

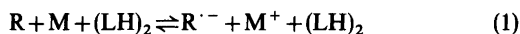
The Effect of Solvent on the Structure of the Radical Ions Formed from Phenazine, an EPR and ENDOR Study

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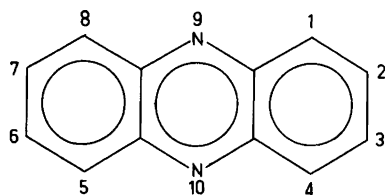
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In liquid ammonia by sodium reduction phenazine (R) yielded the radical anion $R^{\cdot-}$; in acetonitrile by electrolysis $R^{\cdot-}$ at the cathode and RH_2^+ at the anode, simultaneously; and in different carboxylic acids RH_2^+ . The effect of the solvent was most evident in the coupling constants of the radical ions of phenazine in positions 1, 4, 5, 8 and 9, 10.

If the solvent is a weak proton donor, phenazine will react with alkali metals [M metal, $(LH)_2$ solvent]

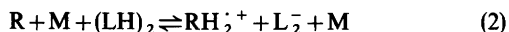


and the phenazine radical anion is formed [eqn. (1)]. An example is the reaction of phenazine in liquid ammonia with sodium.



Phenazine (R)

If the solvent is a strong proton donor, the reaction (2) takes place.



Here the solvent acts as an oxidant. The reaction involves the coordinative addition of two protons to the nitrogen atoms of phenazine^{1, 2} and the formation of a diprotonated radical ion having the structure of a radical anion.³ A good example of this is the reaction of phenazine in trifluoroacetic

acid where Tl^{3+} , usually used as an oxidant in this solvent, is unnecessary.³

The aim of the present study was to investigate solvation and the coordination and exchange reactions of protons of solvents of different proton donating abilities. Phenazine was selected as the test molecule.

The reaction has a clear effect on the coupling constants of phenazine radical. Changes in the coupling constants are nevertheless small when similar solvents are used. Where possible, ENDOR spectra, which carry the accuracy of the measurements one order higher than EPR, should therefore be used in determining coupling constants.

EXPERIMENTAL

The phenazine was from Fluka AG; formic-, propionic-, trifluoroacetic- and deuteriotrifluoroacetic acids were from Merck AG and were of analytical grade. The purity of phenazine was tested gas chromatographically.

The ammonia was a Merck product of 99.9% purity. It was distilled into the ampoule under nitrogen atmosphere.⁴ The acetonitrile was purified according to the literature.^{5, 6} Some aluminium oxide was added to the acetonitrile and it was stored connected to the vacuum line. Tetrabutylammo-

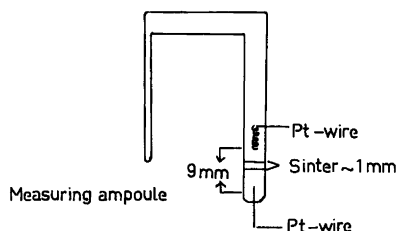


Fig. 1. Electrolytic apparatus.

niumperchlorate (0.1 mol/dm^3) used as the carrying electrolyte was a *p.a.* product from Merck.

The electrolysis was carried out in the apparatus shown in Fig. 1. The anode and cathode were isolated by means of a sinter. By freezing the lower part of the cell with liquid nitrogen, it was possible to pour the wanted radical formed in the upper part into a cuvette for measuring by reversal electrodes. The green RH_2^+ was formed at the anode and the red $\text{R}^{\cdot-}$ was formed simultaneously at the cathode, to be captured in the ampoule for measuring. All samples were prepared under high vacuum.

The EPR spectra were recorded with Varian model E-12 and E-9 spectrometers equipped with Varian variable temperature regulators. Varian 620/L spectrosystem 100 computer facilities were used for the spectrum simulation. The Varian E-12 spectrometer was equipped with a Bruker Physik ENDOR-system B-EN200S.

The coupling constants were measured in liquid phase. The temperature dependence of the coupling constant was measured with all samples down to the freezing point of the sample to allow estimation of the effect of the variation in viscosity of the solvent on the coupling constants. Where possible ENDOR spectra were also measured.

RESULTS AND DISCUSSION

The EPR spectra of the radical ion $\text{R}^{\cdot-}$ of phenazine in liquid ammonia and in acetonitrile are shown in Figs. 2 and 3. Though in both cases there is no

doubt that the radical anion $\text{R}^{\cdot-}$ is involved, the coupling constants of the protons in positions 1, 4, 5, 8 and of nitrogen are slightly different, as shown in Table 1. The ENDOR spectra (Fig. 4) of the same sample as in Fig. 2 clearly shows the nitrogen coupling.

In basic ammonia there are few protons to be obtained and therefore the $\text{R}^{\cdot-}$ anion radical is found. Acetonitrile is a weak Lewis base, but even after the most careful purification it still contains water and hydrogen bonds are formed between phenazine and water more easily than between phenazine and ammonia. Accordingly, the intensity of the nitrogen peak ($m_1(\text{N}) \neq 0$) in Fig. 3 is diminished compared to the simulated spectrum.

According to Table 1, no measurable changes occur in the coupling constants of positions 2, 3, 6, 7, whereas one does find changes in coupling constants

Table 1. Coupling constants (mT) of the radical anion phenazine ($\text{R}^{\cdot-}$).

	1, 4, 5, 8	2, 3, 6, 7	9, 10(N)
EPR			
$\text{NH}_3(1) + \text{Na}$	0.178	0.159	0.523
CH_3CN (cathode)	0.159	0.159	0.536
ENDOR			
$\text{NH}_3(1) + \text{Na}$	0.1789	0.1562	0.5186

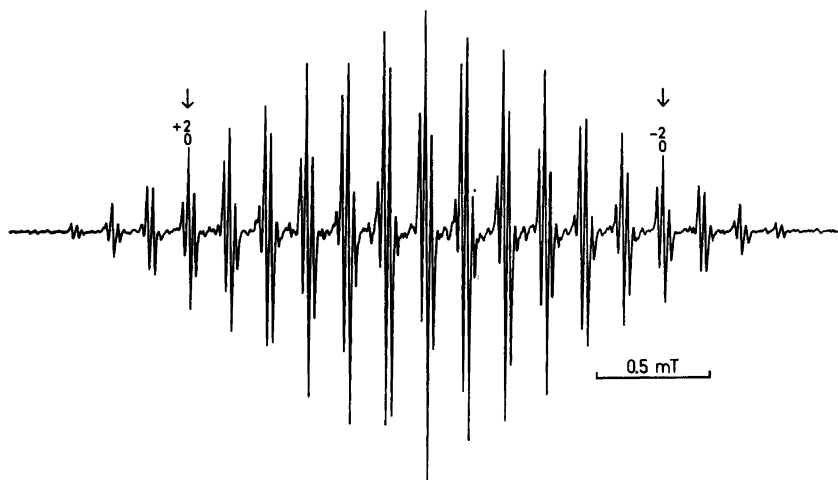


Fig. 2. The EPR spectrum of the phenazine anion radical ($\text{R}^{\cdot-}$) in ammonia with sodium as reducing agent at 253 K.

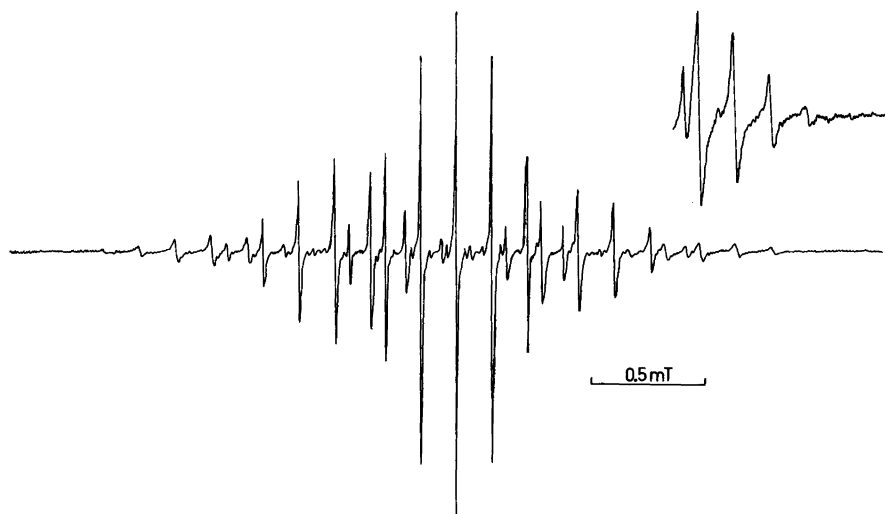
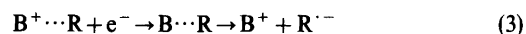


Fig. 3. The EPR spectrum of the phenazine anion radical ($R^{\bullet-}$) in acetonitrile produced at the cathode by electrolysis at 233 K.

of positions 1,4, 5, 8 and of nitrogen when the solvent is changed. In acetonitrile, a hydrogen bond is formed between the oxygen atom of the water molecule and the hydrogen in position 1 (4, 5, 8), while another bond is formed between the nitrogen in position 9 and the hydrogen of the water molecule. The relative changes in the coupling constants in going from ammonia to acetonitrile indicate the formation of the bonds in question. There is no change in the coupling constant of position 2 (3, 6, 7), which means that the corresponding proton does not participate in hydrogen bonding. According to the EPR spectra the molecular symmetry remains unchanged, too, indicating that corresponding hydrogen bonds are formed in position 1, 4, 5, 8 and 9, 10.

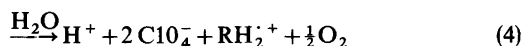
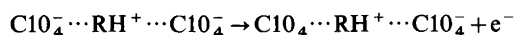
The reactions in acetonitrile during electrolysis (B^+ = tetrabutylammonium ion) are as eqns. (3)–(4).

At the cathode:



There is equilibrium in the solution $R + H^+ \rightleftharpoons RH^+$.

At the anode:



When a carboxylic acid is used as solvent, a hydrogen bond is formed to the oxygen of the carboxylic acid instead of to the water molecule, and the acid donates a proton to the nitrogen of phenazine and forms a coordinative bond. Now the $RH_2^{\bullet+}$ ion radical is formed. The better proton donor the acid is, the more easily $RH_2^{\bullet+}$ is produced and the more easily a hydrogen bond between the carboxylic oxygen and the hydrogen of phenazine at position 1 (4, 5, 8) is formed.

The coupling constant of the proton at position

Table 2. Coupling constants (mT) of the radical ion of dihydrophenazine ($RH_2^{\bullet+}$).^a

	1,4,5,8	2,3,6,7	9,10(N)	9,10(H)
EPR				
CH ₃ CN(Anode)	0.060	0.177	0.610	0.670
CH ₃ CH ₂ COOH	0.064	0.171	0.615	0.660
CH ₃ COOH ³	0.062	0.171	0.610	0.667
HCOOH	0.058	0.171	0.615	0.672
CCl ₃ COOH ³	0.056	0.172	0.612	0.670
CF ₃ COOD	0.056	0.177	0.605	—
CF ₃ COOH ³	0.053	0.173	0.620	0.675
ENDOR				
CF ₃ COOH	0.0532	0.1751	—	—

^a Temperatures in Table 2: 233, 258, 288, 265, 353, 263, 263 and 263 K.

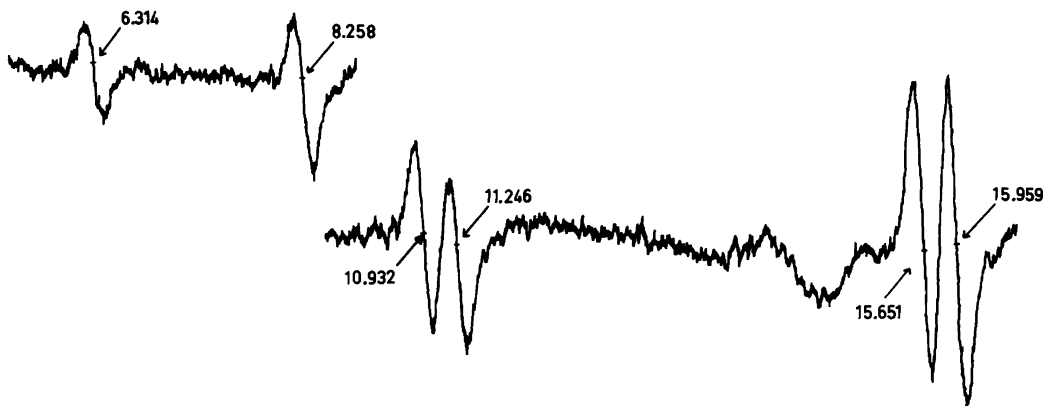
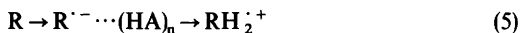


Fig. 4. The ENDOR spectrum of the phenazine anion radical ($R^{\cdot-}$) in ammonia with sodium as reducing agent at 253 K. The nitrogen coupling is seen on the left.

1 (4, 5, 8) of phenazine indicates this change. Comparing the values of coupling constants in Tables 1 and 2 and thinking of the reaction (5) as a continuous event,



the change 0.178 mT \rightarrow 0.159 mT indicates that a hydrogen bond is formed.

Coordinative bonding ($RH_2^{\cdot+}$) between nitrogen and proton leads to a marked change in the values of coupling constants at position 1 (4, 5, 8). At position 2 (3, 6, 7) the change is small and is due to

the noticeable change in spin density elsewhere in the molecule. Even at position 9 (10) the change in the coupling constant of nitrogen is relatively much smaller than that of the proton at position 1 (4, 5, 8). As the ability of the carboxylic acid to donate protons increases, the value of the coupling constant of the proton at position 1 (4, 5, 8) decreases, as shown in Table 2. The ENDOR spectrum in Fig. 5 confirms the interpretation of the EPR spectrum. When the temperature is lowered near to the freezing point of the sample, the line intensities of nitrogens ($m_I(N) \neq 0$) at positions 9, 10 of the $RH_2^{\cdot+}$ radical ion and of protons bonded to them

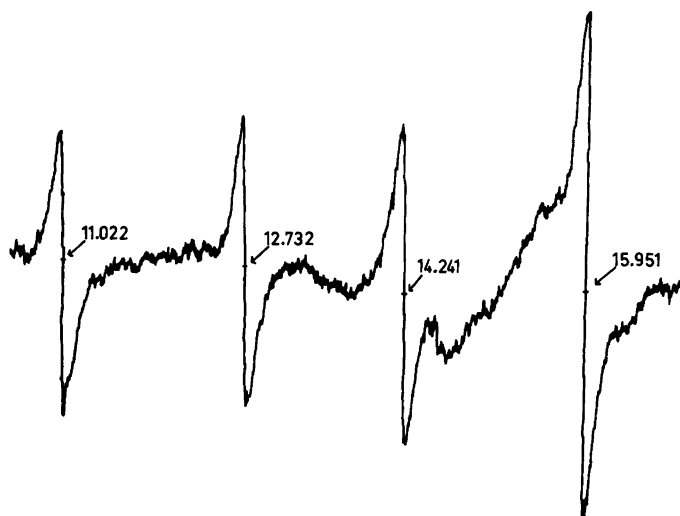


Fig. 5. The ENDOR spectrum of the radical ion ($RH_2^{\cdot+}$) of dihydrophenazine in trifluoroacetic acid at 263 K.

Table 3. The relative intensities of the phenazine radical anion of the ENDOR spectrum when magnetic field is locked to the resonance line alternately on the lower and higher field. Solvent ammonia, at 253 K.

Magnetic field locked	N		1,4,5,8		2,3,6,7	
	Lower	Higher	Lower	Higher	Lower	Higher
$M_1^N = 2, M_1^H = 0$	1	3.6	5	3.5	4.8	3.8
$M_1^N = -2, M_1^H = 0$	2	1.5	1.6	5.9	1.8	5.8

diminish noticeably and the lines broaden; in contrast, the fine structure of the lines of protons at positions 1, 4, 5, 8 and 2, 3, 6, 7 remains. These findings indicate that exchange reactions take place between protons bonded to nitrogen and protons of the solvent. This is seen in the time scale of EPR near the freezing point of the sample. The coupling of the protons (9, 10) was verified with deuterio-trifluoroacetic acid. The unchanging fine structure of the proton at position 1 (4, 5, 8) indicates that the hydrogen bond formed by the carboxylic ion does

not take part in an exchange reaction with the solvent within the EPR time scale.

Lubitz and Nyrönen^{7,8} have shown using triple resonance⁹ with pyrazine anion in liquid ammonia that one can also determine the relative sign of the coupling constant from ENDOR spectra. When the magnetic field is locked to the resonance line on the low-field in Fig. 2 ($M_1^N = 2, M_1^H = 0$), the relative ENDOR intensities in Table 3 are obtained. The intensity of the nitrogen line of the low-field is smaller than that of the high-field. When the magnetic field is locked on the high-field ($M_1^N = -2, M_1^H = 0$) the intensity ratio is reversed. Simultaneously, as one can see in Fig. 6, the intensities of hydrogens change in opposite directions to the nitrogens when the locking of the magnetic field is successively on the low- and high-fields. These results indicate that the coupling constants of nitrogen and protons at positions 1, 4, 5, 8 and 2, 3, 6, 7 have different signs. Since the coupling constant of nitrogen in aromatic compounds is positive, the coupling constants of phenazine anion protons must be negative. This conclusion is consistent with Indo calculations for the phenazine anion.¹⁰

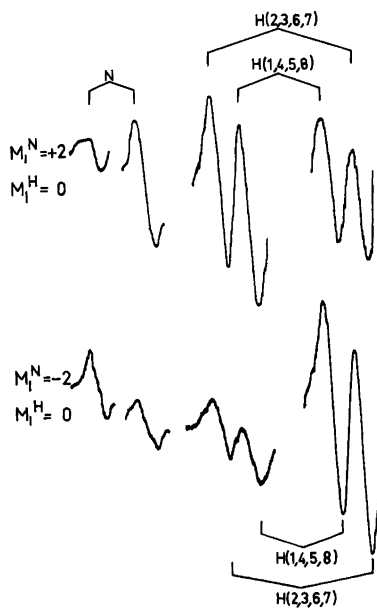


Fig. 6. ENDOR spectra of the radical anion ($R^{\cdot -}$) of phenazine in ammonia with sodium as reducing agent at 253 K. In the upper spectrum the magnetic field was locked to the nitrogen line at the low-field and in the lower spectrum it was locked to the line of nitrogen at the high-field. Nitrogen and protons show opposite changes of intensities in the ENDOR lines.

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