An Isolation and Liquid Phase EPR Spectra of the Cation Radical Salts of N-Methyl and N-Ethylphenothiazinium Perchlorate

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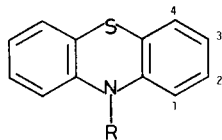Received February 5, 1980

N-Methyl and N-ethylphenothiazines were oxidized with bromine and sodium perchlorate to give stable cation radical salts. Their well-resolved epr spectra were obtained in nitromethane solution. In order to assign the hfs constants, the cation radicals of N-deuteriomethyl and N-deuterioethylphenothiazines were prepared with lead tetraacetate and trifluoroacetic acid in solutions.

Inorganic salts of N,N,N',N'-tetramethyl-p-phenylenediamine [TMPD] cation radical undergo a phase transition and have attracted much attention due to their paramagnetic properties at high temperatures and diamagnetic properties at low temperatures. In the cation radical salt of TMPD perchlorate the phase transition occurs at about $-83°$, as was ascertained from magnetic susceptibilities (1), heat capacity (2), electron paramagnetic resonance (epr) (3), nuclear magnetic resonance (4), and crystal structure determinations (5). Recently it has shown that the cation radical salt of TMPD tetrafluoroborate exhibits a phase transition at about $-82.5°$ (6).

We have been looking for compounds that could form cation radicals by appropriate oxidation. The low ionization potential of phenothiazine, N-methyl and N-ethylphenothiazines made them worth investigating. These compounds form charge-transfer complexes with several electron acceptors (7,8). It was felt that stable salts of substituted phenothiazines could be prepared by using strong oxidizing agents. On the other hand, up until now the unpaired electron spin density distributions of the cation radicals of phenothiazine, N-methyl and N-ethylphenothiazine have been verified by epr spectroscopy due to various chemical preparative or electrochemical methods (9-14). Among the rest, their stable cation radical salts in ratios of 1:1 of the organic molecules and perchlorates are the expected interesting results of various chemical and physical properties (8). We wish to report the isolation of the cation radical salt based on N-methyl and N-ethylphenothiazinium perchlorates and their intense well-resolved epr spectra in solution.

The preparation of the N-methylphenothiazinium perchlorate cation radical salt by oxidizing N-methylphenothiazine with iodine/silver perchlorate in ethanol was reported in 1974 by Litt and Radovic (8) and by Shine and co-workers (15), using Billon's method (16). These methods give high yields, but the purity of the N-methylphenothiazinium perchlorate cation radical salt obtained was not good. This compound exists as a hydrate (one water molecule); the nonhydrated salt decomposes in several hours (dec. above 120°) (8). Therefore, pure N-methylphenothiazinium perchlorate cation radical salt was prepared and isolated by oxidizing N-methylphenothiazine with bromine and sodium perchlorate (17) at low temperature in acetone. The pure product has a melting point range of 195-196° dec. Indeed, the isolated salt is a complete contact ion-pair (N-methylphenothiazine: perchlorate = 1:1) and is stable for over three years in the air.
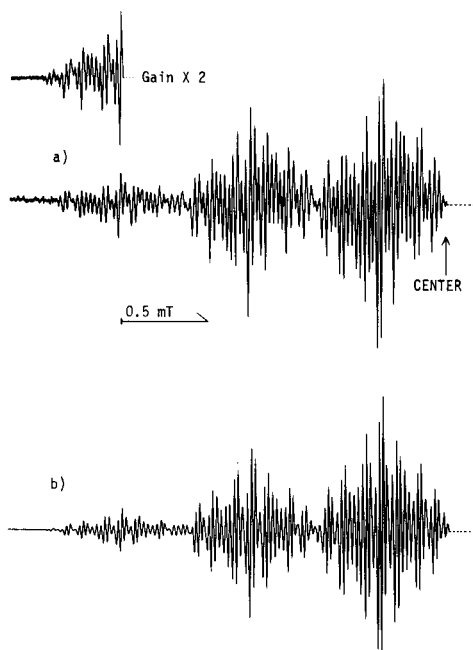

Figure 1. (a) Low-field portion of the observed epr spectrum for the cation radical salt of N-methylphenothiazinium perchlorate in nitromethane at $-60°$. (b) Half-spectrum simulated by means of hfs constants listed in Table I: lineshape, Lorentzians; linewidth, 0.008 mT.

$R = CH_3, C_2H_5, CD_3, \text{ and } C_2D_5$

Structure 1

Results and Discussion.

Cation Radical Salts.

Epr Spectra.

An intense well-resolved epr spectrum of N-methyl-phenothiazinium perchlorate cation radical salt in nitromethane solution at −60° is displayed in Figure 1a. The spectrum is exactly the same as that obtained by other workers who oxidized the compound in nitromethane (14), sulfuric acid (12), or via electrochemical means (11). The computer-simulated spectrum using the values listed in Table I is shown in Figure 1b. This spectrum is in good agreement with the observed one. Table I also contains details of the epr spectra reported by others (12,14) for comparison. The assignments of hyperfine splitting [hfs] constants to hydrogen atoms in various molecular positions are made on the basis of the reported MO calculation (12).
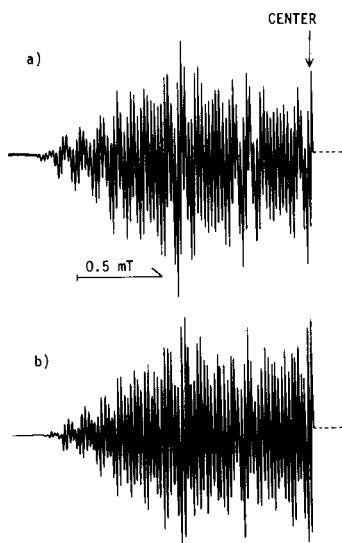
The epr spectrum of N-ethylphenothiazinium perchlorate cation radical salt in nitromethane at −30° was observed as a well-split hyperfine structure as shown in Figure 2a. Good agreement with experimental values (Figure 2a) was obtained by spectrum simulation (Figure 2b), employing the splittings given in Table I. Analysis of the spectrum indicate that the hydrogen atoms have separate hfs constants (0.216, 0.099, 0.080 and 0.023 mT) in the heteroaromatic ring and two splittings (0.374 and 0.018 mT) due to the β and γ-protons in the ethyl group, and that there is splitting (0.753 mT) due to the nitrogen atom (17a).
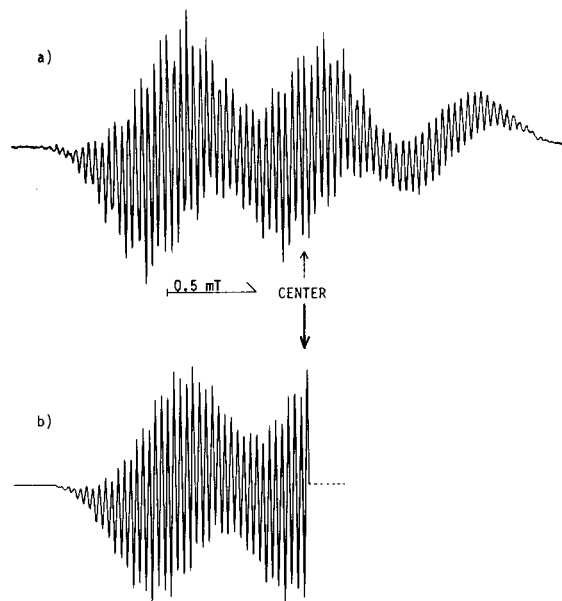

Figure 2. (a) Low-field portion of the observed epr spectrum for the cation radical salt of N-ethylphenothiazinium perchlorate in nitromethane at −30°. (b) Half-spectrum simulated by means of hfs constants listed in Table I: lineshape, Lorentzians; linewidth, 0.008 mT.

Figure 3. (a) The observed epr spectrum for the cation radical of N-deuteriomethylphenothiazine in carbon tetrachloride at −30°. (b) Half-spectrum simulated by means of hfs constants listed in Table I: lineshape, Lorentzians; linewidth, 0.008 mT.

Table I

The hfs Constants and the g-Values of some N-Substituted Phenothiazine Cation Radicals

Cation Radical	hfs Constants (mT)								
	a_1^H	a_2^H	a_3^H	a_4^H	a^N	a_β^H	a_γ^H	g-value	
Calcd., N-methylphenothiazine	−0.112	−0.051	−0.191	+0.034	0.738	.....	———	———	Ref. 12.
N-methylphenothiazinium perchlorate	0.101	0.077	0.224	0.026	0.765	0.742	———	2.0050	This work
N-methylphenothiazine	0.100	0.076	0.220	0.029	0.750	0.723	———	———	Ref. 12.
	0.098	0.073	0.212	0.024	0.749	0.724	———	2.0052	Ref. 14.
N-deuteriomethylphenothiazine	0.076	0.070	0.217	0.037	0.764	0.112 (a)	———	2.0050	This work
N-ethylphenothiazinium perchlorate	0.099	0.080	0.216	0.023	0.753	0.374	0.018	2.0051	This work
N-ethylphenothiazine	0.094	0.094	0.211	....	0.751	0.372	.....	2.0052	Ref. 14.
N-deuterioethylphenothiazine	....	....	....	....	0.74	.....	.....	2.0051	This work

(a) This is the hfs constant due to the deuterium atoms of the deuteriomethyl group.

In order to ascertain the analytical data as shown in Table I, the cation radicals of N-deuteriomethyl and N-deuterioethylphenothiazine were prepared using lead tetraacetate, trifluoroacetic acid and acetic anhydride (10:1) in solution. In Figure 3a the observed epr spectrum of N-deuteriomethylphenothiazine cation radical is shown in carbon tetrachloride at $-30°$. The high field broadening of the main spectrum, attributed to anisotropy in the g-tensor and the nitrogen hfs constant (18), causes the high-field ^{33}S satellite to be almost completely obscured. The ^{33}S satellites are expected to be broader than the main signal, there being a further contribution to the linewidth from dipolar interactions due to the anisotropy in the ^{33}S hfs (18). The computer-simulated spectrum using the listed values in Table I is displayed in Figure 3b. In this case, Figure 3a agrees well with Figure 3b and the hfs constant due to the deuterium of the deuteriomethyl group was 0.112 mT. Therefore, the proportion of the hfs constants of the proton and deuterium (a^H/a^D) was found to be approximately 6.625 for the cation radical of N-methylphenothiazinium perchlorate and N-deuteriomethylphenothiazine (19). On the other hand, as shown in Figure 4, the
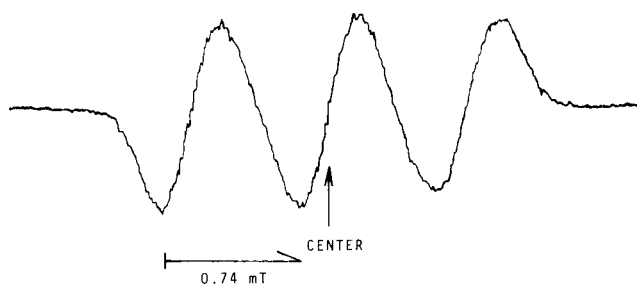

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0.74 mT

Figure 4. The observed epr spectrum for the cation radical of N-deuterioethylphenothiazine in nitromethane at $-20°$.

epr spectrum of N-deuterioethylphenothiazine cation radical measured three broad splittings of about 0.74 mT due to the nitrogen, because of the hfs constants for the deuterioethyl group must overlap the hfs constants of the ring protons.

As shown in Table I, good agreement is also obtained between the calculated (McLachlan) and the experimental hfs constants as reported by others (9-14) for protons and the nitrogen atoms in N-methyl and N-ethylphenothiazinium perchlorate cation radical salts. In conclusion it is clear that these salts are a highly pure complex of cation radical pairs. We particularly feel that the magnetic and physical properties will be of interest in these salts.

EXPERIMENTAL

Measurement.

The epr spectra were observed by means of an X-band epr spectro-

meter (JEOL ME-3) with 100 kHz field modulation over the temperature range from 25 to $-60°$. The magnetic field was calibrated by the hyperfine splitting of ^{14}N of the peroxylamine disulfonate ion. The spectral simulations were carried out with a JEOL spectral computer (model JEC-6) and at the Data Processing Center, Kyoto University (FACOM M-190 computer). The visible spectra of the absorption spectra were measured with Shimazu UV MPS-50L spectrometer at room temperature. The ir spectra were obtained using a JASCO S-G5 IR spectrometer.

N-Methylphenothiazine.

N-Methylphenothiazine was prepared according to the method of Gilman, et al. (20). A mixture of 6 g. of crude phenothiazine in 5 ml. of absolute methanol and 7 g. of methyl iodide was heated at 90° for 24 hours in a sealed tube. The yield of N-methylphenothiazine melting at 100°, after crystallization from ethanol, was 6.2 g. (96.4%).

N-Ethylphenothiazine.

N-Ethylphenothiazine was prepared according to the method of Gilman, et al. (20). A mixture of 5 g. of crude phenothiazine, in 12 ml. of absolute ethanol and 5 g. of ethyl bromide was heated at 110° for 24 hours in a sealed tube. The yield of N-ethylphenothiazine melting at 103° after crystallization from ethanol was 5.5 g. (96.3%).

N-Deuteriomethyl and N-Deuterioethylphenothiazine.

N-Deuteriomethyl and N-deuterioethylphenothiazine were prepared using the deuteriomethyl iodide and deuterioethyl bromide in a similar manner as in the preparation of N-methyl and N-ethylphenothiazine. The purity of the deuterated compounds was checked by ^{1}H-nmr.

N-Methylphenothiazinium Perchlorate.

The cation radical perchlorate salts of N-substituted phenothiazines were synthesized according to the method of Michaelis and Grannick (17). One g. N-methylphenothiazine was dissolved in a solution of 9 ml. of water and 40 ml. of acetone containing 6 g. of sodium perchlorate. The mixture was then cooled to $-10°$; 30 ml. of 0.126N aqueous bromine solution was added dropwise. The crystals were filtered and washed several times with small portions of ice-cold acetone:ether (1:10), yield 0.45 g. (30.7%), m.p. 195-196° dec. The crystals have a brown metallic luster; ir (potassium bromide): ν max, cm^{-1} 1455, 1330, 1260, 1110 (ClO$_4^-$ broad and sharp), 755, 635, 625; visible (dichloromethane): λ max, nm (ϵ), 451 (7500), 520 (23250), 709 (2650), 784 (4425), 880 (4450).

Anal. Calcd. for a 1:1 salt, $C_{13}H_{11}NS \cdot ClO_4$: C, 49.93; H, 3.55; N, 4.48; S, 10.25; Cl, 11.34. Found: C, 49.64; H, 3.43; N, 4.40; S, 10.27; Cl, 11.42.

N-Ethylphenothiazinium Perchlorate.

One g. of N-ethylphenothiazine was dissolved in a solution of 7 ml. of water and 40 ml. of acetone containing 5 g. of sodium perchlorate. The mixture was then cooled to $-10°$; 30 ml. of 0.126N aqueous bromine solution was added dropwise. The crystals were filtered and washed several times with small portions of ice-cold acetone:ether (1:10), yield 0.70 g. (48.7%), m.p. 182-184° dec. The crystals have a brown metallic luster; ir (potassium bromide): ν max, cm^{-1} 1455, 1330, 1250, 1110 (ClO$_4^-$ broad and sharp), 760, 638, 628; visible (dichloromethane): λ max, nm (ϵ), 452 (11450), 519 (27500), 711 (5550), 782 (7050), 878 (7200).

Anal. Calcd. for a 1:1 salt, $C_{14}H_{13}NS \cdot ClO_4$: C, 51.46; H, 4.01; N, 4.29; S, 9.81, Cl, 10.85. Found: C, 51.29; H, 3.98; N, 4.29; S, 10.04; Cl, 10.65.

Acknowledgment.

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