DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ RESEARCH REPORT No. 5

# ON THE EPR, ENDOR AND VISIBLE ABSORPTION SPECTRA OF SOME NITROGEN CONTAINING HETEROCYCLIC COMPOUNDS IN LIQUID AMMONIA

BY TIMO NYRŎNEN

Academic Dissertation for the Degree of Doctor of Philosophy



Jyväskylä, Finland ISBN 951-678-093-8 DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ RESEARCH REPORT No. 5

# ON THE EPR, ENDOR AND VISIBLE ABSORPTION SPECTRA OF SOME NITROGEN CONTAINING HETEROCYCLIC COMPOUNDS IN LIQUID AMMONIA

BY

TIMO NYRÖNEN

Academic Dissertation for the Degree of Doctor of Philosophy

To be presented, with the permission of the Faculty of Mathematics and Natural Sciences of the University of Jyväskylä for public criticism in Auditorium II-212 on December 15 th, 1978, at 12 o'clock noon

> Jyväskylä, Finland ISBN 951-678-093-8

URN:ISBN:978-952-86-0533-1 ISBN 978-952-86-0533-1 (PDF) ISSN 0357-346X

University of Jyväskylä, 2025

Copyright 1978 Jyväskylän yliopisto

### PREFACE

The experimental work described in this publication was carried out at the Department of Chemistry, University of Jyväskylä from 1975 until 1977.

I wish to express my gratitude to my teacher, Professor Jorma Eloranta, Ph.D., whose interest and encouragement were of great help throughout the course of this work.

My thanks also go to Mr. Reijo Mäkinen, M.Sc., for his assistance in several experiments. I also wish to thank my collagues, especially Mr. Esa Salo, Ph.Lic., for his advice in the electrolytical radical preparation.

I am indebted to Mr. Roger Price, B.Sc., for inspecting the language, to Miss Raili Koskinen for drawing the pictures and to Mrs. Sirkka-Liisa Nupponen who patiently typed the final form of this publication.

I am grateful to Professor K. Möbius, Ph.D., Professor H. Kurreck, Ph.D., and Mr. W. Lubitz, Ph.D., Freie Universität, Berlin for giving the possibility to the ENDOR measurements and for the help in the practical work.

This work was supported by the grant from the Neste Oy Foundation and is gratefully acknowledged.

Finally, I owe a great depth of gratizude to my family for their support and understanding.

Jyväskylä, November 1978

## CONTENTS

I	INTRODUCTION	1
1.	The purpose of this study	1
2.	On the solvated electrons in the liquid ammonia-	
	sodium system	2
3.	Liquid ammonia as a solvent	7
4.	On the theory of the EPR and ENDOR spectroscopy	11
5.	On the theory of molecular orbital calculations	17
II	THE EXPERIMENTAL DETAILS	22
6.	The starting material and equipment	22
7.	The preparation of the radicals	24
8.	The measuring equipment	25
9.	The computer programs	26
III	RESULTS AND DISCUSSION	27
10.	On the kinetics of the solvated electrons and on	
	the formation of the $(NH_2)_2$ -radical	27
11.	The visible absorption spectra of the radicals	32
12.	The EPR spectra of the anion radicals	35
13.	The EPR spectra of the protonated anion radicals	42
14.	The ENDOR spectra recorded	55
15.	The molecular orbital calculations	59
	SUMMARY	69

REFERENCES

### I INTRODUCTION

## 1. The purpose of this study

Both solvated electrons and nitrogen containing heterocyclic compounds have been the subject of several investigations. The nature and the reactions of the solvated electrons have been studied with various theoretical and experimental methods<sup>1</sup>, and hitherto several conclusions has been reported. In this study the solvated electrons are investigated using electron paramagnetic resonance (EPR) spectroscopy and the main interest is directed to the kinetics of the decay of the solvated electrons in the liquid ammonia-sodium system. The nitrogen containing heterocyclic compounds are interesting not only due to their biological importance, but also due to their particular reactions in the liquid ammonia-sodium system<sup>2</sup>. The following compounds were selected for this work: pyridine, pyrazine, pyridazine, pyrimidine and s-triazine. Their structures are shown by Fig. 1.1.



Pyridine

Pyrazine

Pyridazine Pyrimidine

s-triazine

Fig. 1.1. The structures of the compounds under investigation.

Plenty of theoretical and experimental data about these compounds has been published, s-triazine being perhaps least investigated. The properties of the anion radicals of these compounds have been measured with various spectroscopic methods and the results usually have been in accordance. The aim during this study was also to test the suitability of liquid ammonia as a solvent in EPR and ENDOR measurements and to investigate the radical spectra of the nitrogen heterocyclic compounds in circumstances where both solvated electrons and protons are present in excess. The idea for this investigation arose during some hydrogenation experiments in liquid ammonia and was confirmed when some aromatic radicals were observed in the liquid ammonia-sodium system. Since the indentification of the

radicals can be aided by other spectroscopic methods than EPR or ENDOR, the visible absorption spectra of the radicals producing the EPR spectrum were measured immediately after the EPR measurements. The results obtained in this work are considered in the light of some semi-empirical molecular orbital calculation methods, viz. the INDO-method and the MINDO/3-method.

2. On the solvated electrons in the liquid ammonia-sodium system

According to the literature, the first one to dissolve sodium in liquid ammonia was Weyl<sup>3</sup>. The result was, as also observed later, a deep indigo coloured solution. The liquid ammonia-sodium solution is not the only one that exhibits solvated electrons but they are observed in many other systems<sup>4</sup>. This is why the liquid ammonia-sodium system is only a minor part of the wide field of the investigations of solvated electrons.

The alkali metal and ammonia solutions form a complex composition, which has led to the following division in relation to the metal concentration<sup>5</sup>:

- 1. Very dilute solutions (  $< 0.005 \text{ mole/dm}^3$ )
- 2. Relatively strong solutions ( 0.005 1.0 mole/dm<sup>3</sup>)
- 3. Strong solutions ( > 1.0 mole/dm<sup>3</sup>)

The classification is rather coarse, but explains the multitude of the models presented in the literature, since none of the theoretical considerations cover the whole concentration range. The formation of the solvated electrons from the alkali metal can be presented as follows<sup>6</sup>:

$$M \rightleftharpoons M^{+} + e^{-}$$
(2.1)

The following equilibria depict the behaviour of the alkali metals in liquid ammonia:

M <sup>+</sup> + e <sup>-</sup>	≓ M	(2.2)
M ≓ 1/2	<sup>M</sup> 2	(2.3)
e ≓ ≓ 1/2	(e <sub>2</sub> ) <sup>2-</sup>	(2.4)
M + e 🗧	$\rightarrow$ M <sup>-</sup> , where	
м+	is the alkali metal cation,	
М	is either an ion pair on expanded metal monomer,	
<sup>M</sup> 2	is either a four ion cluster or an expanded metal	

dimer, (e<sub>2</sub>)<sup>2-</sup> is an electron pair in solvent cavity, M is either alkali anion monomer or an ion pair (e<sup>-</sup>...M<sup>+</sup>...e<sup>-</sup>)

There is strong evidence for the existence of the alkali anions, but investigations have been carried out in strong concentrations  $^{7,8}$ . The alkali metal and ammonia solutions have been studied with almost every spectroscopic method. If we compare e.g. optical measurements, we notice that the spectra obey Beer's law in the defined concentration range. The absorption peaks are characterized by a symmetry and in particular by broadening at higher energies. The high pressure (>10 MPa) and the cation added to the solution result in a similar effect, but lower pressure (<10 MPa) and increase of temperature and concentration transfers the peak toward lower energies  $^{9-11}$ .

The EPR spectrum of the alkali metal and ammonia solution consists of a singlet whose line width depends on the metal, the concentration and the temperature. The EPR measurements of the solvated electrons were initiated by Hutchinson et al. and were thereafter performed by several groups 12-14.

From EPR spectra, it can be concluded that an unpaired electron exists in the alkali metal and ammonia solutions. The changes in the shape of the peak due to temperature and concentration changes seem normal phenomena, but the increase of the g-factor as the temperature is lowered is exceptional.

The relaxation times calculated from the EPR-spectra are almost equal and they are shortened as the concentration increases and prolonged as the temperature rises. According to the EPR measure-

ments and the electrical conductivity of the solutions, a rapid transfer of the electron from one state to another in the mutual equilibrium of the electron pair and the unpaired electron might take place, and this could explain the existence of the singlet. The disappearence of the blue color of the alkali metal-ammonia solution in the sealed ampoule and the return of the color with the UV exposure gives the reason to assume that a discharge and a charge of the excited state occurs 15-18. The transparent alkali metal-ammonia solution does not produce an EPR spectrum, either.

Several scientists agree that the electron is transferred between the states ls  $\rightarrow$  2p. The corresponding emission, however, has not been observed <sup>19,20</sup>.

In dilute solutions, the equilibrium (2.2) is valid, but Jolly has also observed the equilibrium <sup>21</sup>.  $NH_2^- + 1/2 H_2 \rightleftharpoons e^- + NH_3$  (2.6)

The reaction partly explains the disappearence of the solvated electrons. Saito has measured the decay of the solvated electrons with the EPR spectroscopy and reports the rate of the decay being  $3.3 \cdot 10^{-4} \text{ s}^{-1}$  in the dark conditions and  $1.5 \cdot 10^{-3} \text{ s}^{-1}$  in the light The amine radical  $NH_2$  has been studied both theoretically and spectroscopically. The coupling constants reported by McWeeny and Sutcliffe are for nitrogen 28.90 G and for protons 67.03 G  $^{23}$ . One of the most comprehensive and detailed theoretical models for the solvated electrons has been developed by Jortner et al.<sup>24</sup> The proceeding theoretical attempts include the works of Ogg  $^{25}$ , Land et al. <sup>26</sup> and Becker et al..<sup>27</sup> The model built up by Jortner et al. could be named as the cavity model, since it assumes that the electrons are in the cavity formed by ammonia molecules. The initial philosophy is based on the assumption, that the excess electron in polar or in nonpolar solvents can be either quasi-free or localized  $^{24}.$  The ground state energy  ${\tt E}_{\pi}$  of the system can be written in terms of two contributions: the electronic energy  $E_{\rho}$ and the medium rearrangement energy  ${\rm E}_{_{\rm M}}$  , so that

 $E_{T} = E_{e} + E_{M}$ (2.7)

The second term in Eq.(2.7) involves the structural modifications induced in the medium due to the presence of the excess electron, so that in general  $E_M \ge 0$ . The quasifree electron state can be described by a plane wave; which is scattered by the atoms or molecules constituting the dense liquid. Under these circumstances it is expected that the liquid structure is not perturbed by the presence of the excess electron, so that  $E_M = 0$ . The electronic energy of the quasifree electron state denoted by  $V_O$  is determined by a delicate balance between short-range repulsions and longrange polarization interactions, so that  $E_T$  (quasifree) =  $V_O$  (2.8)

The wavefunction for the excess electron tends to zero at large distances from the localization center. Since this involves the rearrangement of the liquid, it requires the investment of energy. It is convenient to specify the configuration of the system with a configurational coordinate R, which is the mean cavity radius. The total energy of the system can be written

$$E_{T}(R) = (localized) = E_{e}(R) + E_{M}(R)$$
(2.9)

The most stable configuration of the localized state is obtained by minimizing the total energy with respect to R:

$$\partial E_m(R) / \partial R = 0$$
 at  $R = R_0$  (2.10)

To assess the energetic stability of the localized excess electron state in liquid, one has to compare the energy of the localized state with that of the quasifree state. The general stability criterion for the localized state implies that,

$$E_{T}(R) < V_{O}$$
(2.11)

The electronic energy can be computed utilizing an electrostatic microscopic short-range attraction potential, a Landau-type potential for long-range interactions and a Wigner-Seitz potential for short-range repulsive interactions. The kinetic energy of the electron is also included. The medium rearrangement in polar solvents is a complicated phenomen and the following contributions to  ${\rm E}_{\rm M}$  have to be considered.

- 1. The energy needed to form a void in the liquid.
- 2. The volume pressure work.
- The long-range polarization energy of the medium required for the orientation of the permanent dipoles to form the potential well.
- The dipole-dipole repulsion between the oriented dipoles in the first coordination layer on the cavity boundary.
- Short-range repulsions between the reoriented solvent molecules on the cavity boundary.
- 6. The energy required for the rupture of hydrogen bonds.

The model can be described as a ball, where the electron is located in the center and around each electron is a small number, N, of symmetrically distributed solvent molecules which constitute the first solvation layer. In the computations, the number of N is usually 4, 6, 8 or 12.

Fig. 2.1. shows the model and the distances involved.



Fig. 2.1. Definitions of the distances involved in the cavity model.

The symbols are as follows:

r, is the void radius of the cavity,

- r is the effective solvent radius,
- $\tilde{a}$  is the effective hard core of the molecules located at a distance  $r_d$  from the centre of the cavity,
- ${\bf r}_{_{\rm C}}$  is the distance, where the continuum begins,
- R is the distance between the cavity center and the hard core of the solvent molecules.

Each of the N solvent molecules has a dipole moment, assumed to be at its center, is of finite size and has an isotropic polarizability.

The absorption peak computed using this model is predicted to be due to the transfer ls  $\rightarrow 2p$  and is symmetrical and temperature dependant. The number of ammonia molecules was 4 and the electronic energy was varied so that  $V_0 = 0.0, +0.5$  and -0.5 eV. The theoretical results, however, can not explain the breadth and the unsymmetry of the experimental spectra.

3. Liquid ammonia as a solvent

Liquid ammonia has been widely used as a solvent and as a reagent in numerous syntheses. Its reactions in various circumstances have been extensively rewieved by several authors  $^{28}$ ,  $^{29}$ . Liquid ammonia has been used as a solvent in IR, UV and EPR spectroscopy, but hitherto not in ENDOR spectroscopy.

It is understandable that the mechanisms involving syntheses in liquid ammonia are not agreed. This has led to competing schools of thought even in this narrow sector of chemistry. There are two major groups, which perhaps can be regarded as leading groups, viz., Hückel-Bretschneider  $^{30}$  and A.J. Birch schools  $^{31}$ . The aim in this work, however, was not to perform total syntheses with known methods, but to investigate the intermediate states of the protonation process. If we were to compare the method used here

to the known methods, it mostly resembles the Hückel-Bretschneider way to do the reduction. The other alternatives undoubtedly would give interesting results, too, if investigated e.g. with the method used in this study. The synthesis of the dihydropyridazine was attempted, but the yield was always the starting material, i.e. pyridazine. No reference was found in the literature to the hydro derivatives of the diazabenzenes being isolated as pure compounds. It can be concluded that the hydro derivatives immediately oxidize back to the starting material when exposed to air. Of course, the reduction in liquid ammonia-sodium system is usually performed in a nitrogen athmosphere. According to the present theories, the reduction may proceed in two different ways <sup>32</sup>, either by

- I the reversible addition of one electron to the substrate to give an anion radical which protonates to a radical capable of dimerising or of undergoing further addition of an electron and a proton, or
- II the reversible addition of two electrons to the substrate either simultaneously or consecutively to give a dianion capable of receiving two protons.

These reactions can be written in a general form as follows. The letter R denotes the substrate.

I<br/>R + e  $\rightarrow$  R.(3.1)2R. + 2H  $\rightarrow$  HR -----RH.(dimer)(3.2a)R. + H  $\rightarrow$  RH.(3.2b)RH. + e  $\rightarrow$  RH.(3.2b)RH. + e  $\rightarrow$  RH.(3.3)RH + H  $\rightarrow$  RH.(3.4)

$$\begin{array}{c} \text{II} \\ \text{R} + 2e^{-} \rightleftharpoons \text{R}^{2^{-}} \end{array} \tag{3.5} \\ \text{R}^{2^{-}} + 2\text{H}^{+} \rightleftharpoons \text{RH}_{2} \end{aligned} \tag{3.6}$$

Moorthy et al. have investigated the intermediate products of the reduction of pyrazine, pyridazine and pyrimidine with UV-spectrc-scopy  $^{33}$ . They performed the reduction radiolytically in the water with the presence of t-butanol.

The reduction of pyridazine is suggested to proceed in the following way:

$$e_{aq}^{-} + N = \left[ \begin{array}{c} & & \\ & &$$

$$\left[\begin{array}{c} & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

$$\left[ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

The radical ( N H had the absorption maximum at 265 nm. The radical anion of the pyrazine had the absorption maximum at 340 nm and the diprotonated cation radical of the pyrimidine at 240 nm and at 325 nm.

Based on the results to be presented later the reduction of some diazabenzenes in the liquid ammonia-sodium system may proceed in the following way:

Na  $\rightleftharpoons$  Na<sup>+</sup> + e<sup>-</sup> (3.10)

$$R + e^{-} \qquad \overrightarrow{R} \qquad (3.11)$$

$$2Na^{+} + 2NH_{3} + e^{-} \implies (NH_{2})_{2}^{-} + 2H^{+} + 2Na$$
 (3.12)

$$RH_2 + e^- \longrightarrow RH_2^-$$
 (3.16)

The protons required for the reductions process are but poorly available in ammonia due to the low self-ionization, but protonation frequently occurs because of the high basicity of the intermediate anion radicals. The limited self-ionization that ammonia can undergo is as follows:

$$\text{NH}_3 \qquad \qquad \text{H}^+ + \text{NH}_2 \quad \text{or} \qquad (3.17)$$

 $2NH_3 \qquad \qquad NH_4^+ + NH_2^- \qquad (3.18)$ 

Therefore, in liquid ammonia, ammonium salts are protonic acids, amides capable of giving rise to amide ions are bases, and substances capable of donating a proton to an ammonia molecule are acids. The auto-ionization has been shown to have a  $pK_a$  of 34 (at 240 K) and so for a substance to show markedly acidic properties in liquid ammonia, and for its salts to escape extensive solvolysis, the  $pK_a$  should be less than this value. Since the  $pK_a$  for the auto-ionization of water is approximately 14 it is clear that a large number of substances with  $pK_a$  values in the range 14-34 which do not behave as acids in aqueous solution will be capable of acidic behaviour in liquid ammonia <sup>34</sup>.

The reduction mechanism presented by equations (3.10) - (3.16)does not agree with the experimental results for the pyridine and pyrazine. Pyridine dimerizes to 4,4 -dipyridyl radical but pyrazine forms a very stable anion radical. The behaviour of the pyridine has been investigated in other reductive circumstances, too, and the dimerization has occurred in most cases. The behaviour of the pyražine can not be explained without the formation of the  $(NH_2)_2^{-}$  radical. The coupling constants of the pyrazine anion radical and the  $(NH_2)_2^{-}$  radical are partically the same  $^{77}$ .

The pK<sub>a</sub> value of pyrazine, pyridazine and pyrimidine in water are 0.65, 2.96 and 1.30, respectively <sup>35, 36</sup>. The pK<sub>a</sub> value of striazine is not known. All these substances show the acidic behaviour in liquid ammonia whose pK<sub>a</sub> is 34. The protonation or the non-protonation cannot, of course, be explained solely on the basis of the pK<sub>a</sub> values since the pK<sub>a</sub> values are determined in water and thus are not valid in liquid ammonia.

4. On the theory of the EPR and ENDOR spectroscopy

The electron paramagnetic resonance (EPR) investigation is the observation of the energy required to reverse the direction of an electron spin in the presence of a magnetic field. The electron possesses a magnetic moment by virtue of its spin, and in the presence of an applied field the two permitted orientations ( $\prec$  and  $\beta$ ) have different energies  $^{37}$ .

The apparatus therefore consists of a magnet capable of providing a homogenous field, a microwave source and a device for detecting whether the incident radiation is absorbed.

The EPR experiment is performed by maintaining a constant microwave frequency and sweeping the applied field until the coincident radiation is absorbed at this field. The sample must be paramagnetic and may be solid, liquid or gas. If the microwave frequency is  $\gamma$  then each photon carries the energy h $\gamma$ , and the applied field is  $\overline{H}$ . The resonance condition is given by Equation

 $h \nu = g \beta H$ , where

(4.1)

g is simply called a g-factor which takes into account the possibility that the local field is not exactly equal to H.

The structure of the EPR spectrum is due to the hyperfine interaction of the electron and the magnetic nuclei. A magnetic nucleus (such as a proton) gives rise to a local magnetic field which, depending on the relative orientation of the nuclear spin and the applied field can increase or decrease the local field experienced by the electron spin.

The EPR spectra are generally displayed in the first derivative form since this facilitates interpretation. The lines are separated from each other in terms of the magnetic field and the distances are expressed in Gauss although MHz would be preferable.

Presently, the EPR is a basic tool for analyzing the structure of radicals and the kinetics of radical reactions. The applications of EPR techniques are found in many areas ranging from technology to biological systems.

According to the nature of this work the theory of ENDOR spectroscopy is limited to the isotropic case, the radicals in solution.

This limitation simplifies the inspection in the following way:

- the g-factor and the hyperfine coupling constant of the compound are described by a scalar due to the rapid motion of the molecule,
- the Hamiltonian operator for the energy presentation is much simpler in the isotropic case than in the anisotropic case.

ENDOR is the abbreviation from the words <u>Electron Nuclear</u> Double Resonance. This means that during the experiment the sample is radiated with two frequencies, the microwave frequency and the radiofrequency. ENDOR is a combination of EPR and NMR <sup>38</sup>.

The first ENDOR measurement in the solid phase was carried out in 1959  $^{39}$ . It took, however, five more years until the first liquid phase measurement succeeded  $^{40}$ . The reasons were purely

technical. The development of high power radiofrequency amplifiers has solved the problem. Due to the shorter relaxation times in solution, more power is needed than in the solid phase.

The Hamiltonian operator can be expressed in general as follows

$$\hat{H} = \hat{H}_{0} + \hat{H}(t) + \hat{E}(t)$$
, where (4.2)

 $\widehat{H}_{o}$  is the time-independent part which defines the energy levels of the system and consequently the transition energies.

 $\widehat{H}(t)$  is the perturbation term describing the spin-lattice relaxation and thus the line widths of the spectrum.

 $\widetilde{E}\left(t\right)$  includes the interaction of the system with two resonance frequencies.

The time-independent part, the spin Hamiltonian operator is defined by equation

$$\widehat{H}_{o} = g \mathcal{B}_{e} \widehat{B}_{o} \widehat{S}_{z} - g_{n} \mathcal{B}_{n} \Sigma B_{o} \widehat{I}_{zi} + h A_{i} \widehat{S}_{z} \widehat{I}_{zi}, \qquad (4.3)$$

where h is Planck's constant,  $\beta_e$  is the Bohr magneton,  $\beta_n$  is the nuclear magneton,  $\hat{S}_z$  is the Z-component of the electron spin angular momentum,  $\hat{T}_z$  is the Z-component of the nuclear spin angular momentum and A is the hyperfine coupling constant.

In EPR the effective spin Hamiltonian consists of the interaction between the electron and the magnetic field and of the hyperfine coupling. ENDOR also takes the interaction between the nucleus and the magnetic field into consideration.

Fig. 4.1. shows the energy levels of a radical where the unpaired electron is coupled with four equivalent protons <sup>41</sup>.



Fig. 4.1. The energy levels and the EPR and ENDOR transitions in the case where the unpaired electron is coupled with four equivalent protons.

In the EPR experiment the sample is radiated with the fixed microwave frequency and the magnetic field is swept resulting in five equidistant lines with binomially distributed intensities. In the ENDOR experiment the sample is radiated with two frequencies, the microwave frequency is used to saturate the transition  $\Delta m_s = \pm 1, \Delta m_i = 0$  in the fixed magnetic field. Additionally, a radiofrequency field of varying frequency is applied saturating the NMR transitions  $\Delta m_i = \pm 1$  of the nuclei coupled to the unpaired electron. The results is that the EPR transitions are not saturated by the NMR transitions, provided that both transitions have energy levels in common. In a ENDOR spectrum, therefore, the enhanced EPR signal intensity is plotted against the NMR frequency, showing that ENDOR is a variant of NMR, the unpaired electron serving as the detector.

Because of the pumping of the microwave transitions and the quantum transformation from NMR to EPR, ENDOR is more sensitive than NMR by a factor of roughly  $10^5$ . Compared with EPR, however, one loses at

least a factor of 10. On the other hand, one gains in resolution because every group of equivalent nuclei, no matter how many nuclei are involved, contributes only 2 ENDOR lines due to the first order degeneracy of the NMR transitions within these groups for a given  $m_s$  state. This gain in resolution can be very drastic especially for low symmetry radicals. The 2 ENDOR lines are displayed for every nucleus in a radical (I =  $\pm$  1/2) at the following frequencies

 $\gamma$  ENDOR =  $\gamma_n + A/2$ , where (4.4)

 $\, \nu$  n is the nuclear Larmor frequency.

gation of other nuclei.

For the protons A/2 is generally smaller than  $\gamma_n$  so that both ENDOR lines are symmetrically displayed about  $\gamma_n$  and separated by A.

In principle, the ENDOR experiment can be applied to any magnetic nucleus (I  $\neq$  0) but the results strongly depend on the experimental conditions. The majority of ENDOR spectra published hitherto deal with the protons, but some other nuclei e.g. <sup>2</sup>H, <sup>14</sup>N, <sup>13</sup>C, <sup>19</sup>F are investigated, too <sup>42-47</sup>. The transitions of the proton and the fluorine nucleus are achieved with moderate radiofrequencies but for nuclei with a gyromagnetic ratio considerable smaller than that of protons, large NMR fields are to be expected. This has been a limiting factor in the investi-

Many manufacturers produce ENDOR accessories but working scientists have usually built or at least modified equipment for their own purposes.

As an example of an ENDOR spectrometer, Fig. 4.2. shows the block diagram of the equipment in Freie Universität, Berlin. It has been constructed by prof. Möbius and his co-workers  $^{48,49}$ .



Fig. 4.2. The block diagram of the ENDOR spectrometer in Freie Universität, Berlin.

The spectrometer operates with the continuous wave principle. The resonator is water-cooled due to the high NMR power. The first ENDOR equipment for the recording of liquid phase spectra operated with a pulsed wave in order to avoid overheating of the resonator.

In the spectrometer shown by Fig. 4.2. the fixed field is modulated with 280 Hz and the radiofrequency field is modulated with 20 kHz. Due to this phase sensitive detection the ENDOR lines are displayed as the first derivative form.

The development of multi resonance spectroscopy is in continuous progress. The ENDOR spectrometer is Freie Universität, for instance, can be applied to TRIPLE resonance investigations. This means the electron-nuclear-nuclear triple resonance. This experiment can be used to determine the relative signs of the coupling constants. Möbius et al. have published several TRIPLE experiments 50,51. In the future, the electron-èlectron-nuclear-nuclear quadruple resonance spectrometer may be possible. This would be a combination of ENDOR and ELDOR techniques which would result in the number of the nuclei producing the spectrum together with the coupling constants with relative signs 52.

5. On the theory of the molecular orbital calculations

In 1965 Pople, Santry and Segal published an important article considering the further development of quantum chemistry. They showed that if the ZDO approximation is employed to all valence electrons certain conditions must be met. These conditions deal with the independence of the resulting energies and the electron densities with respect to the choice of the co-ordinate axes and the hybridization base. A closer inspection of the methods presented in the article is subjected to the CNDO approximation 53,54. The earlier SCF calculations for the electron systems were dependant on the choice of the molecular axis. If the molecule were not symmetrical the results would heavily depend on the choice of the axes. This can be distinguished by looking at the typical two-electron integral in the ZDO approximation 55.

$$(p_A^2 + s_B^2) = \int p_A p_A dt_A \int s_B s_B dt_B$$
(5.1)

Suppose, that  $\mathbf{p}_{A}$  is directed along the vector in the xy-plane so that it can be divided into the components  $\mathbf{p}_{X_{A}}$  and  $\mathbf{p}_{Y_{A}}$  as follows:

$$p_{A} = \cos \theta p_{X_{A}} + \sin \theta p_{Y_{A}}$$
(5.2)

By inserting this into equation (5.1) the integral becomes

$$((\cos\theta p_{X_{A}} + \sin\theta p_{Y_{A}})^{2} | s_{B}^{2}) = \cos^{2}\theta (p_{X_{A}}^{2} | s_{B}^{2}) + \sin\theta (p_{Y_{A}}^{2} | s_{B}^{2}) + 2\sin\theta \cos\theta (p_{X_{A}}^{2} p_{Y_{A}}^{2} | s_{B}^{2})$$
(5.3)

The third integral in the right-hand side of (5.3) would be

neglected in the ZDO approximation since  $\mathbf{p}_X$  and  $\mathbf{p}_Y$  are orthogonal. Therefore, a requirement is presented

$$(p_A^2 | s_B^2) = \cos^2 \theta (p_{X_A}^2 | s_B^2) + \sin^2 \theta (p_{Y_A}^2 | s_B^2)$$
 (5.4)

If this equation is valid for all values of  $\boldsymbol{\theta}$  , the following equality must exist

$$(p_{X_{A}}^{2} | S_{B}^{2}) = (p_{Y_{A}}^{2} | S_{B}^{2}) = (p_{A}^{2} | S_{B}^{2})$$
 (5.5)

By expanding this argument it can be stated that the integral  $(p_A^2 \mid S_B^2)$  must be independant of the direction of the  $p_A$ -orbital. Since the combination  $(p_X^2 + p_Y^2 + p_Z^2)$  has a spherical symmetry it must be the same as  $(S_A^{'2} \mid S_B^2)$  where  $S_A^{'}$  is a spherical orbital with the same radical function as the  $p_A$ -orbital. If the hybridization invariance of the ZDO basis is required, then

$$(s_{\rm A}^{\prime 2} | s_{\rm B}^{2}) = (s_{\rm A}^{2} | s_{\rm B}^{2})$$
 (5.6)

The SCF approximation where all the integrals type ( $\mu\nu$  1/2 ) are not considered unless  $\mu = \nu$  and  $\rho = \sigma$ , is called the CNDO method (Complete Neglect of Differential Overlap). The elements in the Fock matrix in the CNDO method are calculated according to the following equations

$$F_{\mu\nu} = H_{\mu\nu} + P_{\rho\sigma} \left[ (\mu\nu)\rho\sigma' \right] - 1/2 (\mu\rho)\sigma' \right]$$
(5.7)

$$P_{\rho c} = 2 \sum_{i}^{\infty c} c \rho_{i} c \sigma_{i}$$
(5.8)

$$(u_{\mathcal{N}} \cup \mathcal{I}) = \iint \varphi_{\mathcal{N}}(1) \phi_{\mathcal{V}}(1) \frac{1}{\lambda_{12}} \phi_{\mathcal{N}}(2) \phi_{\mathcal{I}}(2) d\mathcal{T}_{1} d\mathcal{T}_{2}$$
(5.9)

 $F_{tttt} = 1/2 (I_{\mu t} + A_{\mu t}), I_{\mu} \text{ is the ionization potential,}$ (5.10)  $A_{\mu} \text{ is the electron affinity.}$ 

In their article Pople et al. presented a number of parameters for practical calculations. Later on they changed some of them. The present version of the CNDO method is called CNDO/2.

This method takes into consideration the electron-electron repulsion with the simpliest possible manner. Consequently, the phenomena between two electrons with parallel or opposite spins especially in the same atom are not handled. Since, due to the asymmetry of the wave function, the electrons with parallel spins can not occupy the same volume element, this leads to the fact that two electrons on the different orbitals of the same atom have a smaller average repulsion if they have parallel spins. This difference can be seen from the equation of the two-electron exchange integral

$$(\mu \nu \, \mu \nu) = \iint \phi_{\mu} (1) \phi_{\mu} (2) \, r_{12}^{-1} \phi_{\nu} (1) \phi_{\nu} (2) \, d\mathcal{I}_{1} \, d\mathcal{I}_{2}$$
(5.11)

where  $\oint \mu$  and  $\oint \gamma$  are on the same atom. These integrals are neglected in the CNDO method whatever the spins are. Dixon was the first to modify the CNDO theory in order to retain the one-electron exchange integrals. He called the modification EM2DO (Exchange Modified Zero Differential Overlap) <sup>56</sup>. When Pople's group made a similar modification, the method was given the name INDO. This name has remained <sup>57, 58</sup>. The INDO method retains all the one-electron repulsion integrals some of which might vanish due to symmetry. The elements in the Fock matrix have the forms

$$F_{\mu\mu} \stackrel{M}{=} U_{\mu\mu} + \sum_{\rho(M)} P_{\rho\sigma} \left[ (\mu^2 | \rho^2) - 1/2 (\mu c | \mu c) + \sum (P_{AA} - Z_A) \right] MA (5.12)$$

$$F_{\mu\nu} \stackrel{M}{=} 1/2 P_{\mu\nu} \left[ 3(\mu \mu | \nu) - (\mu \mu | \nu) \right] \mu \text{ and } \nu \text{ in the atom } M (5.13)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - 1/2 P_{\mu\nu} \mathcal{Y}_{MN}, \mu$$
 in the atom M and  $\nu$  in the atom N(5.14)

The one-electron repulsion integrals are usually defined by the Slater-Condon parameters. These are repulsion integrals after the integration of the angular coordinates. The non-vanishing integrals are of the form

$$(S(1SS)) = (pxpx | ss) = F^{o} = \lambda MM$$
 (5.15)

$$(s px | s px) = G^{1}/3$$
 (5.16)

$$(px py | px py) = 3F^2/25$$
 (5.17)

$$(px px | px px) = F^{0} + 4F^{2}/25$$
 (5.18)

(5.19)

 $(px px | py py) = F^{0} - 2F^{2}/25$ 

The Slater-Condon parameters  $F^{\circ}$ ,  $G^{1}$  and  $F^{2}$  are two-electron integrals. If a non-zero value is given for  $F^{2}$ , the mutual interaction of two electrons on different p-orbitals is then included.

The parameters  $G^1$  and  $F^2$  are determined semi-empirically whereas  $F^0$  can be calculated theoretically like Pople et al. have done or semi-empirically like e.g. Ohno and Klopman  $^{58}$ ,  $^{59}$ . The parametrization of the INDO method is very similar to the CNDO method, the main difference is the integrals  $F^2$  and  $G^1$  included in the INDO method.

Since the spin densities result from the INDO method, the isotropic hyperfine coupling constants can be calculated using the equation

$$a_N = K_N \cdot S$$
, where (20)

 $K_N$  is a constant specific to each magnetic nucleus N under consideration, and  $\zeta$  is the spin density associated with the valence s orbital of atom N <sup>60</sup>. There have been attempts to calculate  $K_N$  theoretically but the results have been unsatisfactory, nevertheless the conversion of the spin densities into the coupling constants is theoretically well established <sup>61</sup>. When a sufficient amount of experimental data is available,  $K_N$  may be evaluated by fitting a straight line  $a_N = f(\zeta)$ , where  $\zeta$  represents the calculated spin densities. The slope of the line is then  $K_N$ . In the INDO program, 141 experimental points have been used to evaluate  $K_N$  for the protons, the value of  $K_N$  being 539.86 G, whereas only 29 points were used to determine the  $K_N$  value for nitrogen <sup>62</sup> The INDO method suffers from the uncertainty of

nitrogen <sup>62</sup>. The INDO method suffers from the uncertainty of the conversion of the spin densities into the coupling constants, but increasing spectroscopic data will compensate for this.

Due to the fundamental difference in the philosophy concerning the semi-empirical calculations, Dewar and Baird made three modi-fications to the original INDO method <sup>63, 64</sup>.

These modifications involved

- the one-electron integrals which were now evaluated with the PNDO method developed by Dewar and Baird,
- the two-electron integrals which were evaluated according to the method of Ohno and Klopman,
- the resonance integrals which were evaluated using the ionization potentials.

The computer program used in the calculations was called MINDO/1. Intensive progress of the theory was carried out and as an intermediate result the improved computer program MINDO/2 was published. The principal theoretical improvement involved the core repulsion integrals  $^{65}$ .

Since the molecular properties strongly depend on geometry a Simplex-algorithm was added to the MINDO/2 program to be used in optimization of the molecular geometry. The optimization was made with respect to the pre-selected variables such as bond lengths and bond angles in order to minimize the heat of formation. The slowness and some disturbing features of the MINDO/2 program activated the further improvement of the theory and the program. In 1975 Dewar published a totally improved theory and the program MINDO/3. It was described as an end point of this theory. The parameters used in the program are results of the enormous amount of calculations where the energies of some standard molecules were minimized with respect to bond lengths and bond angles. The Slater exponents in the program. The values of the exponents used for instance in the INDO program. The values of the exponents are the results of several experimental calculations

Table 5.1. shows the values of Slater exponents used in MINDO/3 and INDO programs.

Element			MINDO/3	INDO
	n	ns	np	ns and np
Н	1	1.30000		1.2000
В	2	1.211156	0.972826	1.3000
С	2	1.739391	1.709645	1.625
N	2.	2.704546	1.870839	1.950
0	2	3.640575	2.168448	2.275
F	2	3.111270	1.419860	2.925
Si	3	1.629173	1.381721	1.383
Ρ	3	1.926108	1.590665	1.600
s	3	1.719480	1.403205	1.816
Cl	3	3.430887	1.627017	2.033

Table 5.1. The Slater exponents used in The MINDO/3 and INDO programs.

The MINDO/3 method evaluates the ground state energy of the molecule, the heat of formation, the dipole moment etc. In addition, the same quantities can be evaluated also for the anion and the cation radicals but not the spin densities. Lately a version of the MINDO/3 program capable of performing unrestricted Hartree-Fock calculations has been reported <sup>69</sup>. The program was not available for this study but is now obtainable from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, U.S,A.

### II THE EXPERIMENTAL PART

## 6. The starting material and equipment

The substances used as a starting material were prepared by Fluka AG and were purum grade reagents. Their purity was checked with the gas chromatograph Varian Autoprep 705 using the Se 30 solumn and diethyl ether as solvent. The ammonia used in the experiments was made by Merck AG and was 99.9 % pure. The purity of ammonia was checked with the mass spectrometer. The use of liquid ammonia as solvent sets certain requirements and limitations while preparing the samples. Since ammonia is a gas at room temperature (293 K) and at normal pressure it must be liquefied in the cold at 200 K. An ethanol bath was used and it was cooled with liquid nitrogen. The cuvettes had to be constructed with care in order to tolerate the pressure caused by ammonia at room temperature. The vapour pressure of liquid ammonia at 278 K is 1.2 MPa.

Fig. 6.1. shows the model of the cuvettes used in this work.



Fig. 6.1. The models of the EPR and the optical cuvettes used.

The other part of the cuvettes was bent in order to regulate the concentration. The optical part of the cuvettes was made from Pyrex glass which limits measurements to the visible region. A commercial quartz cuvette did not tolerate the pressure caused by ammonia at room temperature but exploded. The round cuvettes made from quartz glass were also unsuitable.

## 7. The preparation of the radicals

The leading of gaseous ammonia into the cuvette was carried out using the arrangements shown by Fig. 7.1.



Fig. 7.1. The system used in the preparation of the radicals.

One end of the cuvette was kept in the cold bath and during the preparation pure nitrogen gas was introduced into the cuvette (AGA Oy, 99.99 ...%). Next the gaseous ammonia was introduced and the amount liquefied was usually 2-3 cm<sup>3</sup>. After this, a freshly cut piece of sodium (about 1 mg) was added and when the sodium had dissolved, the sample substance was introduced. The upper end of the cuvette was sealed with a rubber cork and the lower end was cooled in liquid nitrogen. The cuvette was transferred to the high vacuum line and when the pressure was less than 10<sup>-5</sup> torr, the cuvette was sealed off. This order of the manipulations proved to be best because the formation of the radical very often could be seen immediately after adding the sample substance. Small amounts of hydrogen

are formed when sodium and ammonia react, but with this system it is possible to wait until the hydrogen has been removed. A coarse rule was that if the cuvette did not explode within two hours after preparation it would tolerate further on. Some exceptions, of course, appeared. The major advantage of this method for preparing EPR samples is that it is quite rapid. The average time taken to make a sample was about one hour.

#### 8. The measuring equipment

The measurements of the EPR spectra were performed with Varian E 12 and E 9 X-band spectrometers. The E 12 spectrometer was equipped with the temperature regulation unit and with the dual cavity E 231. The E 9 spectrometer was also equipped with the temperature regulation unit and with the field-frequency lock. Both during the measurements and the simulation of the spectra Varian 620/L computer was utilized connected primarily to the E 9 spectrometer.

The ENDOR spectra were measured in the Freie Universität Berlin in the department of molecular physics and in the department of the organic chemistry. The block diagram of the ENDOR spectrometer in the department of molecular physis is shown in Fig. 4.2, page 16. The spectrometer has been constructed from the accessories of several manufacturers. The magnets, the microwave source and the control board was made by Varian, the type was E 12. The NMR amplifiers was made by IFI, the type 404 A. The NMR oscillators were made by Hewlett-Packard and the resonator was selfmade, the type being  $TM_{110}$ .

The ENDOR spectrometer in the department of organic chemistry was AEG X-20. Both spectrometers were equipped with the temperature regulation units made by AEG.

The measurements of the visible spectra were performed using a Beckman DK-2A spectrophotometer.

The irradiation of the samples was done either with the UV lamp Philips 57413/40 MG or with a flash apparatus Metz Mecablitz, which had a flash duration of  $2 \cdot 10^{-3}$  s and a power of 130 J <sup>70</sup>. The EPR spectra were measured over a temperature range from 200 to 293 K using a 100 kHz modulation frequency. The g-values of

the radicals were determined using the pyrene anion radical as a standard. It has the g-value 2.002724  $^{71}$ . The irradiation of the radicals was performed either in the Dewar vessel or directly in the cavity after the cover plate was removed.

The kinetic measurements were aided by the Varian 620/L computer and by the software program 994002-B, which punched the spectra on to the paper tape for further operations.

#### 9. The computer programs

During this and earlier work the following programs from the Quantum Chemistry Program Exchange (QCPE) library were modified for the Univac 1108 computer  $^{72}$ :

QCPE	137	MINDO/1
QCPE	209	ESREXN
QCPE	250	ATCOOR
QCPE	249	VSS
QCPE	261	CNINDO
QCPE	261	CNINDO (for the calculation of the second row
		INDO calculations)
QCPE	246	MIEHM
QCPE	281	CNINDO (for the calculation of the NMR coupling
		constants)
QCPE	279	MINDO/3
QCPE	312	GEOMIN
		HUCKEL (from Heilbronner and Bock)

Except for the MINDO/3 program, all the others are stored in this order in the same magnetic tape in the library of the computing centre of the University of Helsinki. This nine track tape has the label U04825. The label of the tape containing the MINDO/3 program is U05955. The instructions to use the programs and the necessary instructions of the Univac 1108 EXEC-8 language are available at the department of physical chemistry, department of chemistry, University of Jyväskylä. The cartesian co-ordinates of the molecules were calculated with the QCPE 136 program  $^{73}$ , which is modified for the Honeywell 1644 time-sharing system with some additions<sup>74</sup>.

The molecular orbital calculations were performed with the QCPE programs 261, 279 and 312. The calculation was carried out in the remote batch environment with the Univac 1108 computer using the Honeywell 1644 computer as a terminal. The paper tapes produced by the Varian 620/L were handled with the Honeywell 1644 computer using the program made for this purpose. The program is named VARKIN and after reading the paper tape it calculates the first order rate constant using the least squares method.

## III RESULTS AND DISCUSSION

10. On the kinetics of the solvated electrons and on the formation of the  $(NH_2)_2$  radical

The sodium-ammonia sample in the EPR cuvette loses it's characteristic blue color in a relatively short time, if the sample is stored in the dark. The light sensitivity of the solvated electrons has gained more attention lately  $^{75}$ .

The sodium-ammonia sample becomes transparent and does not produce the EPR spectrum if the measurement is done in the darkness. A very small amount of light, however, is enough to produce the typical EPR spectrum, the narrow singlet, which disappears again in the darkness. The kinetic measurements were done under conditions, where the only external light was produced by the oscilloscope screen and by the control lamp in the microwave source of the spectrometer. In the first hand, the sample was given enough light that the signal of the solvated electrons could be observed. The system was locked to the maximum of the peak using the field-frequency lock and the field to be swept was set to zero. The dimension of the x-axis was then time. The total sweep time was given to the computer and when the sweep started the irradiation was performed directly to the sample in the cavity.

The increase of the peak and the following decrease were stored in the computer memory, from where they were punched onto paper tape. Fig. 10.1. shows a typical spectrum and explains the arrangement of the measurement.



Fig. 10.1. The measuring arrangement for the decay of the solvated electrons along with a typical spectrum.

The measurement were performed with three different sodium-ammonia solutions.

Solution

1. about 1 mg Na and 2 cm<sup>3</sup> NH<sub>3</sub> 2. "6"""""" 3. "15"""""" Further, the measurements were done at different temperatures in order to determine the possible activation energy. Since the decay of the solvated electrons proceeds through a long-lived triplet state  $^{76}$ , the reaction was calculated assuming first order kinetics. The equilibrium in Eg. (2.6), page 4 is assumed. The rate constant was calculated according to the equation:

 $k = 1/t \ln (Y_{max}/(Y_{max} - Y_{t})), \text{ where}$  (10.1)

t = the time in seconds  $Y_{max}$  = the maximum height of the peak  $Y_t$  = the height of the peak at time t

Table 10.1. shows the rate constants of the solutions 2 and 3 at various temperatures.

Table 10.1. The rate constants of the decay of the solvated electrons in two different sodium-ammonia solutions at various temperatures.

Solution 2

Solution 3

Т	(K)	the ra	ate	const.	(s	· <sup>_</sup> )	Т	(K)	the	rat <u>e</u>	const.	( ຣີ	⊥)

288	1.69.10-3	288	$1.05 \cdot 10^{-3}$
285	1.44.10-3	285	$7.94 \cdot 10^{-4}$
283	1.25.10-3	283	6.92·10 <sup>-4</sup>
280	1.00.10-3	280	5.62.10-4
277	9.33.10-4	277	4.78·10 <sup>-4</sup>

٦

Since the rate constant depends on the temperature, the activation energy can be calculated using the Arrhenius equation,  $k=A\cdot \exp(-E/RT)$ .

Table 10.2. shows the results for the solutions 2 and 3.

Table 10.2. The activation energies of the solvated electrons in two different sodium-ammonia solutions.

Solution	E kJ/mol
2	44
3	47

Solution 1 showed an exceptional behaviour. The spectrum due to the solvated electrons, however, was obtained momentarily and after that, the spectrum showed by Fig. 10.2.



Fig. 10.2. The EPR spectrum of a dilute sodium-ammonia solution at 295 K.

The coupling constants measured from the spectrum are presented in the Table 10.3. along with the coupling constants of the pyrazine anion radical.

Table 10.3. The coupling constants of the (NH<sub>2</sub>)<sup>2</sup> radical and the pyrazine anion radical at room temperature.

coupling constants (G)

(NH<sub>2</sub>)<sub>2</sub> Pyrazine

 $a_N = 7.25$   $a_N = 7.24$ 

$$a_{\rm H} = 2.70$$
  $a_{\rm H} = 2.72$ 

The possible existence of pyrazine as an impurity in ammonia was excluded with a mass spectrometer  $^{77}$ . No peak with the m/e value 80 appeared. The radical obtained and presumably having the formula  $(NH_2)_2$  also disappears in the dark. Its' kinetics was investigated in a similar manner to the kinetics of the solvated electrons.

Table 10.4. shows the rate constants at various temperatures.

Table 10.4. The rate constants of the decay of the (NH<sub>2</sub>)<sub>2</sub> radical at various temperatures.

temperature (K) rate constant (s<sup>-1</sup>)

296
 
$$2.08 \cdot 10^{-3}$$

 273
  $1.20 \cdot 10^{-3}$ 

 253
  $8.91 \cdot 10^{-4}$ 

The value of the activation energy is 16 kJ/mol. This radical has also been observed in another occasion during this work, namely after the formation of the pyridazine anion. The first stage of the reaction was the formation of the radical anion as presented on page 10, and after it had disappeared the radical  $(NH_2)_2^{-1}$  was formed and after its' decay the reaction proceeded, viz.
$$R + e^{-} \xrightarrow{R^{+}} R^{-}$$
  
2 Na<sup>+</sup> + 2NH<sub>3</sub> +  $e^{-} \xrightarrow{(NH_2)_2} + 2H^{+} + 2Na$  etc

According to the results, the formation of the  $(NH_2)_2$  radical mostly depends on the concentration of the sodium-ammonia solution because it could not be observed in the more concentrated solutions.

If the third substance is added to the solution, the rate of the formation and the decay of the  $(NH_2)_2$  radical are affected by the rate of the protonation, since the  $(NH_2)_2$  radical has an acidic function in the sodium-ammonia solutions.

11. The visible absorption spectra of the radicals

The visible absorption spectra of the radicals were measured at room temperature using the sodium-ammonia solution as a reference. The measurements suffered from the lack of temperature control, and the radical concentration altered during the measurement. This was caused due to the development of the heat affecting the evaporation of the ammonia and its' condensation to the cooler parts of the cuvette. No references have been found in the literature to the visible absorption spectra of the radicals under investigation in liquid ammonia. The reference spectra have been measured in other solvents. Dodd et al. have measured the absorption spectra of the pyridine anion, the pyrazine anion, the pyridazine anion and the pyrimidine anion both in the visible and in the UV regions  $^{78}$ . The radicals were prepared by sodium reduction using tetrahydrofuran as a solvent. Their results in the visible region along with the results obtained in this work are presented in the Table 11.1.

Table 11.1. The absorption maxima of some nitrogen heterocyclic radical anions.

The absorption maxima (nm)

anion	Dodd et al.	this work
pyrazine	364	370
pyridazine	351	350
pyrimidine	330	-
4.4'-dipyridyl	335	340

The true absorption spectrum of the pyrimidine radical anion was not obtained in this work due to the rapid protonation of the radical.

In addition, the absorption spectra of the protonated species of the pyrimidine, pyridazine and s-triazine were measured. The measurements were always carried out immediately after the measurement of the EPR spectrum in order to conserve the radical producing the EPR spectrum.

Fig. 11.1. shows the absorption spectra of the protonated forms of pyrimidine, pyridazine and s-triazine and their absorption maxima are presented in the Table 11.2.



Fig. 11.1. The absorption spectra of the protonated radical forms of pyrimidine, pyridazine and s-triazine in the sodium-ammonia solution.

Table 11.2. The absorption maxima of the protonated radical forms of pyrimidine, pyridazine and s-triazine in sodiumammonia solution.

radical	absorption maxima (nm)
pyrimidine -H2+	482 and 510
pyridazine -H2.	440
pyridazine -H2.	342
s-triazine -H2	342

The protonated radical form of pyrimidine always showed two maxima which gives reason to suggest that more than one species exists in the sample. This may also be due to the formation of an ion pair. The existence of more than one radical is also supported by the EPR spectrum. The protonated radical form of pyrimidine was pink by the color.

The protonated radical form of s-triazine showed only one absorption maximum.

Two different protonated radical forms are exhibited by pyridazine. Their absorption spectra clearly differ which is inherent in the structural changes in the course of the protonation reaction.

12. The EPR spectra of the anion radicals

The compounds showing the EPR spectra of the anion radicals conststent with the literature were pyrazine, pyridazine, pyridine and 4,4'-dipyridyl  $^{79-86}. \label{eq:compound}$ 

Fig. 12.1. shows the EPR spectrum of the pyrazine anion radical along with the simulated spectrum. The hyperfine coupling constants are presented in the Table 12.1.

Table 12.1. The hyperfine coupling constants (HFC) of the pyrazine anion radical.

nucleus	HFC (G) <sup>≭</sup>	4
<sup>5</sup> a <sub>N</sub> (1,4)	7.24	6 NL 2
<sup>5</sup> a <sub>H</sub> (2,3,5,6)	2.72	5 N 3



Fig. 12.1. The EPR spectrum of the pyrazine anion radical at 223 K (upper) along with the simulated spectrum.

concentration was observed, but the suitable concentration for the measurement could be adjusted.

The anion radical of pyridazine is not stable in the sodiumammonia system but protonates although fairly slowly. Fig. 12.2. shows the EPR spectrum of the pyridazine anion radical along with the simulated spectrum. The hyperfine coupling constants are presented in Table 12.2.

Table 12.2. The hyperfine coupling constants of the pyridazine anion radical.

nucleus HFC (G)

<sup>5</sup>a<sub>N</sub> (1,2) 6.00

<sup>3</sup>a<sub>H</sub> (4,5) 6.41

<sup>3</sup>a<sub>H</sub> (3,6) 0.08



The values of the coupling constants slightly differ from the values presented by Stone and Maki<sup>81</sup>. They also stated that the radical is unstable. The assignment of the coupling constants is based on results of Stone and Maki. The line width alteration due to temperature could not be measured because of instability.

Both the EPR spectrum of the 4,4'-dipyridyl anion radical and the pyridine anion radical were obtained from pyridine in this order. Fig. 12.3. shows the EPR spectrum of the 4,4'-dipyridyl anion radical along with the simulated spectrum. The hyperfine coupling constants are presented in the Table 12.3. The assignment of the coupling constants is based on the results of Ward <sup>83</sup>.



Fig. 12.2. The EPR spectrum of the pyridazine anion radical at 240 K (upper) along with the simulated spectrum.

Table 12.3. The hyperfine coupling constants of the 4,4'-dipyridyl anion radical.



The anion radical of 4,4'-dipyridyl proved to be stable except under irradiation with UV-light. The irradiation produced the radical anion of pyridine whose spectrum is shown by Fig. 12.4. along with the simulated spectrum. The hyperfine coupling constants are presented in the Table 12.4.

Table 12.4. The hyperfine coupling constants of the pyridine anion radical.

3:55

nucleus HFC (G)

- <sup>3</sup>a<sub>N</sub>(1) 6.31
- <sup>3</sup>a<sub>H</sub>(3,5)
- <sup>3</sup>a<sub>H</sub>(2,6) 0.70

<sup>2</sup>a<sub>H</sub>(4) 9.63

The coupling constants of the pyridine anion radical are consistent with values presented in the literature  $^{82,84}$ . The assignment of the coupling constants is based on the results presented in the reference 84. The radical obtained by the irradiation vanished quite rapidly as can be seen from the decreasing intensities in the spectrum. The radical anion of 4,4'-dipyridyl appeared



Fig. 12.3. The EPR spectrum of the 4,4'-dipyridyl anion radical at 223 K (upper) along with the simulated spectrum.



Fig. 12.4. The EPR spectrum of the pyridine anion radical at 233 K (upper) along with the simulated spectrum.

after it. The peak due to the solvated electrons was not observed in either spectra though exposed to UV-light.

The radical anion of pyrimidine corresponding to the spectra published was not obtained. The anion stage of pyrimidine must be so short that it can not be measured using the methods in this work. The same conclusion can be made in the case of s-triazine, no anion radical was observed. The literature, however, does not give any information about the anion radical of s-triazine which supports its' instability.

13. The EPR spectra of the protonated anion radicals

When the radical is made in the sodium-ammonia system, it gives reasons for the argument, that the protonated radicals formed are anions by their electronic structure and not cations although they may have a positive charge. Based on the model on page 10 the first stage of the reaction is the formation of the anion radical. If the formation of the  $(NH_2)_2^-$  -radical is now excluded, the progress of the reaction can be followed. The most concrete substance in this sense was pyridazine because its' protonation was partially so slow that some stages could be measured.

Fig. 13.1. shows the EPR spectrum of the diprotonated pyridazine anion radical along with the simulated spectrum. The hyperfine coupling constants are presented in Table 13.1.

Table 13.1. The hyperfine coupling constants of the diprotonated pyridazine anion radical

4.20

0.25

0.75

4.45

nucleus HFC (G) <sup>5</sup>a<sub>N</sub>(1,2) <sup>3</sup>a<sub>u</sub>(3,6)  $^{3}a_{1}(4,5)$ <sup>3</sup>a<sub>u</sub>(1',2')





Fig. 13.1. The EPR spectrum of the diprotonated pyridazine anion radical at 223 K (upper) along with the simulated spectrum.

Compared with the anion of pyridazine one proton triplet coupling has appeared and the coupling constant of the nitrogens has markedly diminished. The assignment of the coupling constants is based on the theoretical calculations. Although the results are quite poor, the order of the magnitude of the coupling constants can be cstablished.

Zeldes and Livingston have prepared the cation radical of the 1,2dihydropyridazine photolytically in acetone-isopropanol solution <sup>87</sup>. They report the following coupling constants for the cation radical of the 1,2-dihydropyridazine:

 ${}^{5}a_{N}^{}(1,2)$  7.81 G,  ${}^{3}a_{H}^{}(3,6)$  - 0.92 G,  ${}^{3}a_{H}^{}(4,5)$  - 5.80 G and

<sup>3</sup>a<sub>u</sub>(1',2') - 6.53 G.

These values differ clearly from the values obtained in this work. Depending on the amount of the solvated electrons the diprotonated anion of pyridazine either remains in this stage or reacts further. If an excess of the solvated electrons is present the reaction proceeds to the end as presented on page 10.

This diprotonated anion of pyridazine was also prepared in lithiumammonia solution and the EPR spectrum obtained was identical to the spectrum in Fig. 13.1.

The third alternative approach to the matter is to try an electrolytical preparation of the diprotonated anion radical of pyridazine. The electrolysis was carried out in the following way: about 3 mm of pyridazine in the glass capillary tube was transferred to the cuvette. Then 66 mg of tetrabutylammoniumperchlorate, 1.5 cm<sup>3</sup> acetonitrile and a small amount of Al<sub>2</sub>O<sub>3</sub> was added. The anode was a platinum wire and the cathode was platinum gauze. The voltage was 3 Volts, but the current could not be measured due to technical reasons. A red wine colored radical was obtained giving the EPR spectrum shown by Fig. 13.2. along with the simulated spectrum. The hyperfine coupling constants are presented in Table 13.2.

The radical formed was very unstable, which can be seen from the decreasing intensities. The interpretation was rendered difficult due to the relatively large noise in the spectrum.



Fig. 13.2. The EPR spectrum of the diprotonated pyridazine radical produced by the electrolysis at 223 K (upper) along with the simulated spectrum.

Table 13.2. The hyperfine coupling constants of the diprotonated pyridazine radical produced by electrolysis.



The coupling constants are not the same as with the radicals obtained in sodium-ammonia and lithium-ammonia solutions, but according to the formation, the radical is very probably the same. The electrolytical preparation may proceed as follows:

R	+	H+	RH <sup>+</sup>	(13.1)
rh+	+	$H^+$	$\mathbb{RH}_2^{2+}$	(13.2)
RН2-	++	e <sup>–</sup>	RH <sup>+</sup> <sub>2</sub>	(13.3)

This diprotonated anion of pyridazine does not form via the anion formation of pyridazine, but the final results presumably are equal by their structure.

It has been stated earlier that if solvated electrons are present in excess in the sodium-ammonia solution the reaction proceeds from the diprotonated anion stage to the end. Finally, the dihydropyridazine anion radical is obtained. To avoid the confusion it is better to distinguish the dihydro and the diprotonated species from each other. This will be explained later. The EPR spectrum of the dihydropyridazine anion radical is depicted in Fig. 13.3. along with the simulated spectrum. Table 13.3. shows the hyperfine coupling constants derived from the spectrum.



Fig. 13.3. The EPR spectrum of the dihydropyridazine anion radical at 223 K (upper) along with the simulated spectrum.

Table 13.3. The hyperfine coupling constants of the dihydropyridazine anion radical.





Compared with the diprotonated pyridazine anion, the number of the nuclei has remained the same in the dihydropyridazine anion but the coupling constants have changed. The assignment of the coupling constants is really uncertain in this case, because it is not supported even by the theoretical calculations. To give reasons for the fact that the both radicals are anions, the situation can be examined in the light of a simple energy level description.

R + e		R	<u> </u>
			the anion radical
	$\rightleftharpoons$	RH.	no changes
RH° + H <sup>+</sup>	<u></u>	RH <sup>+</sup> <sub>2</sub>	no changes
			the diprotonated anion



The reaction proceeds to the dihydropyridazine anion form providing that a sufficient amount of solvated electrons are present. Such a sample in the sodium-ammonia system was prepared which, due to the lack of solvated electrons, remained at the diprotonated anion stage. The sample was put into the EPR spectrometer and in order to get the reaction to proceed, a flash irradiation was used. At first a straight line was recorded by the spectrometer which might refer to the formation of the neutral dihydropyridazine. When the irradiation was continued the spectrum of the dihydropyridazine anion radical shown in Fig.13.3. was recorded. This reaction was reversible, for when the irradiation was ceased the EPR spectrum of the diprotonated pyridazine anion radical could be observed. It can be concluded that the hydration is sensitive to the amount of the solvated electrons. The energetic inspection was not possible since the irradiation was made with mixed wavelengths of light. Pyrimidine reacted in the sodiumammonia system to give the diprotonated anion radical only. The reaction proceeds so rapidly to this stage that the intermediates could not be measured with the EPR spectrometer. Even slow increase of the temperature when the ammonia was still frozen at 180 K and then turned to liquid at 200 K did not help. The reaction had already taken place. The EPR spectrum obtained from the diprotonated pyrimidine anion radical is shown in Fig.13.4. both in the 40 Gauss and in the 10 Gauss scale.

The values of the coupling constants presented in the literature for the pyrimidine anion radical and for the dihydropyrimidine cation radical are not in agreement with the values obtained from this spectrum  $^{87-89}$ . The interpretation of the spectrum is not unambiguous because there is probably a very stable ion pair between the diprotonated pyrimidine anion and the Na<sup>+</sup> -ion. The hyperfine coupling constants obtained from the ENDOR spectrum are presented in Table 13.4. Based on the ENDOR spectrum one coupling seems to be missing.

Table 13.4. The hyperfine coupling constants of the diprotonated pyrimidine anion radical.

17DO (0)

nucleus	HFC (G)		
<sup>5</sup> a <sub>N</sub> (1,3)	3.110		
<sup>3</sup> a <sub>H</sub> (4,6)	1.590		6
<sup>2</sup> a <sub>H</sub> (5)	1.770		5
<sup>2</sup> a <sub>H</sub> (2)	0.045		
<sup>3</sup> a <sub>H</sub> (1', 3')	4.80	(EPR)	

The coupling constants of 4.80 G is not present in the ENDOR spectrum but in the EPR spectrum. The simulated spectrum of the diprotonated pyrimidine anion radical calculated with the values in the Table 13.4. is shown by Fig. 13.5.

If pyrimidine in the sodium-ammonia system produces a mixture of the radicals, only one can be detected with the ENDOR spectrometer but both are seen in the EPR spectrum, as a mixture, unfortunately. The assignment of the coupling constants is uncertain due to the unreliability of the theoretical considerations.



Fig. 13.4. The EPR spectrum of the diprotonated pyrimidine anion radical aL 240 K in the 40 Gauss (upper) and in the 10 Gauss scale.



Fig. 13.5. The simulated spectrum of the diprotonated pyrimidine anion radical using the coupling constants in the Table 13.4.

S-triazine showed quite similar behaviour as pyrimidine, only one EPR spectrum was obtained. The spectrum is not due to the anion radical of s-triazine but due to the diprotonated anion. The EPR spectrum is shown by Fig. 13.6. along with the simulated spectrum.

The hyperfine coupling constant are presented in the Table 13.5.

Table 13.5. The hyperfine coupling constants of the diprotonated s-triazine anion radical.



<sup>5</sup>a<sub>N</sub>(1,3) 3.43

<sup>3</sup>a<sub>N</sub>(5) 0.51

- <sup>3</sup>a<sub>H</sub>(4,6) 1.02
- <sup>3</sup>a<sub>µ</sub>(1', 3') 1.53

<sup>2</sup>a<sub>H</sub>(2) ~

The proton coupling in position 2 can not be seen in the EPR spectrum thus it must be outside the detection limits of the spectrometer. Based on the interpretation and on the simulation of the spectrum it looks like two protons are joined with the s-triazine. The third proton addition was not observed. No literature references are found concerning the anion, cation or the diprotonated radicals of s-triazine in any solvent. The assignment of the two proton couplings is uncertain. Although the diprotonated s-triazine anion radical was stable towards external irradiation, some reaction unobservable by the EPR spectrometer proceeded in the cuvette because the samples without exception exploded within three weeks of preparation.

The phenomenon might be partially explained by the use of s-triazine in the explosives industry 90.

One way to identify the radicals is their g-values. Some g-values measured during this work are collected in Table 13.7. In solution the g-values of the different radicals do not vary very much but the differences are distinctive.



Fig. 13.6. The EPR spectrum of the diprotonated s-triazine anion radical at 240 K (upper) along with the simulated spectrum.

Table 13.7. The g-values of some radicals in sodium-ammonia solution.

radical	g-value
pyrazine anion	2.00360
pyridazine anion	2.00350
diprotonated pyrimidine anion	2.00278
diprptonated pyridazine anion	2.00344
diprotonated s-triazine anion	2.00333
dihydropyridazine anion	2.00320

14. The ENDOR spectra recorded

According to the literature only a few  $^{14}$ N ENDOR experiments are performed in solution  $^{91,92}$ . The nuclear frequencies of the nitrogen and the proton in the same magnetic field differ so markedly that the coupling of the nitrogen can hardly be seen simultaneously with the protons.

Another important requirement for the succesful ENDOR experiment is the enchancement of radiofrequency field especially in the case of nitrogen. When using liquid ammonia as a solvent, the anisotropy of the nitrogen can not be much larger than that of the protons because the signals of the nitrogen could be observed simultaneously with the protons in the same ENDOR spectrum. Figs. 14.1, 14.2 and 14.3. show the ENDOR spectra of the pyrazine anion, the 4,4' -dipyridyl anion and the diprotonated pyrimidine anion at 210 K, respectively. The coupling constants are presented in the Table 14.1.



Fig. 14.1. The ENDOR spectrum of the pyrazine anion at 210 K.





56



Fig. 14.3. The ENDOR spectrum of the diprotonated pyrimidine anion at 210 K.

Table 14.1.	The hyperfine coupling constants of	the pyrazine
	anion, the 4,4 -dipyridyl anion and	the diproton-
	ated pyrimidine anion.	
radical	HFC (MHz)	HFC (G)
nvrazine anio	n	
pyruzine unit	511	
-		
<sup>5</sup> a <sub>N</sub>	20.286	7.245
5	7 614	2 719
ан	/:014	2.715
A A' 2'	1	
4,4 -dipyrid	yl anion	
<sup>5</sup> a,	10.135	3.620
IN		
5		
а <sub>н</sub>	6./40	2.407
5 <sub>a</sub>	1.340	0.479
H		
diprotonated		
arproconacca	nion	
pyrimidine a		
_		
<sup>5</sup> a <sub>N</sub>	8.708	3.110
3	4 452	1 500
а <sub>н</sub>	4.452	1.590
2 <sub>a,,</sub>	4.956	1.770
п		
2	0.100	0.045
a <sub>H</sub>	0.126	0.045

 ${}^{3}a_{\overset{}_{H}}$  (in nitrogens) not detected

In all cases the coupling of the nitrogen can be observed in the high frequency part. In addition, the  $B_{NMR}^{eff}$  required was very small, in the of the diprotonated pyrimidine anion about 40 W, which only is 1/10th of the normal requirement in solution. The microwave power used was also reasonable, only about 1,5 mW. Both the values of pyrazine anion and the 4,4'-dipyridyl anion correspond to the values obtained with the EPR. One coupling, however, seems to be missing in the ENDOR spectrum of the diprotonated pyrimidine anion. This coupling was not found above 16.8 MHz although searched. The coupling of the sodium remain undetectable, too. Due to the technical limitations as well as due to the time limitations the ENDOR spectra of the other radicals could not be measured. The theoretical inspections of the experimental results is difficult without additional experiments. The main attention was paid to the suitability of the ammonia as the solvent for the ENDOR experiments. Also, the coupling constants were of more interest than the relaxation systems. The situation would have been enlighted by TRIPLE resonance measurements because the relative signs of the coupling constants would have been characterized. The liquid ammonia, however, proved to be a good solvent for the ENDOR experiments in order to simultaneously investigate the couplings of the nitrogens and the protons in the solution because the  $B_{\mbox{NMR}}^{\mbox{eff}}$  to be used is rather small and not much microwave power is required to saturate the EPR line.

## 15. The molecular orbital calculations

The molecules under investigation in this work are widely used as "test molecules" when developing the molecular orbital theory and its' methods of calculation 93-99. Therefore some of the results presented here were previously published. The principal attention has been paid to the structural inspection of the neutral and radical hydro forms of pyridazine. The structural investigation has been made with the aid of the MINDO/3 program. The coupling constants are calculated using the INDO program together with the energy minimizing version of it, called GEOMIN. No special features are included in the calculations, e.g. the solvent effect is neglected. The input data for all the programs consists of the structural information of the molecules, the bond lengths, the bond angles and the dihedral angles <sup>100-104</sup>. The INDO program reads this data in the form of the cartesian coordinates whereas the MINDO/3 program automatically calculates the coordinates. Although the bond lengths and the bond angles of some molecules are known from X-ray data they were only seldom utilized to establish the initial structural guess since this led to undesired unsymmetry, which reflected e.g. in the values of the calculated coupling constants. The mutual stability of the molecules can be compared with the MINDO/3 method. Tjebbes has experimentally determined the heats of formation of pyrazine, pyridazine and pyrimidine. The experimental heat of formation of pyridine has been taken from Ref. 68.

Table 15.1. shows the experimental and the calculated heats of formation of the compounds under investigation.

Table 15.1. The heats of formation of pyridine, pyrazine, pyridazine, pyrimidine and s-triazine, kcal/mol (kJ/mol).

compound	experimental	calcd. (MINDO/3)
pyridine	34.1 (142.7)	35.4 (148.2)
pyrazine	46.9 (196.3)	42.5 (177.9)
pyridazine	66.5 (278.4)	25.1 (105.1)
pyrimidine	47.0 (196.7)	36.8 (154.0)
s-triazine	not found	34.5 (144.4)

Except in the case of pyridazine, the experimental and the calculated results are in good agreement. According to the calculations pyridazine is the most stable molecule whereas the experimental results show the opposite order. Table 15.2. shows some calculated and experimental bond lengths and bond angles for these molecules. The planar structure was assumed in the calculations.

Table 15.2.	Some experimental and calculated bond lengths and
	bond angles of pyridine, pyrazine, pyridazine,
	pyrimidine and s-triazine.

compound	bond	bond len	gth (nm)	angle	bond an	gle ( <sup>0</sup> )
		exptl.	calc.		exptl.	calc.
pyridine	CN	0.1340	0.1333	CCN	123.1	119.3
	$C_2C_3$	0.1395	0.1404	CCC	118.5	119.2
	$C_3C_4$	0.1394	0.1394	CCH	121.8	120.5
	C <sub>2</sub> H	0.1084	0.1101			
	С <sub>4</sub> Н	0.1077	0.1101			
pyrazine	CN	0.1334	0.1334	CCN	122.4	119.6
	CC	0.1378	0.1406	CNC	115.1	120.7
	СН	0.1105	0.1112	CCH	120.3	122.7
pyridazine	CN	_	0.1387	CCN	119.0	114.0
	$C_1C_2$		0.1396	$C_1 C_2 C_3$	117.3	120.5
	$C_3C_4$		0.1402	CCH		121.9
	NN		0.1214			
	СН		0.1111			
pyrimidine	C <sub>1</sub> N <sub>2</sub>	0.1315	0.1329	CNC	115.1	115.4
	N <sub>2</sub> C <sub>3</sub>	0.1337	0.1338	NCC	122.5	122.8
	$C_3C_4$	0.1373	0.1414	CCC	116.3	128.1
	CH	663	0.1108	CCH		118.6
s-triazine	CN	0.1338	0.1326	CNC	127.0	119.9
	CH		0.1124	NCH	204	119.0

The common feature of the MINDO/3 method seems be the tendency to over estimate the aromatic CH-bonds.

The structural optimization of the dihydro forms of pyridazine may be justifiably uncertain because no experimental results are available. On the other hand, such situations cannot even be inspected without sophisticated computer programs. Since the protons are joined with the nitrogens, this may lead to the nonplanar structure of dihydro pyridazine. Further, the protons may be either in cis, cis-positions or in cis, trans-positions.

The optimum structures with respect to the heat of formation were sought for the neutral molecules whose coordinates were employed in the calculation of the radical forms. The results of the calculations are collected in Table 15.3.

Based on the calculations, the non-planar structure with the protons in cis, cis-positions seems favorable. The energy differences between the structures are not large and when calculating the optimum structures of the dihydro anion radicals the results were as follows:



the heat of formation 54.7 kcal/mol (229.0 kJ/mol)

the heat of formation 55.5 kcal/mol (232.3 kJ/mol)

The energy difference is only 0.8 kcal/mol (3.3 kJ/mol) but now favoring the cis, trans-position of the protons. In addition, the heat of formation of the neutral monohydro pyridazine was calculated giving 51.2 kcal/mol (214.3 kJ/mol).

63

Table 15.3. The calculated structural parameters of the dihydroforms of pyridazine.



x) the dotted line refers to the molecular plane

The calculated heat of formation of the diprotonated pyridazine cation radical was 194.9 kcal/mol (815.8 kJ/mol). This is not in agreement with the proceeding of the reaction. The problem during the calculation is that it is not possible to calculate the positively charged radical with the anion structure. The initial situation may be described as follows:



The energy order of the reactions, however, is supported by the results obtained with the GEOMIN program. The energies are calculated for the underlined species shown below.

)

the reaction st	ages	energy (A.U.
R + e 🛁	R.,	- 52.3940
$R^{-} + H^{+} \longleftarrow$	RH	- 53.2715
RH + H +	+ 	- 53.8422
$RH_2 + e \rightarrow$	RH <sub>2</sub>	- 54.0355
RH <sub>2</sub> + e →	RH <sub>2</sub> .	- 53.9222

When calculating the structures were assumed to be planar though this may not be the case according to the results obtained with the MINDO/3 method. The reason for the use of the planar structures was the immoderate results obtained for the calculated hyperfine coupling constants using the nonplanar structures. Especially the coupling constants of the protons bonded to the nitrogens were too large if the deviation from the planarity was assumed in the calculation. Joela and Pyykkö <sup>106</sup> have investigated this weakness of the INDO method and stated that if the orbital energies go to the wrong order during the Extended Hückel type initial guess used in the INDO method they remain in the wrong order in the course of the SCF iteration cycles. Consequently, the total wave function has the wrong symmetry to the end of the calculation. The tracing of the right orbital energies was attempted, but the results did not improve. The reason may be due to the unsuitability of the tracing method for the nitrogen containing systems, since the method was originally developed for the hydrocarbons. As an example the calculated coupling constants of the nitrogens and the protons bonded with them in the case of the dihydro pyridazine anion are presented for the planar and for the non-planar structures:

nucleus

HFC (G)

	planar	non-planar
N	0.44	23.7
H (in N)	- 1.48	33.2

Table 15.4. shows the calculated hyperfine coupling constants of the pyridazine anion and its' hydroform radicals.

Since the minimization of the total energy did not bring any essential improvement for the values of the coupling constants, the rest of the calculations were performed without energy minimization. The results of the calculations are presented in the Table 15.5.

Table 15.4. The calculated hyperfine coupling constants obtained with the GEOMIN program for the pyridazine anion and for the mono- and dihydro pyridazine radicals.



Table 15.5. The calculated hyperfine coupling constants of the pyridine coupling constants of the pyridine anion, the 4,4'-dipyridyl anion, the diprotonated pyrimidine anion, the diprotonated s-triazine anion and the pyrazine anion.

radical	position	HFC (G) calculated
	1 2 3 4	7.50 3.55 0.17 9.87
$\left[ \sqrt{2} + \sqrt{2}$	2 3 4	1.82 0.78 3.90
$ \begin{bmatrix} H \\ 1 \\ 0 \\ 5 \\ 4 \end{bmatrix} $	1,3 (N) 1,3 (H) 2 5 4,6	2.00 - 3.75 1.01 4.04 - 11.99
$\left(\begin{array}{c} 5\\ 4\\ 1\\ 3\\ 1\\ 1\\ 1\\ 2\end{array}\right)^{1}$	1,3 (N) 5 (N) 1,3 (H) 6,4 2	4.89 7.49 6.88 8.28 3.20
$\left[\begin{array}{c} 1 \\ 1 \\ 2 \\ 5 \\ \mathbf{N} \\ 4 \\ 3 \\ 3 \\ 1 \\ $	1,4 2,3,5,6	7.21 2.64 (taken from ref. 80)

The results are satisfactory for the anions but not so good for the hydro form radicals.
The heat of formation of  $(NH_2)_2$  -radical according to the MINDO/3 calculations was 33.2 kcal/mol (139.0 kJ/mol) which shows the radical to be as stable as the compounds under investigation in their ground state. This would explain the formation of the  $(NH_2)_2$  -radical before the protonation process as in the case of pyridazine. The radical was not observed with the other compounds. The calculated coupling constants of the planar  $(NH_2)_2$  -radical have been reported previously  $10^7$ . Based on the MINDO/3 calculations the  $(NH_2)_2$  -radical is not planar.

Table 15.6. shows the calculated bond lengths and bond angles with respect to the minimum energy.

Teble 15.6. The calculated bond lengths and bond angles of the  $(NH_2)_2$  -radical with the MINDO/3 program.

Numbering of the molecule

1 2 3



bond	bond length (nm)	angle	bond angle (o)
1-2, 2-3			
4-5, 5-6	0.1095	1-2-3	104.4
2-4	0.2066	1-2-4	146.0
3-5	0.2135		

The structure proposed by the MINDO/3 program seems rather unreliable remembering that the radical, especially with respect to the coupling constants, resembles the pyrazine anion radical. The theoretical calculations, of course, can not repeat the experimental conditions but their support is important for method testing purposes. Further development of the calculation methods is needed.

## 16. Summary

The protonation process of some nitrogen containing heterocyclic compounds was investigated. The radicals were prepared using liquid ammonia as solvent and sodium metal as reducing agent. The kinetics of solvated electrons were followed with the EPR spectrometer. The excess of solvated electrons in sodium-ammonia solution was generated using flash equipment and the decay of the resulting peak was measured. The evaluation of the rate constant was performed assuming first order kinetics. The decay of the solvated electrons was measured at various temperatures in order to determine the activation energy. The most dilute sodium-ammonia solution produced a radical for which the formula  $(NH_2)_2$  was suggested on ref. 77. This radical was light sensitive as were the solvated electrons. The compounds under investigation were pyridine, pyrazine, pyridazine, pyrimidine and s-triazine.

The anion radical of pyrazine was formed in the sodium-ammonia solution and no further protonation was observed. Pyridine first gave the anion radical of 4,4' -dipyridyl which turned to the pyridine anion after UV irradiation. The process was reversible. Pyrimidine reacted in sodium-ammonia solution giving the mixture of the radicals which could be seen in the absorption spectrum in the visible region. S-triazine formed the diprotonated anion radical in the sodium-ammonia system but the anion of s-triazine was not observed. The slow protonation of pyridazine was followed by recording the EPR spectra and the visible absorption spectra at various stages. The protonation is suggested to proceed as follows (R denotes the starting material):

$$R + e^{-} \qquad R^{+}$$

$$R^{-} + H^{+} \qquad RH^{+}$$

$$RH^{+} + H^{+} \qquad RH^{+}_{2}$$

$$RH^{+}_{2} + e^{-} \qquad RH^{+}_{2}$$

$$RH^{+}_{2} + e^{-} \qquad RH^{+}_{2}$$

The suitability of liquid ammonia as solvent in ENDOR spectrocopy, not only in EPR spectrocopy, was tested by recording the ENDOR spectra of the pyrazine anion, the diprotonated pyramidine anion and the 4,4' -dipyridyl anion. Due to the diminished anisotropy of the nitrogen in sodium-ammonia solution, it can be recorded simultaneously with the protons. Hence liquid ammonia is a very suitable solvent also for the ENDOR experiments. The INDO method was employed in the evalution of the coupling constants for the radicals obtained. The calculation was not very succesful for the protonated species but overestimated the coupling constants especially for the non-planar structures. The MINDO/3 method aided the determination the optimum geometries of the diprotonated pyridazine radicals as well as the geometries of pyridazine, pyrimidine and s-triazine in their ground state.

## REFERENCES

- Electrons in Fluids, ed. J. Jortner and N.R. Kestner, Springer Verlag, Berlin - Heidelberg - New York, 1973.
- Organic Reactions in Liquid Ammonia, Vol. 1, Part 2, ed. H. Smith, Interscience Publ., A Division of John Wiley & Sons, New York - London, 1963.
- Gmelins Handbuch der anorganischen Chemie, Verlag Chemie GmBH, Weinheim, BRD, 22, part 2 (1969) 259.
- Ber. Bunsenges. physik. Chem. <u>75</u> (1971) 607 722. (The volume is dedicated to the solvated electrons)
- Alger, R.S., Electron Paramagnetic Resonance, Interscience Publ., New York, (1968) 291 - 297.
- 6. Catterall, R., Symons, M.C.R., J. Chem. Soc. (1965) 3763.
- Arnold, E., Patterson, A., Jr., J. Chem. Phys. <u>41</u> (1964) 3089, 3098.
- Golden, S., Guttman, C., Tuttle, T.R., Jr., J. Am. Chem. Soc. 87 (1965) 135.
- 9. Gold, M., Jolly, W.L., Inorg. Chem. 1 (1962) 818.
- Clark, H.C., Horsfield, A., Symons, M.C.R., J. Chem. Soc. (1959) 2478.
- 11. Douthit, R.C., Dye, J.L., J. Am. Chem. Soc. <u>82</u> (1960) 4472.
- 12. Hutchinson, C.A., Pastor, R.C., J. Chem. Phys. <u>21</u> (1953) 1959.
- 13. Kaplan, J., Kittel, C., J. Chem. Phys. 21 (1953) 1429.
- Fowles, G.W.A., McGregor, W.R., Symons, M.C.R., J. Chem. Soc. (1957) 3329.
- 15. Windwer, S., Sundheim, B.R., J. Phys. Chem. 66 (1962) 1254.

```
16. O'Reilly, D.E.O., J. Chem. Phys. 35 (1961) 1856.
```

```
17. Levy, R.A., Phys. Rev. 102 (1956) 31.
```

- 18. Pollak, V.L., J. Chem. Phys. <u>34</u> (1961) 864.
- 19. Jortner, J., J. Chem. Phys. 30 (1959) 839.
- Huppert, D., Strume, W.S., Rentzepis, P.M., J. Chem. Phys.
   63 (1975) 1205.
- 21. Jolly, W.L., Kirschke, E., Inorg. Chem. 6 (1967) 855.
- 22. Saito, E., in Metal Ammonia Solutions, Proc. Coll. Weyl II, ed. J.J. Lagowski and M.J. Sienko, Butterworths, London, 1970, 487.

- 23. McWeeny, R., Sutcliffe, B.T., Mol. Phys. 6 (1963) 493.
- Copeland, D.A., Kestner, N.R., Jortner, J., J. Chem. Phys. 53 (1970) 1189.
- 25. Ogg, Jr., R.A., J. Am. Chem. Soc. 68 (1946) 155.
- 26. Land, R.H., O'Reilly, D.E., J. Chem. Phys. 46 (1967) 4496.
- Becker, E., Lindqvist, R.H., Alder, B.J., J. Chem. Phys. 25 (1956) 971.
- 28. Holy, N.L., Chem. Rev. 74 (1974) 243 277.
- Hückel, W., Fortschr. chem. Forsch. Ed 6/2, July 1966, 197 - 206.
- Hückel, W., Bretschneider, H., Justus Liebigs Ann. Chem. 540 (1939) 157.
- 31. Birch, A.J., Quart. Rev. Chem. Soc. 4 (1950) 69.
- 32. Ref. 2., pp. 151 154.
- 33. Moorthy, P.N., Hayon, E., J. Phys. Chem. 78 (1974) 2615.
- 34. Ref. 2., pp. 39.
- Brigwell, P.J., Johnson, C.P., Katritzky, A.R., Naeem, S., Tarhan, H.O., Walker, G., J. Chem. Soc. (B) (1967) 1233.
- Albert, A., Katritzky, A.R., ed. Physical Methods in Heterocyclic Chemistry, Vol. I, Academic Press, New York, 1963.
- Atkins, P.W., Quanta, A Handbook of Concepts, Clarendon Press, Oxford, 1974 61 - 64.
- 38. Möbius, K., Ber. Bunsenges. physik. Chem. 78 (1974) 1116.
- Kevan, L., Kispert, L.D., Electron Spin Double Resonance Spectroscopy, John Wiley & Sons, New York, 1976, p. 96.
- 40. Hyde, J.S., Maki, A.M., J. Chem. Phys. <u>40</u> (1964) 3117.
- 41. Möbius, K., Dinse, K-P., Chimia 26 (1972) 461.
- 42. Dinse, K-P., Möbius, K., Biehl, R., Plato, M., in XVII Congress Ampere, ed. V. Hovi, North-Holland Publishing Co. 1973, 419.
- van Willingen, H., Plato, M., Biehl, R., Dinse, K-P., Möbius, K., Mol. Phys. 26 (1973) 793.
- 44. Dinse, K-P., Möbius, K., Plato, M., Biehl, R., Haustein, H., Chem. Phys. Lett. 14 (1972) 196.
- 45. Lubitz, W., Dinse, K-P., Möbius, K., Biehl, R., Chem. Phys. 8 (1975) 371.

- 46. Lubitz, W., Biehl, R., Möbius, K., J. Magn. Reson. <u>27</u> (1977) 411.
- 47. Lubitz, W., Dissertation, Freie Universität Berlin, 1977.
- 48. Dinse, K-P., Dissertation, Freie Universität Berlin, 1971.
- 49. Dinse, K-P., Möbius, K., Biehl, R., Z. Naturforsch. 28 a (1973) 1069.
- Biehl, R., Plato, M., Möbius, K., J. Chem. Phys. <u>63</u> (1975) 3515.
- Möbius, K., Biehl, R., in Multiple Electron Resonance Spectroscopy, ed. M.M. Dorio and J.H. Freed, Plenum Press, New York, 1977.
- 52. Private discussion with Dr. R. Biehl, Freie Universität, Berlin.
- 53. Pople, J.A., Santry, D.P., Segal, G.A., J. Chem. Phys. <u>43</u> (1965) S 129.
- 54. Pople, J.A., Santry, D.P., Segal, G.A., J. Chem, Phys. <u>43</u> (1965) S 136.
- 55. Murrell, J.N., Harget, A.J., Semi Empirical Self -Consistent Field Molecular Orbital Theory of Molecules, Wiley - Interscience, Belfast, 1972.

```
56. Dixon, R., Mol. Phys. 12 (1967) 83.
```

- 57. Pople, J.A., Beveridge, D.L., Dobosh, P.A., J. Chem. Phys. <u>47</u> (1967) 2060.
- 58. Ohno, K., Theoret. Chim. Acta 2 (1964) 219.
- 59. Klopman, G., J. Am. Chem. Soc. 86 (1964) 4550.
- Beveridge, D.L., Dobosh, D.A., J. Chem. Phys. <u>48</u> (1968) 5532.
- 61. Atherton, N.M., Hinchliffe, A., Mol. Phys. 12 (1967) 349.
- Pople, J.A., Beveridge, D.L., Approximate Molecular Orbital Theory, McGraw-Hill Book Company, New York, 1970.
- 63. Dewar, M.J.S., Baird, N.C., J. Chem. Phys. 50 (1969) 1262.
- 64. Dewar, M.J.S., Baird, N.C., Sustmann, R., J. Chem. Phys. <u>50</u> (1969) 1275.
- 65. Dewar, M.J.S., Haselbach, E., J. Am. Chem. Soc. 92 (1970) 590.
- 66. Bingham, R.C., Dewar, M.J.S., Lo, D.H., J. Am. Chem. Soc. <u>97</u> (1975) 1285.

- Bingham, R.C., Dewar, M.J.S., Lo, D.H., J. Am. Chem. Soc. 97 (1975) 1294.
- Bingham, R.C., Dewar, M.J.S., Lo, D.H., J. Am. Chem. Soc. 97 (1975) 1302.
- 69. Bischof, P., J. Am. Chem. Soc. 98 (1976) 6844.
- Private correspondence with Metz Apparatenwerke, Fürth, Bayern, BRD.
- Segal, B.G., Kaplan, M., Fraenkel, G.K., J. Chem. Phys. 43 (1965) 4191.
- 72. QCPE 137, MINDO, Baird, N.C.
  - QCPE 209, ESREXN, Heinzer, J.
  - QCPE 250, ATCOOR, Nordlander, J.E.
  - QCPE 249, VSS, Giessner-Prettre, C.
  - QCPE 261, CNDO/2-3R, Hase, H.L., Schweig, A.
  - QCPE 246, MIEHM, Spanget-Larsen, J.
  - QCPE 281, CNINDO/74, Dobosh, P.A., Ostlund, N.S.

QCPE 279, MINDO/3, Dewar, M.J.S., Metiu, H., Student, P.J., Brown, A., Bingham, R.C., Lo, D.H., Ramsden, C.A., Kollmar, H., Weiner, P., Bischof, P.K.,

QCPE 312, GEOMIN, Purcell, K.F., Zapata, J. HUCKEL, Heilbronner, E., Bock, H., Das HMO\_Modell und seine Anwendung.

Verlag Chemie, Weinheim, 1970.

- 73. QCPE 136, COORD, Baird, N.C., Dewar, M.J.S.
- 74. Eloranta, J., Nyrönen, T., Finn. Chem. Lett. (1974) 193.

```
75. Ref. 1., pp. 73 - 75.
```

- 76. Eloranta, J., Linschitz, H., J. Chem. Phys. 38 (1963) 2214.
- 77. Eloranta, J., Nyrönen, T., Finn. Chem. Lett. (1977) 91.
- 78. Dodd, J.W., Hopton, F.J., Hush, N.S., Proc. of the Chem. Soc. Feb. (1962) 61.
- 79. Carrington, A., dos Santos-Veiga, J., Mol. Phys. 5 (1962) 21.
- 80. Hinchliffe, A., Int. J. of Quant. Chem. Vol. XI (1977) 767.
- 81. Stone, E.W., Maki, A.H., J. Chem. Phys. <u>39</u> (1963) 1635.
- 82. Talcott, C.L., Meyers, R.J., Mol. Phys. 12 (1967) 549.
- 83. Ward, R.L., J. Am. Chem. Soc. 83 (1961) 3623.
- Buick, A.R., Kemp, T.J., Neal, G.T., Stone, T.J., J. Chem. Soc. (A) (1969) 1609.

- Chaudhuri, J., Kume, S., Jagur-Grodzinki, J., Szwarc, M., J. Am. Chem. Soc. 90 (1968) 6421.
- 86. Henning, J.C.M., J. Chem. Phys. 44 (1966) 2139.
- 87. Zeldes, H., Livingston, R., J. Phys. Chem. 76 (1972) 3348.
- 88. Sevilla, M.D., J. Phys. Chem. 74 (1970) 805.
- 89. Geske, D.H., Padmanabhan, G.R., J. Am. Chem. Soc. <u>87</u> (1965) 1651.
- Private discussion with H. Helama, M.Sc., Kemira Oy, Vihtavuori.
- 91. Leniart, D.S., Vedrine, J.C., Hyde, J.S., Chem. Phys. Lett. 6 (1970) 637.
- 92. Dinse, K-P., Möbius, K., Plato, M., Biehl, R., Haustein, H., Chem. Phys. Lett. 14 (1972) 196.
- 93. Miller, R.L., Lykos, P.G., Schmeising, H.N., J. Am. Chem. Soc. 84 (1962) 4623.
- 94. Fischer Hjalmars, I., Sundbom, M., Acta Chem. Scand. <u>22</u> (1968) 607.
- 95. Del Bene, J., Jaffé, H.H., J. Chem. Phys. 48 (1968) 1807.
- 96. Del Bene, J., Jaffé, H.H., J. Chem. Phys. 50 (1969) 563.
- 97. Kato, H., Katô, H., Konishi, H., Yonezawa, T., Bull. Chem. Soc. Japan 42 (1969) 923.
- 98. Calacco, V., Org. Magn. Recon. 6 (1974) 5.
- 99. Almlöf, J., Roos, B., Wahlgren, V., Johansen, H., J. Electron Spectrosc. 2 (1973) 51.
- 100. Innes, K.K., Byrne, J.P., Ross, I.G., J. Mol. Spectrosc. 22 (1967) 125.
- 101. Bak, B., Hansen Nygaard, L., Rastrup Andersen, J., J. Mol. Spectrosc. 2 (1958) 361.
- 102. Wheatley, P.J., Acta Cryst. 13 (1960) 80.
- 103. Merrit, J.A., Innes, K.K., Spectrochim. Acta 16 (1960) 945.
- 104. Lancaster, J.E., Stoicheff, B.P., Can. J. Phys. <u>34</u> (1956) 1016.
- 105. Tjebbes, J., Acta Chem. Scand. 16 (1962) 916.
- 106. Pyykkö, P., Joela, H., Chem. Phys. Lett. 31 (1975) 574.
- 107. Ref. 77. p. 93.