containing 10 to 100 micromoles of parent

compound per 10 cc. of solution was cooled to about -75°C. Current was

passed through the cell starting at 1 μa, gradually being increased

until ESR signals could be observed. Then the current was adjusted to

maximize signal intensity and resolution. It was often necessary for

the "solvated electron" concentration to be so great as to produce the

single intense signal that appears slightly to the high field side of

the center of the radical anion spectrum in several of the figures.

In general, no M_I linewidth dependence was observed. The apparent

variation in signal intensity between the high and low field extreme in

some of the spectra presented is due to a change in radical concentration

during the 20 to 30 minute period of the field sweep. It was often

found that the best spectra were obtained under conditions of precarious

and short lived dynamic balance among the concentrations of parent

compound, radical anion, and "solvated electron" in the vicinity of the

cathode. The coupling constants corresponding to the various radical

anions discussed in this paper along with related data from other works

are listed in Table I. Results pertinent to each anion studied are

discussed in the following sections.

2.3 Mono-Nitrogen Radical Anions

Pyridine

The pyridine radical anion is first observed at ~ 20 μa. The

spectrum consists of 34 lines grouped in sets of 3 and 4. The number

of lines observed is less than the theoretically possible 54 because

the coupling constants $A(N)$ and $A(4)$ happen to be linearly dependent

on $A(1)$ and $A(2)$. The individual linewidths at this low current are

about 0.5 gauss. When the current is gradually raised to maximum of

240 μa (the maximum current was limited by the 110 volts available from

the power supply and by the conductivity of the solution) there is an

increase in signal intensity and decrease of linewidth to 0.15 gauss.

After 45 minutes of continuous electrolysis at this current the lines

narrow further (80 milligauss or less) and additional splitting in some

of the central lines is observed. This splitting corresponds to a

resolution of the linear independence of $A(4)$. A trace of the spectrum

recorded under these conditions is shown in Figure 1. Along with the

increased resolution, a 25% increase in conductivity is observed, then

the signal begins to decay and is completely gone in 10 to 15 minutes.

If the voltage is turned off the signal reappears reaching a maximum

intensity in about 5 minutes. It then decays with a "half life" of

1 to 1.5 minutes. The "half life" for decay at the 40 μa level is

0.75 minutes. All "half lives" are taken as the time necessary for the

signal intensity to decrease by a factor of two. Quantitative studies

of decay rates were not undertaken.

It should be pointed out that current levels quoted are only

qualitatively reproducible. The exact values depend on such factors

as solute concentration and presence of traces of O_2, water, and other

impurities. The exact values are mentioned only to give an idea of the

type of experiment performed.

4-Picoline (4-Methylpyridine)

4-picoline behaves in much the same way as pyridine in liquid

ammonia. Reduction is observed at about 15 µa. There is a similar

increase in radical concentration and decrease in line width as the

current is increased. The spectrum as shown in Figure 2 consists of

81 out of the theoretically possible 108 line. The strong central line,

not expected in a radical containing an odd number of equivalent protons,

is due to the accidental equality $A(CH_3) = 2A(N)$. Continued electrolysis

at maximum current results in decay and eventual disappearance of the

signal. After the voltage is turned off the signal attains maximum

strength within 5 to 8 minutes and decays with a 1 minute "half life."

3,5-Lutidine (3,5-Dimethylpyridine)

The 3,5-lutidine radical anion was prepared in order to compare

results obtained in liquid ammonia with those obtained by chemical

reduction (9, 12). Signal is observed at 20 to 25 µa and the best spectrum

is obtained at approximately 70 µa. This current is significantly less

than the corresponding values for the pyridine and 4-picoline radical

anions. The linewidth was decreased from 0.5 to 0.2 gauss, but could

not be further reduced. The spectrum obtained is shown in Figure 3.

Only 50 of the 126 possible lines are resolved due to the fairly broad

lines and the near equalities $A(N) = 7 A(CH_3)$ and $A(2) = 3A(CH_3)$.

Continued electrolysis at or above 70 μa causes the signal to decrease

and the conductivity to increase. The signal grows back when the voltage

is shut off and then decays with a 4 minute "half life." The observations

indicate that the 3,5-lutidine radical anion is somewhat more stable

than the pyridine or picoline radical anions. The difference in the

hyperfine coupling constants as measured in the two solvent systems

(see Table I) was at first consideration surprising, especially considering

the good agreement in the case of pyrazine radical anion measured in a

wide variety of systems. This will be discussed in a later section.

2.4 Di-Nitrogen Compounds

Pyrazine (1,4-Diazine)

This radical too, was prepared in order to form a basis for comparing

results obtained in liquid ammonia with those obtained using other

techniques (1, 5, 7, 9, 16, 34, 35, 36). An observable quantity of

radical anion is formed with only 1 μa of current. The best signal is

obtained at 7 to 10 μa. Above 10 μa the signal intensity decreases but

returns to the original level if the current is reduced or set to zero.

The pyrazine radical anion is quite stable in liquid ammonia. There is

no noticeable decay of signal after two hours at zero current.

Pyrimidine (1,3-Diazine)

In contrast to pyrazine, pyrimidine radical anion is not observed until the current is raised to 20 μa. Between 20 and 100 μa the spectrum consists of nine broad lines which begin to show additional splitting as the 100 μa level is approached. Continued electrolysis at 125 μa produces a well resolved spectrum consisting of eleven equally spaced quartets. This is shown in Figure 4a.

The four lines of equal intensity can be assigned to the two non-equivalent protons in positions numbered 2 and 5. Eleven equally spaced lines of relative intensities 1:2:3:4:5:6:5:4:3:2:1 can be generated in two ways from two equivalent nitrogen nuclei and two equivalent hydrogen nuclei. If $A(H)$ is equal to the observed spacing then $A(N) = 2 A(H)$, or if $A(N)$ is equal to the observed spacing then $A(H) = 3 A(N)$. The latter case was chosen as the correct assignment on the basis of the observed broadening of the 4th and 5th groups of lines. The computed spectra shown in Figures 4b and 4c show the effects of unresolved inequalities for the two assignments.

Increasing the current above the 125 μa level resulted in a decrease of signal strength. Original intensity was restored when the current was dropped back to 125 μa. After several hours of electrolysis new lines began to appear towards the center of the spectrum indicating the formation of a new species. This second spectrum was not intense enough to analyze or identify.

2.5   N-Oxide Radical Anions

Pyridine N-Oxide

Radical anion is produced in observable quantity at current as low as 2 μa. This is in part due to a high concentration of parent compound (about ten times that of most of the other compounds run). The spectrum consists of 14 lines each about 1 gauss wide. After several hours of electrolysis at maximum current (150 μa) these lines resolve into triplets with a line width of 0.20 to 0.25 gauss. This spectrum is shown in Figure 5. Eventually the conductivity of the solution increases and the radical decays. The signal grows back when the voltage is turned off and then decays with a "half life" of 2 minutes. Prolonged electrolysis results in the growth of additional sharp lines towards the center of the spectrum. The separation of these lines is the same as for the corresponding lines in the pyridine radical anion spectrum. It has been previously observed that chemical reduction of pyridine N-oxide in liquid ammonia yields both pyridine and 4,4'-dipyridyl (13).

4-Picoline N-Oxide

At 5 μa a signal consisting of six triplets having a linewidth of about one gauss is observed. Increasing the current up to 100 μa has no effect on the line width or resolution. Several attempts including prolonged electrolysis at various current levels and variation in parent compound concentration failed to resolve the expected small triplet splittings or to remove the $A(N) = A(CH_3)$ equality. Continued electrolysis at currents greater than 100 μa yielded a new spectrum which could be identified as that of the 4-picoline radical anion. Comparison

with computed spectra indicate that it is reasonable to assume a small

unresolved triplet splitting of 0.25 to 0.30 gauss and a difference of

up to 0.5 gauss in the values of $A(N)$ and $A(CH_3)$. It was not possible

to decide which of the two is larger. The spectrum is shown in Figure 6.

2,6-Lutidine N-Oxide

A signal consisting of eighteen lines of linewidth 1 gauss is

observed at 5 to 10 µa. It was necessary to electrolyze at maximum

current (180 µa) for several hours before further splitting could be

resolved. The spectrum is shown in Figure 7. No decay of signal,

increase in conductivity or production of 2,6-lutidine was observed.

2.6 Discussion of Experimental Observations

In the liquid ammonia electrolyses described above, most of the

interesting reactions occur in a small area above the cathode (a platinum

bead sealed in the bottom of a 4 mm quartz tube). The volume involved

is roughly 2% of the total solution volume. The processes of interest

are equilibria of the sort:

$$A + e^- = A^- \qquad (a)$$

$$A^- + e^- = A^= \qquad (b)$$

$$A^= + A = 2A^- \qquad (c)$$

$$A^- + A = A + A^- \qquad (d)$$
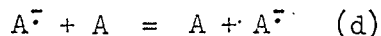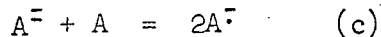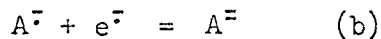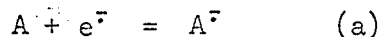
where A represents the parent compound of interest (and e^- is the

"solvated electron" in all its possible forms). Also to be considered

are the irreversible decay processes such as:

$$A^- \rightarrow B \qquad (e)$$

$$A^= \rightarrow C \qquad (f)$$

The products are in general unknown, but the importance of these processes is to give the decrease in concentrations of A^- and $A^=$. The concentration of e^- can be controlled by adjusting the current passing through the electrolytic cell. The parent compound concentration at the cathode is determined variously by the initial concentration, the rate at which it is being used up and the rate of diffusion from the bulk solution into the cathode area. Constants for the equilibria (a) - (c) are functions of the reduction potentials and solvation energies of the species involved.

Using preceeding considerations as a guide, one can propose probable explanations of the phenomena observed during electrolyses of the various nitrogen heterocyclics. The decrease of radical anion concentration at higher current levels can be attributed to dianion formation. An increase in electron concentration coupled with an increase in the concentration of radical anion and/or a decrease in parent compound concentration in sufficient amount would favor reaction (b) instead of (a). The dianion is also a likely species to yield monoanion when the electron concentration is drastically reduced. The decay of the dianion could proceed either by (b) reversed or by (c). Both are possible depending upon the relative amount of A..

Another question of interest concerns the formation of pyridine and picoline from the respective N-oxides. The high current level necessary to bring about the deoxygenation and the observation that prolonged electrolysis and current levels less than that necessary to form significant concentrations of dianion suggest that the dianion is an intermediate in this process.

The width of the lines in an ESR spectrum can often give information about the processes going on in a solution. If the exchange reaction (d) took place with a frequency on the order of 10^6 sec^{-1} it would make a significant contribution to the line width of many organic radical anions (which typically have linewidths of 0.1 to 1 mc). If the concentration of parent molecule were to decrease by a large factor the exchange rate would also drop and there would be a corresponding decrease in the linewidth of the spectrum. The decrease in linewidth in the spectra of radical anions in liquid ammonia observed at increasing current levels is evidence for a linewidth contribution of this sort.

3. DETERMINATION OF NITROGEN HYPERFINE COUPLING PARAMETERS

The equations derived by Karplus and Fraenkel (14) for the interpretation of C-13 hyperfine coupling constants have been adapted to explain N-14 coupling in a variety of situations (1, 15, 16). To first order in a situation where the nitrogen is bonded to two carbon atoms the N-14 hyperfine splitting is bilinear in ρ_N (the electron spin density on the nitrogen atom) and $\rho_C + \rho_C'$ (the electron spin densities on the carbon atoms bonded to the nitrogen) and can be written

$$A(N) = (S_N + 2Q_{CN}{}^N)\rho_N + Q_{NC}{}^N(\rho_C + \rho_{C'}) \tag{1}$$

where S_N represents the contribution of nonbonding electrons including the $N(1s^2)$ and the lone pair electrons. The constant $Q_{CN}{}^N$ represents the contribution due to electrons associated with the carbon-nitrogen bonds. We shall replace the quantity $(S_N + 2Q_{CN}{}^N)$ by a single symbol $Q_N{}^N$ since the two contributions are not separable in the present series of compounds and will probably remain constant. The quantity $Q_N{}^N$ would have different components and hence a different numerical value if derived for a nitrogen atom in a different molecular framework and possibly in very different solvents.

One finds in the literature many determinations of the parameters $Q_N{}^N$ and $Q_{NC}{}^N$. These are summarized in Table II. These calculations all involved data from molecules containing one or more positions of unknown spin density. The numbers presented are therefore dependent on the reliability of molecular orbital calculations and on an estimate of Q_H, the parameter in McConnell's (18) equation relating proton hyperfine coupling to spin density on the adjacent carbon atom.

$$A(H) = Q_H\rho_C \tag{2}$$

Using only the coupling constants for pyridine, pyrazine and pyrimidine radical anions we have been able to calculate values for $Q_N{}^N$ and $Q_{NC}{}^N$, as well as determining a value for Q_H. The major assumption underlying this determination is the validity of equations (1) and (2). Our calculation involved the simultaneous solution of equations of the type:

$$A(N) = Q_N{}^N(1 - \sum_i A(i)/Q_H) + Q_{NC}{}^N(\sum_s A(s)/Q_H) \tag{3}$$

$$A(N) = \tfrac{1}{2}Q_N{}^N(1 - \sum_i A(i)/Q_H) + Q_{NC}{}^N(\sum_s A(s)/Q_H) \tag{4}$$

where i is summed over all carbon atoms in the ring and s is summed over the carbon atoms adjacent to the nitrogen atom in question. Equation (3) applies to the pyridine radical anion and equation (4) applies to the pyrazine and pyrimidine radical anions. The assumption that $\Sigma \rho_j = 1$ (j summed over all atoms in the ring) is implicit in the derivation of (3) and (4).

In these equations one must know the signs of the A values while our ESR data only determine their magnitudes. It is well known that Q_H is negative and the sign of $A(N)$ appears to be positive (19, 20) in most situations. In the case of pyrimidine radical anion simple Hückel theory places a node at carbons 2 and 5, but unrestricted SCF calculations yield a small negative spin density. For pyrimidine we have assumed that A(2) and A(5) are positive. The only other positions where the sign of A is questionable are the 3,5 positions of pyridine. Hückel and unrestricted SCF type calculations give contradictory answers. In this case if equations (3) and (4) are solved assuming A(3) > 0 for pyridine one obtains $Q_N{}^N = +27.7$, $Q_{NC}{}^N = +6.4$ and $Q_H = -17.5$ gauss. While the nitrogen Q values are reasonable, Q_H is not. On the other hand, if A(3) < 0 for pyridine then one obtains the values listed in Table II together with a very reasonable $Q_H = -24.5$ gauss.

Additional evidence for the probable Q values are shown in Figure 8.

Here the three radical anions, pyridine, pyrazine and pyrimidine are

utilized in pairs in equations (3) and (4) to solve for Q_N^N and Q_{NC}^N

as a function of Q_H. It can be seen that the pair pyrimidine and

pyrazine for Q_N^N and pyrimidine and pyridine for Q_{NC}^N give solutions

which are largely independent of Q_H. For this reason we can be confident,

within the accuracy of equations (3) and (4), of the values of Q_N^N and

Q_{NC}^N. A second pair, as shown in Figure 8, selects with some precision

the exact value of $Q_H = -24.5$ gauss. Our value of Q_{NC}^N is very close to

zero and thus we confirm the approximate determinations of references

(7), (9), (16) and (17) and do not agree with (5) and (1). In his work

Henning (1) attempted to correct for the deviations from Hückel theory

by making consistent corrections. Since our determinations are

essentially independent of any molecular orbital theory and are only a

test of equations (3) and (4) it would seem that we have established the

best possible values for Q_N^N and Q_{NC}^N for this type of nitrogen

heterocyclic.

4. MOLECULAR ORBITAL CALCULATIONS

4.1 N-Heterocyclics

We have carried out a number of molecular orbital calculations using

both Hückel and McLachlan approximations (21, 22) in order to see how

well simple theory correlates with the experimentally determined spin

densities. For the unsubstituted N-heterocyclics the two necessary

parameters are δ_N which measures the difference between the carbon and

nitrogen coulomb integrals, and γ_{CN} the reduced carbon-nitrogen resonance

integral, both in units of the carbon-carbon resonance integral. Calcu-

lations reported in the literature for excited states and radical anions

of similar molecules use values of δ_N ranging from 0.2 to 1.0 and of

γ_{CN} from 0.8 to 1.2. Pariser and Parr (23) determined a semiemperical

value for $\beta_{CN} = 1.076\beta_{CC}$ by fitting calculations to the electronic

spectra of benzene and s-triazine. Using a value of $\lambda = 1$ for the

McLachlan parameter we have calculated spin densities for $0.5 < \delta_N < 1.0$

and $0.8 < \gamma_{CN} < 1.2$. It appears that the Pariser-Parr value for γ_{CN}

gives the best overall results, and $\delta_N = 0.80$ seems appropriate. It was

observed that the difference in the Hückel and McLachlan spin densities

corresponded to an over-estimation of the importance of the splitting in

the lower "doubly occupied" orbitals. Since the McLachlan parameter λ

is fairly arbitrary, λ was reduced to 0.75. This improves the agreement

between theory and experiment. In fact, any of the experimental spin

densities can be reproduced very well indeed with only small variations

from our "average" parameters. Theoretical McLachlan spin densities

along with those calculated from experimental coupling constants using

the Q values previously determined are listed in Table III. The agree-

ment is excellent.

There have appeared in the literature a number of other SCF calculations

treating pyridine, pyrazine and pyrimidine. Nishimoto (24) lists wave

functions for pyridine, pyrazine and s-triazine calculated using an

LCAO MO SCF framework in the form proposed by Pople (25) with $\gamma_{CN} = 1.076$,

with core integrals estimated from ionization potentials and with two

center coulomb integrals based on an inverse separation approximation.

Nagakura (10) has used these wave functions as a basis set for a

configuration interaction approximation to the orbitals for the pyridine

radical anion. The CI calculation has very little effect on the spin

density distribution, although it does improve energy calculations.

Spin densities for the pyridine radical anion can be calculated from the

lowest unoccupied orbital of the set determined by Nishimoto using the

so-called virtual orbital (VO) approximation. Miller, et. al. (26)

have calculated spin densities for the pyridine and pyrimidine radical

anions using both the VO approximation and an open shell (OS) calculation

based on orbitals determined for the neutral molecules. Their neutral

molecule calculation differs from that of Nishimoto in the inclusion of

penetration integrals in the estimation of diagonal matrix elements,

theoretical calculation of two center coulomb integrals using Slater

type orbitals with adjustable exponent (semiemperically determined),

and an exponential expression for β adjusted to fit the Pariser-Parr

values for β_{CC}(1.39 A) and β_{CN}(1.34 A). Bond distances were determined

as a function of bond order and iterated to self-consistency for the

neutral molecule. Hinchliffe (27) has calculated spin densities for

various radicals including the pyrazine radical anion. He reports values

obtained both from open shell SCF and open shell SCF plus CI approximations

using core integrals estimated from ionization potentials, β values and

two center coulomb integrals as proposed by Pariser and Parr (23) and

starting orbitals calculated by Hückel theory with $\delta_N = 0.5$ and $\gamma_{CN} = 0.8$.

The various SCF spin densities are also included in Table III.

There are some relevant observations that can be made about the

various approximations. First it should be pointed out that spin

densities calculated from closed shell SCF wave functions using VO's

can be closely reproduced by Hückel orbitals calculated with core

integrals related to these used in the SCF calculation. Configuration

interaction seems to have very little effect on spin density distribution

in a closed shell approximation, while Hinchliffe's calculation seems

to indicate that the correction is in the wrong direction in an open

shell basis. Similarly the open shell calculation of Miller et. al.

compared with VO's calculated using the same parameters yields a

correction in the wrong direction for both radical anions considered.

In light of these observations and the success of McLachlan theory,

it would seem worthwhile to carry out calculations such as those done

by Amos and Hall (28) for hydrocarbon radicals, using the unrestricted

open shell SCF model. This model is more flexible than the McLachlan

approximations and may account for the small variations in δ_N. It also

takes into account the spin dependence of electron correlation neglected

in the restricted SCF calculations.

It can be seen from Table I that methyl group substitution brings

about appreciable changes in the spin density distribution of the

pyridine framework. Since the McLachlan theory gives a good description

of the unsubstituted radical anions, it is logical to try to include

the effects of the methyl groups in this type of calculation. We have

determined spin densities using a number of models. For the simple

inductive model we used $\delta_C = -0.1$ and -0.4 for the carbon atom to which

the methyl group is attached. For the hyperconjugation model without

inductive effect we used the parameters of Coulson and Crawford (29)

$\gamma_{CC'} = 0.76$, $\gamma_{C'H} = 2.00$, $\delta_{C'} = -0.1$, and $\delta_H = -0.5$ where C' is the

methyl group carbon atom and H is the pi-type orbital formed from the

hydrogen 1s orbitals. For inclusion of the inductive effect in the

hyperconjugation model we used values of δ_C from -0.1 to -0.5. It was

found that the best agreement was obtained when the changes in spin

density distribution were predicted using the hyperconjugation model

with $\delta_C = -0.2$. These calculated spin densities are included in

Table III.

The calculation of methyl proton hyperfine splittings is still the

subject of some controversy. McLachlan (30) has suggested that in the

valence bond formalism $A(CH_3)$ is proportional to the spin density on

the pi-system carbon atom to which the methyl group is attached and he

estimated the proportionality constant to be 28 gauss. The values used

to explain various experimental determinations of methyl hyperfine

coupling range from 15 to 30 gauss. Levy (31) has derived equations for

calculating the methyl and methylene proton splittings using spin

densities determined by the hyperconjugation model. We have calculated

methyl coupling constants from Levy's equations using the ranges of

δ_N, γ_{CN}, and δ_C previously discussed. We also determined the quantity

$Q_{CH_3}^{eff.} = A(CH_3)/\rho_t$, where $A(CH_3)$ is the calculated coupling constant and

ρ_t is the total spin density associated with the methyl group, i.e.

$\rho_H + \rho_{C'} + \rho_C$. For all of the methyl substituted pyridines studied

$Q_{CH_3}^{eff.}$ varied by only 2 gauss over the range of parameters used and

was constant from molecule to molecule for equivalent sets of parameters.
The value of $Q_{CH_3}^{eff.}$ predicted by these calculations is 25 gauss. An
experimental value can be determined using our values for Q_N^N, Q_{NC}^N and
Q_H to calculate the spin densities. For the 4-picoline radical anion
$Q_{CH_3}^{eff.}$ = 27.3 gauss and for the 3,5-lutidine radical anion $Q_{CH_3}^{eff.}$ = 24.1
gauss. Although the range is greater than can be explained by simple
theory, the average of 25.7 gauss is in good agreement with the predicted
value. The variation could indeed be an indication of deviation from
the relations assumed in equations (3) and (4).

The variations observed in the 3,5-lutidine radical anion coupling
constants in electrolytic and chemical reduction systems remains to be
considered. It has been proposed (5a, 32) that the dimerization of
pyridine observed in alkali metal/ether systems involves complexes such
as I and II. Although the dimerization of 3,5-lutidine is made sterically

I   II   III
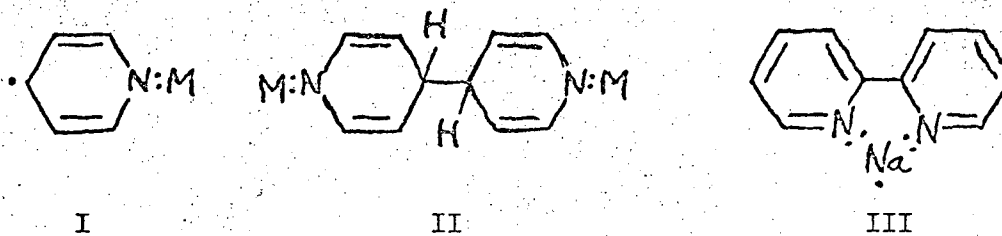
unfavorable by the presence of the methyl groups, it is not unlikely that
a complex like I would form in the presence of an alkali metal cation.
Further evidence of a nitrogen lone pair electron---alkali metal inter-
action has been reported by Zahlan et. al. (33). They observed the ESR
spectrum of a sodium 2,2'-dipyridyl complex which they suggested has the
structure III. This type of interaction would certainly perturb the

spin density distribution and would also change the value of Q_N^N.

Donation of the lone pair electron to a nitrogen alkali metal bond would

in simple theory have the effect of increasing δ_N. With this variation,

McLachlan theory does indeed predict changes in spin density in the

appropriate directions.

On the other hand, the system pyrazine/alkali metal/ether has been

extensively studied by a number of workers (12, 34, 35a,b). It is found

that the pyrazine radical anion coupling constants are independent of

cation, temperature, and choice of solvent. Line-width alteration and

other theoretical and experimental considerations have led to the

proposal that the cation is above (or below) the plane of the radical

anion rather than in the plane of the anion as is suggested for pyridine

and 2,2'-dipyridyl. Calculations by Atherton (36) indicate that the

interaction is predominantly with the pi-electrons rather than with the

nitrogen lone pair electrons. This being the case, the effect on Q_N^N

and on the spin density distribution would be considerably smaller.

4.2 N-Oxides

The calculation of spin densities in the N-oxide radical anions

involves the evaluation of a number of parameters. Only a few MO treat-

ments of the N-oxides are reported in the literature and these generally

are attempts to explain the unusual chemical behavior of the pyridine

N-oxides. Values used for δ_N range from 0.6 to 2.0, for γ_{NO} from 0.75

to 1.0 while $\delta_O = 1.0$ was common (37, 38). In order to set reasonable

limits on the values of δ_N and δ_O we have used relation (5) suggested

$$\delta_A = d\omega_A - \tfrac{1}{2}[Z_A(AA|AA) - (CC|CC)] \qquad (5)$$

by McWeeny (39) where atom A donates Z_A electrons to the pi system, $d\omega_A$ is the difference in electron affinity of the core atom A from a benzene core carbon atom, and $(AA|AA)$ is the coulomb repulsion integral between two electrons in the same spatial orbital. Using the valence state ionization potentials determined from the tables of Pritchard and Skinner (40) and values of $(AA|AA)$ calculated by Orloff and Sinanoglu (41) we have arrived at the following estimates:

$$\delta_N(Z_N = 1) = 0.8$$

$$\delta_N(Z_N = 2) = 2.0$$

$$\delta_O(Z_O = 1) = 1.75$$

$$\delta_O(Z_O = 2) = 3.5$$

In the MO calculations it is assumed that the oxygen atom donates two electrons to the pi-system. This effect is partially cancelled by the donation of nitrogen lone pair electrons to the oxygen in the σ bond formation and one would expect the δ's to lie between the extremes of $Z = 1$ and $Z = 2$.

Nishimoto and Forester (42) have worked out equations relating the quantities γ_{CC}, γ_{CN}, and γ_{CO} to the pi bond order. Assuming that the quantity γ_{XY} can be approximated by an average of γ_{XX} and γ_{YY}, we have worked out a similar relation for the dependence of γ_{NO} on the pi bond

order, with the result that γ_{NO} should lie between 1.1 and 1.2 for bond

orders of $\frac{1}{4}$ to $\frac{1}{2}$.

With the semiemperical predictions in mind we have determined spin

densities for the following ranges of parameters: $0.75 \leqslant \delta_N \leqslant 2.0$,

$1.5 \leqslant \delta_O \leqslant 2.5$, $0.8 \leqslant \gamma_{NO} \leqslant 1.4$ with $\gamma_{CN} = 1.0$ and 1.076 and using the

methyl group parameters previously discussed. At values of $\gamma_{NO} \geqslant 1.4$

a low lying unoccupied orbital with a node passing through the N-O bond

drops below the orbital occupied by the unpaired electron thus placing

an upper limit on the value of γ_{NO}. It was necessary to approach this

limit in order to account for the large spin density observed in the

N-O entity, therefore γ_{NO} was set equal to 1.2. With $\gamma_{CN} = 1.076$, the

spin densities in the 4 positions were much too large, so a value of

1.00 was used. The choice of δ_N and δ_O was somewhat less well defined.

Several sets of (δ_N, δ_O) in the ranges $1.0 \leqslant \delta_N \leqslant 1.5$ and $1.5 \leqslant \delta_O \leqslant 2.0$

predicted reasonable spin densities. The best description of the pyridine

N-oxide and the 4-picoline N-oxide radical anions corresponded to

$\delta_N = 1.1$ and $\delta_O = 1.5$ but the agreement for the 2,6-lutidine N-oxide

radical anion was considerably improved by increasing δ_O to 2.0. The

theoretical and experimental spin densities are listed in Table III.

Katrizky (43) has concluded from NMR data that the electron density

in position 3 is greater than that in position 2 in neutral pyridine

N-oxide. Using our parameters, the calculated electron densities are in

agreement with this analysis. Previous workers have predicted the

reverse to be true.

Part of the interest in the calculation of spin densities for the

N-oxide radical anions resulted from a desire to examine the nitrogen

hyperfine coupling parameters. In analogy to equation (2) the nitrogen

coupling constant can be written:

$$A(N) = (S_N' + 2Q_{CN}{}^N + Q_{ON}{}^N)\rho_N + Q_{NO}{}^N\rho_O + Q_{NC}{}^N(\rho_C + \rho_{C'}) \qquad (6)$$

where S_N' represents only the $N(1s^2)$ contribution and the other parameters

are similar to those of equation (2). We shall replace the quantity

$(S_N' + 2Q_{CN}{}^N + Q_{ON}{}^N)$ by the symbol $Q_{N\to O}{}^N$ since again the individual

quantities are not separable.

We determined $Q_{N\to O}{}^N$ and $Q_{NO}{}^N$ using the calculated values of ρ_N and

ρ_O and the experimental values of ρ_C listed in Table III along with our

value of $Q_{NC}{}^N$ and the experimental values of $A(N)$ listed in Table I.

The values obtained are $Q_{N\to O}{}^N = \pm 50 \pm 8$ gauss and $Q_{NO}{}^N = \pm 65 \pm 25$ gauss.

The large uncertainty is due to part to the uncertainty in the 4-picoline

N-oxide coupling constants and in part to the fact that the three $A(N)$

equations are nearly dependent. It would be of considerable value to

determine coupling constants for N-oxides not so closely related to

pyridine in order to remove the near dependence and allow a better

determination of the Q values.

Fraenkel (15) has determined the corresponding parameters $Q_{NO_2}{}^N$ and

$Q_{NO}{}^N$ for the nitro group nitrogen hyperfine coupling. He obtained

$Q_{NO_2}{}^N = \pm 99 \pm 10$ gauss and $Q_{NO}{}^N = \pm 36 \pm 6$ gauss. The quantity $Q_{ON}{}^N$

contributes twice to $Q_{NO_2}{}^N$ and only once to $Q_{N\to O}{}^N$ and it must be fairly

large (in absolute magnitude) in order to account for either of the large

Q values to which it contributes. Thus it is reasonable that the para-

meters $Q_{N \to O}^N$ and $Q_{NO_2}^N$ are quite different. Some change in the value of

Q_{NO}^N would be expected due to the differences in the N-O bonds, however

a difference of 14 gauss seems unlikely. Determination of Q_{NO}^N in a

greater variety of cases might shed some light on the problem.

Acknowledgment

Table I

Observed Coupling Constants for Radical Anions in Liquid Ammonia

Heterocyclic Compound[a]	Atom	Heterocyclic	N-Oxide
		A(gauss)	A(gauss)
Pyridine	N	6.28	10.82
	H(2)	3.55	3.04
	H(3)	0.82	0.47
	H(4)	9.70	8.61
4-Picoline	N	5.67	9.89 ± 0.3
(4-methylpyridine)	H(2)	3.80	3.35
	H(3)	0.60	<0.30
	$CH_3(4)$	11.38	9.89 ∓ 0.3
3,5-Lutidine	N	7.40[b]	
(3,5-dimethylpyridine)	H(2)	3.19	
	$CH_3(3)$	1.06	
	H(4)	8.98	
2,6-Lutidine	N	(c)	9.85
(2,6-dimethylpyridine)	$CH_3(2)$		4.25
	H(3)		0.47
	H(4)		8.98
Pyrazine	N	7.22[d]	----
(1,4-diazine)	H	2.72	----
Pyrimidine	N	3.26	----
(1,3-diazine)	H(2)	0.72	----
	H(4)	9.78	----
	H(5)	1.31	----

(a) Rings numbered by standard convention. See, for example, Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland.

(b) Reference 9 obtained 6.21, 3.41, 0.80 and 8.96, respectively, using alkali metal reduction in dimethoxyethane.

(c) A spectrum has been obtained using 2,6-lutidine as the parent compound but we have been unable to assign it.

(d) References 1, 5, 7 and 16 have obtained quite similar values in a number of other solvents.

Table II

Nitrogen-14 Q Values in Conjugated Heterocyclics

Reference	Q_N^N	Q_{NC}^N	Radical Anions
	gauss		
Carrington and Santos Veiga (7)	+25 ± 2	----	pyrazine, 4,4'-dipyridyl, quinoxaline, phenazine, tetraazaanthracine
Ward (5)	+21	+7	pyrazine, 4,4'-dipyridyl
Atherton, Gerson and Murrell (9)	+28.4	-1.5	pyrazine, 3,5-lutidine
Henning (1)	+19.1	9.1	pyrazine, 4,4'-dipyridyl, 1,4- and 1,5-diazanapthylene
Stone and Maki (16)	+30.9 ± 2	-2 ± 4	pyrazine, phenazine
Geske (17)	(+30.9)[a]	-4	2,2'-dipyrimidine
This work[b]	+27.3	-1.7	pyridine, pyrazine, pyrimidine

(a) Assumed value of Reference 16.

(b) Using only equations (3) and (4) and assuming that $A(3) < 0$ for pyridine which gives $Q_H = -24.5$ gauss.

Table III

Experimental and Theoretical Spin Densities

in N-Heterocyclic Radical Anions

Radical Anion	Position	Expt[a]	McLach.[b]	Theory — Others		
				$\underline{VO}^{(c)}$	$\underline{VO}^{(d)}$	$\underline{OS}^{(d)}$
Pyridine	N	0.247	0.275	0.273	0.228	0.206
	2	0.145	0.153	0.114	0.120	0.079
	3	0.033	0.007	0.074	0.071	0.082
	4	0.395	0.403	0.346	0.390	0.476
				$\underline{VO}^{(c)}$	$\underline{OS}^{(e)}$	$\underline{OS+CI}^{(e)}$
Pyrazine	N	0.278	0.291	0.285	0.336	0.379
	2	0.111	0.105	0.102	0.082	0.061
					$\underline{VO}^{(d)}$	$\underline{OS}^{(d)}$
Pyrimidine	N	0.143	0.151		0.181	0.187
	2	-0.029	-0.028		0.000	0.000
	4	0.398	0.402		0.318	0.313
	5	-0.053	-0.078		0.000	0.000
4-Picoline	N	0.227	0.263			
	2	0.155	0.160			
	3	0.024	-0.004			
	4(CH_3)	0.415	0.433			
3,5-Lutidine	N	0.287	0.282			
	2	0.130	0.163			
	3(CH_3)	0.044	0.012			
	4	0.364	0.367			
Pyridine N-oxide	Ox	} 0.363 {	0.065			
	N		0.298			
	2	0.124	0.126			
	3	0.019	0.015			
	4	0.351	0.360			

Table III (continued)

Radical Anion	Position	Expt.[a]	Theory	
			McLach.[b]	Others
4-Picoline N-oxide	Ox N	} 0.350±.012	{ 0.058 0.284	
	2	0.136	0.135	
	3	0.008±.002	-0.002	
	4(CH$_3$)	0.362±.010	0.392	
2,6-Lutidine N-oxide	Ox N	} 0.276±.010	{ 0.054[f] 0.261	0.036[g] 0.253
	2(CH$_3$)	0.160±.005	0.134	0.148
	3	0.019	0.023	0.017
	4	0.366	0.370	0.373

(a) Experimental spin densities are calculated from the coupling constants using Q_H = -24.5 gauss, Q_N^N = 27.3 gauss and Q_{NC}^N = -1.7 gauss along with the restriction that ρ total = 1.

$Q_{CH_3}^{eff}$ = 25 gauss was used in the N-oxides.

(b) See text for discussion of parameters used.

(c) Reference 10, and 24.

(d) Reference 26.

(e) Reference 27.

(f) Calculated using δo = 1.5.

(g) Calculated using δo = 2.0.

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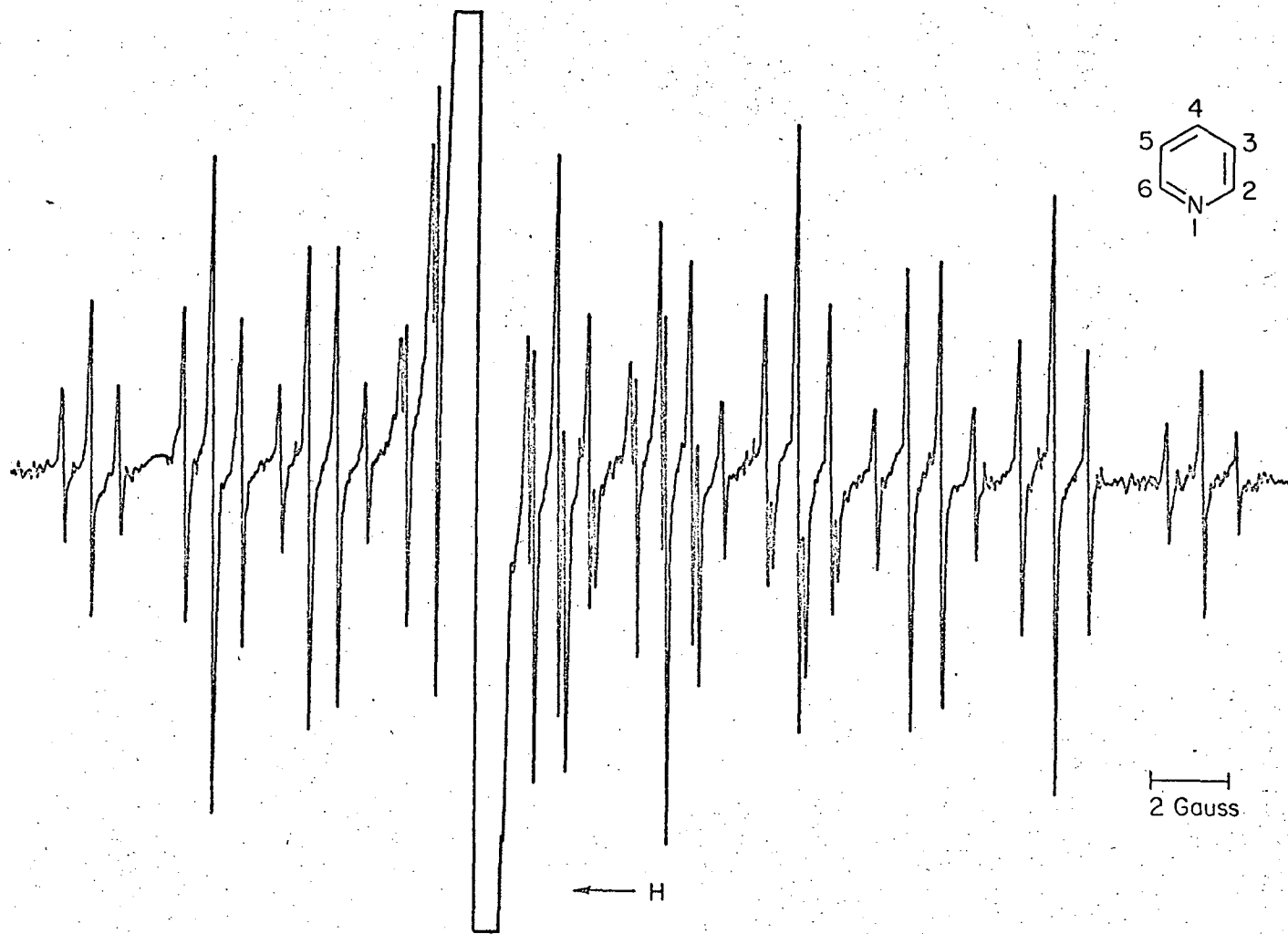
Figure 1.   The ESR spectrum of the radical anion of pyridine in liquid
            ammonia near -75°C.   The strong line is due to the "solvated
            electrons" present in the system under steady state electrolysis.
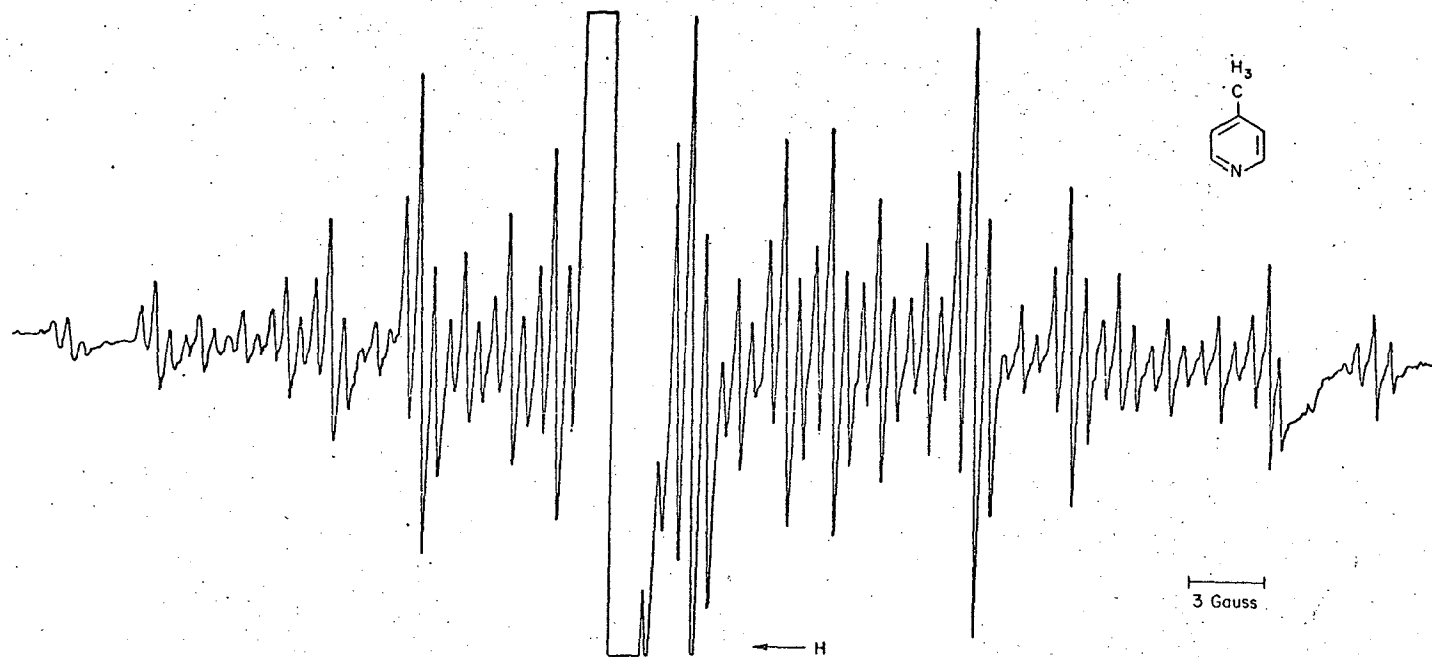
Figure 2. The ESR spectrum of the radical anion of 4-picoline. The intensity variations from one end of this spectrum to the other are largely due to variations with time.

2 Gauss

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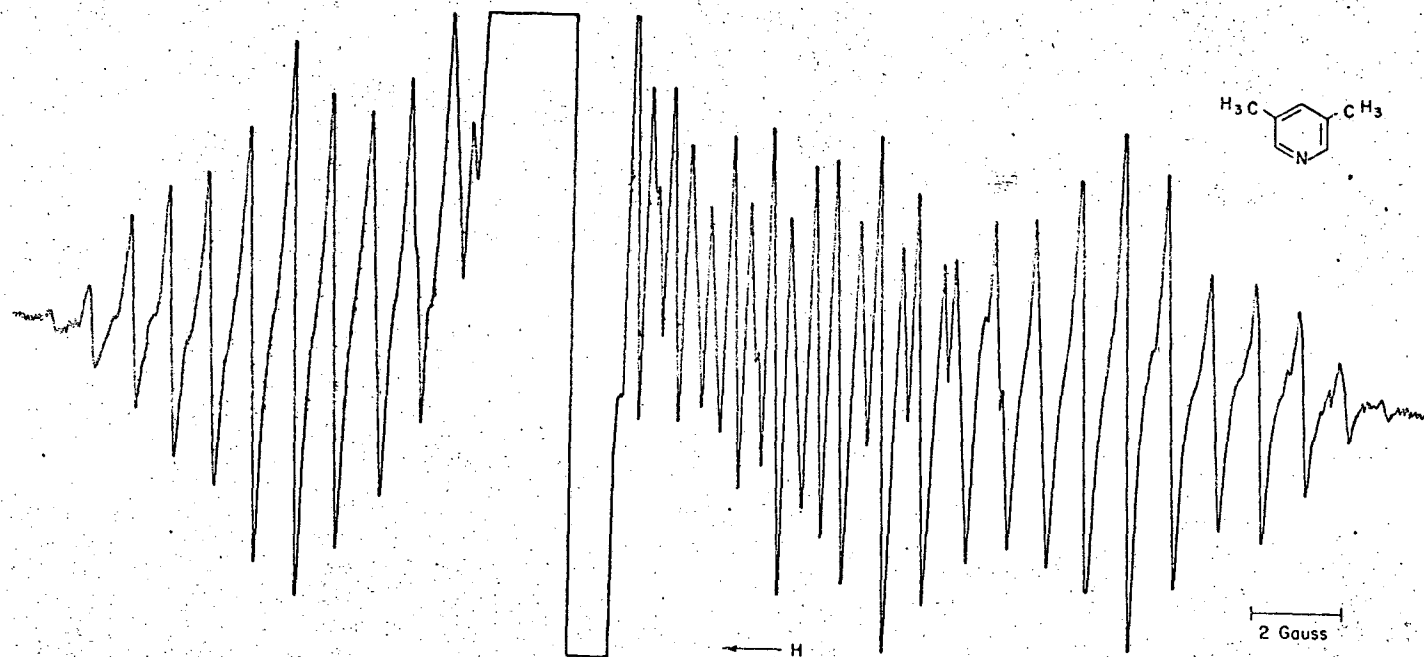
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Figure 3. The ESR spectrum of the radical anion of 3,5-lutidine.
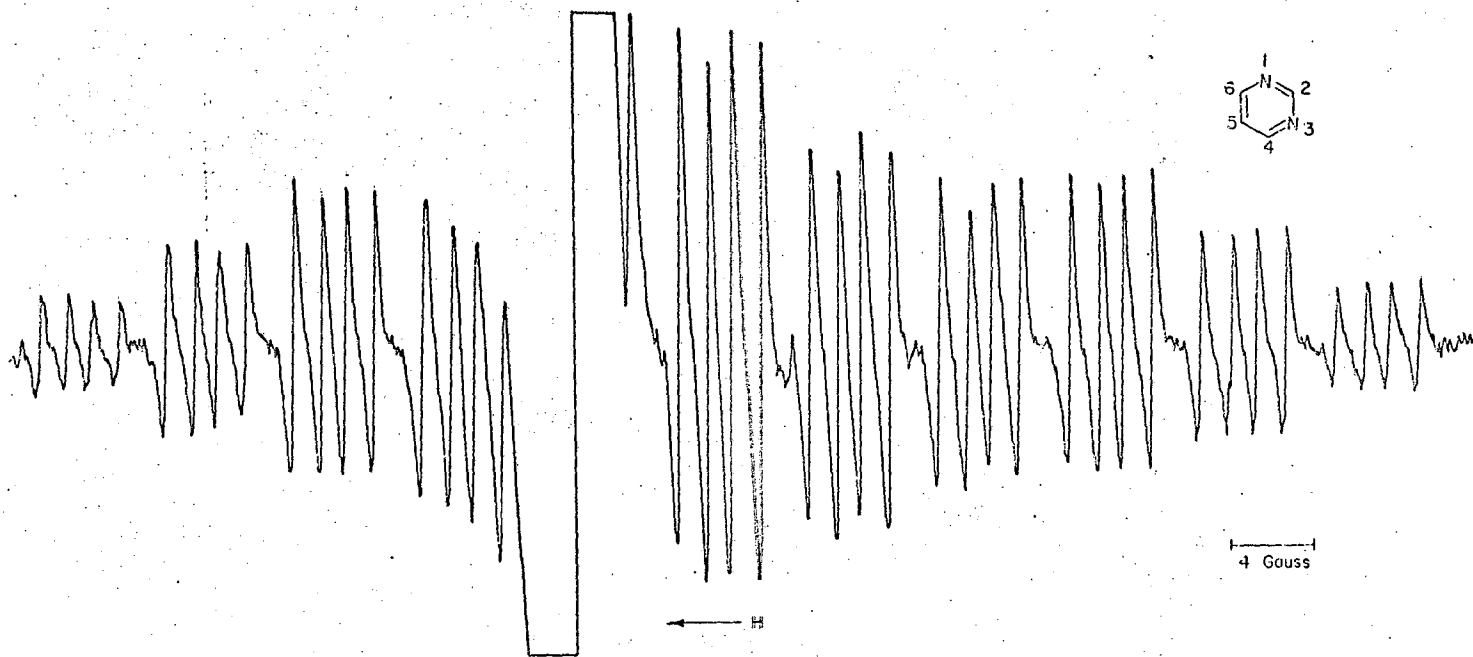
Figure 4. The ESR spectrum of the radical anion of pyrimidine.
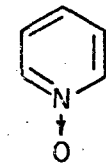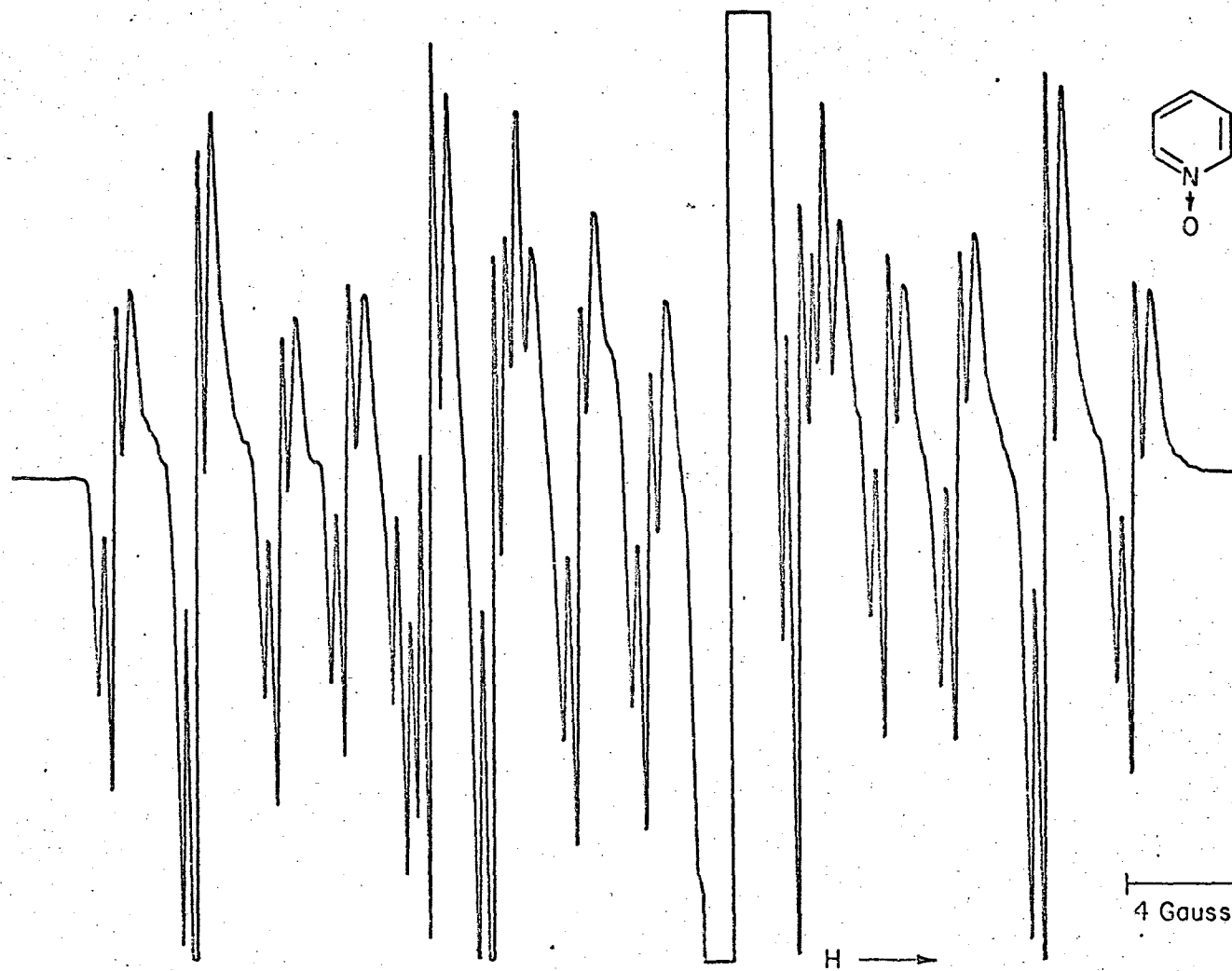
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Figure 5. The ESR spectrum of the radical anion of pyridine N-oxide.
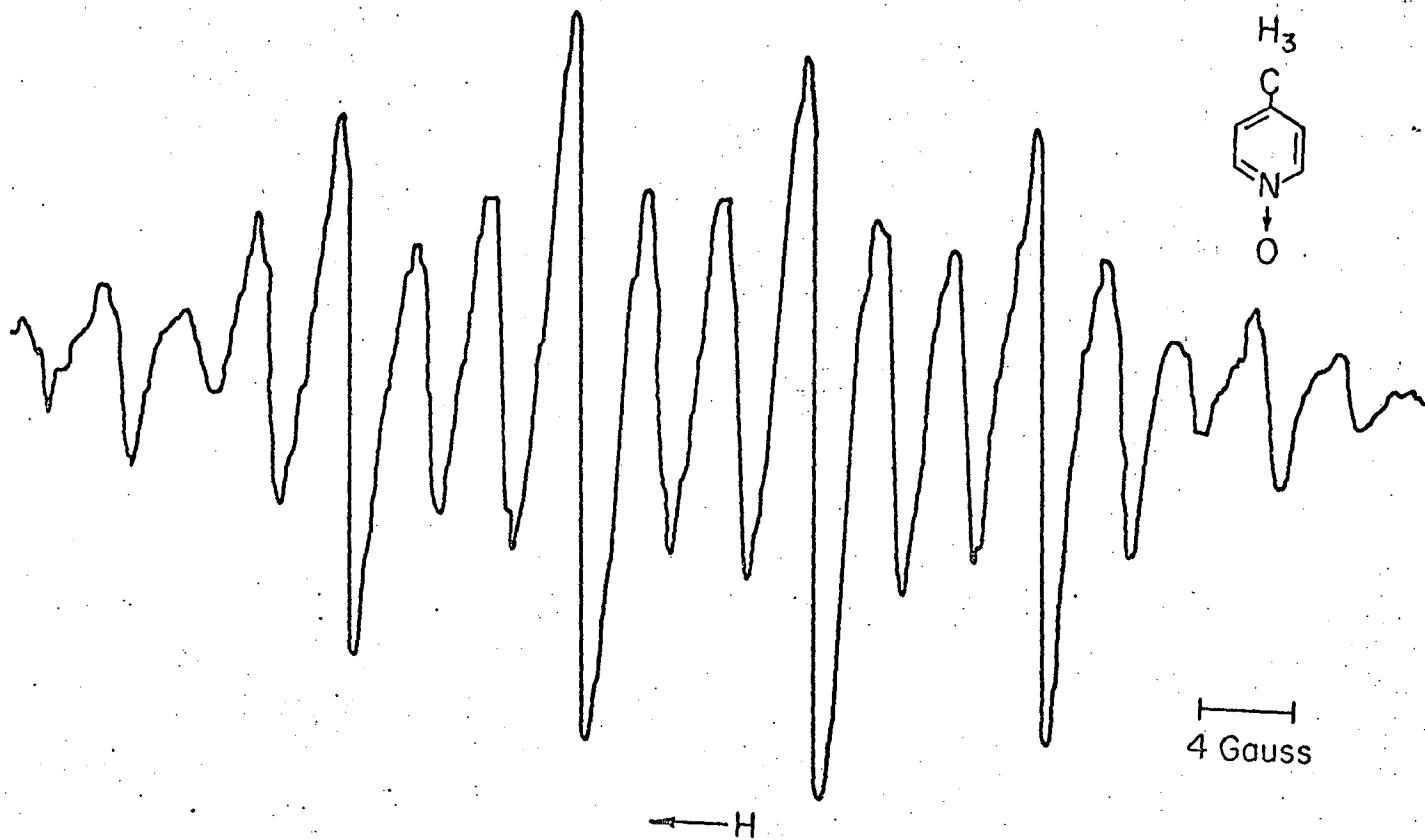
Figure 6. The best ESR spectrum obtained for the radical anion of 4-picoline N-oxide.

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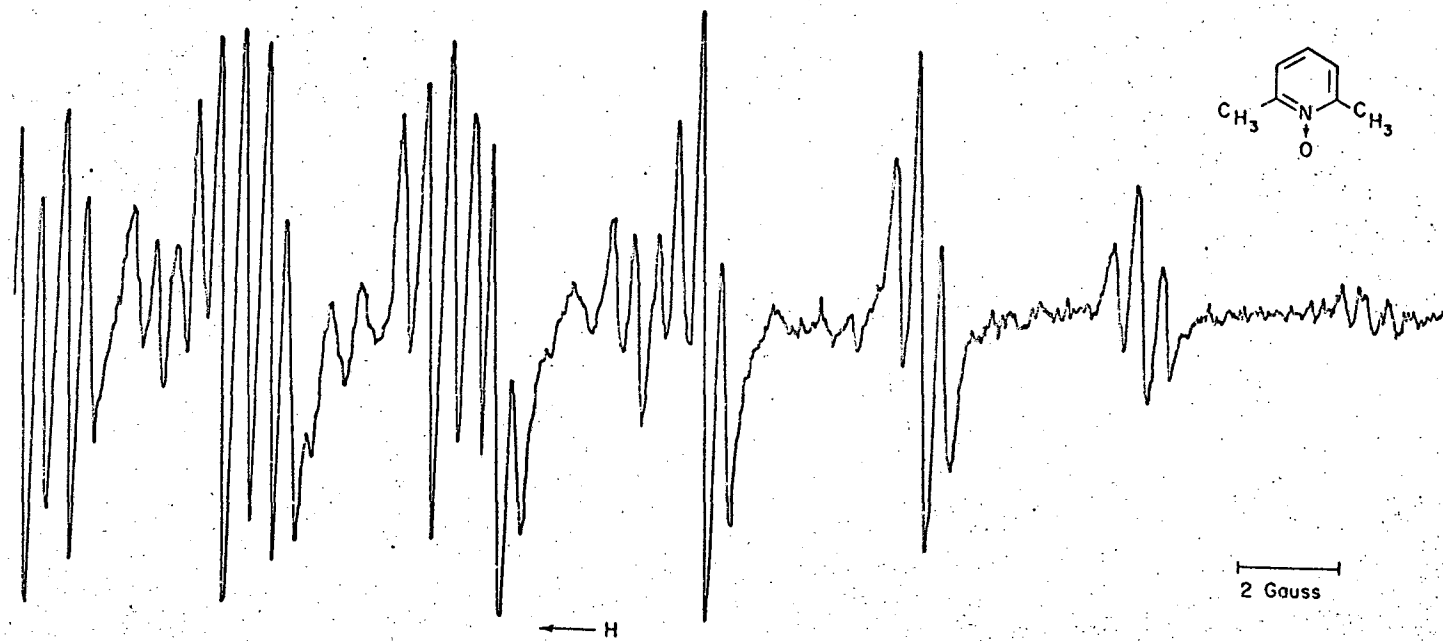
Figure 7. One-half of the ESR spectrum of the radical anion of 2,6-lutidine N-oxide.
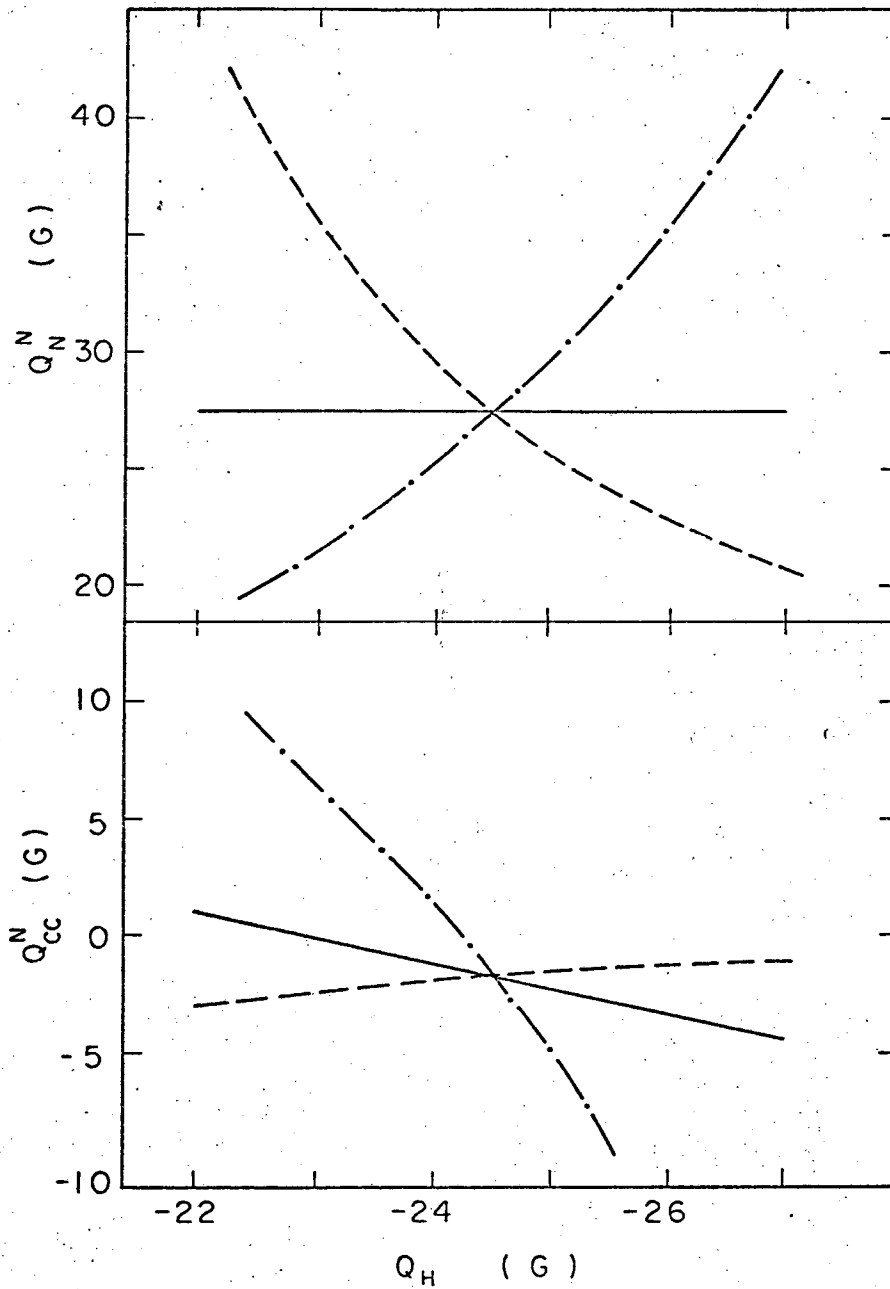
MUB 14131

Figure 8. The determination of Q values by pair-wise solution
of Equations (3) and (4).

---- Pyridine plus pyrimidine
_____ Pyrazine plus pyrimidine
-·-·- Pyridine plus pyrazine