pling constant in the cation radical is expected to be higher for protons adjacent to the dimethylamino group. Such an order was, in fact, observed also for the chemical shifts.

The hyperfine coupling constant for the positive ion of dimethoxybenzene is slightly smaller than that of the benzene cation (2.4 *vs.* 2.9 G, respectively)[22,23] in contrast to our chemical-shift results. However, as the dimethoxybenzene is a better donor than benzene, it is reasonable that a higher amount of charge transfer occurs during the encounter with an oxygen molecule. However, the relatively high hyperfine constant of the methyl protons in the cation radical of 9,10-dimethylanthracene (8.0 G[24,25]) is not reflected in the oxygen-induced chemical shift of these protons, which is similar to the chemical shifts of methyl groups in all other compounds. This last result renders the correlation between the oxygen-induced chemical shifts and the proton hyperfine constants of the cation radicals incomplete. Obviously, further study is needed before a firm conclusion about the origin of the chemical shifts can be made.

Conclusions

The equal relaxation rates induced by dissolved O_2 on proton groups in the same or different molecular species lead to the conclusion that no stable complexes of oxygen with the organic molecules are present in the solutions. The relaxation is caused by a nonspecific dipolar interaction. The small but reproducible shifts, the origin of which is still unknown, may indicate, however, some specific interaction during the short encounters.

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Cation Radical Salts of *N*-Methylphenothiazine and Its Analogs. Synthesis and Characterization

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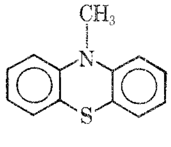
10-Methylphenothiazine and dibenzo-*N*-methylphenothiazine were oxidized with silver perchlorate, hexafluoroantimonate, and tetrafluoroborate to give stable ion-radical salts. All compounds exhibit exponential dependence of conductivity on temperature. Their magnetic behavior has been interpreted on the basis of a linear Ising model involving antiferromagnetic interaction of the unpaired electrons. Only a small fraction of the unpaired electrons participate in conduction.

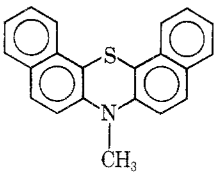
Introduction

Organic salts of TCNQ radical anions have attracted much attention due to their low electrical resistivities, particularly when incorporating an apparently neutral molecule of TCNQ.[1] Recently it has been shown that some simple radical-ion salts of TCNQ exhibit an insulator–metal transition below room temperature.[2,3]

We have been looking for compounds that could form cation radical ions by appropriate oxidation. The low ionization potential of phenothiazine and related compounds made them worth investigating. These form charge-transfer complexes with several electron acceptors.[4,5] It was felt that stable salts of substituted phenothiazines could be formed using string oxidizing agents. We report here the preparation of several salts based on 10-methylphenothiazine (10-MP) and 3,4:5,6-dibenzo-*N*-methylphenothiazine (DiB-N-MP) and their electrical and magnetic behavior. The structural formulas of the two compounds are shown.



10-MP



DiB-N-MP

Experimental Section

Preparation. 10-Methylphenothiazine was obtained by a procedure developed in this laboratory by Litt and Summers.[6]

10-Methylphenothiazine Perchlorate (10-MPClO$_4$). 10-MP (3.3220 g, 0.0156 mol) was dissolved in sufficient 95% ethanol to get an almost saturated solution at about 60° and 1.9760 g (0.0077 mol) of iodine dissolved in 20 ml of ethanol was added. After a few minutes a solution of 3.2280 g (0.0156 mol) of silver perchlorate in 10 ml of ethanol was poured in. A precipitate of AgI formed immediately. The precipitate was allowed to agglomerate and then was filtered off, leaving a red solution of 10-methylphenothiazine perchlorate. After evaporation to dryness *in vacuo* at room temperature the salt had the appearance of a black powder. The crude yield was 4.8232 g (99.3%). The product was recrystallized by dissolving in acetone (saturated solution) adding dioxane (⅓ the volume of acetone) and precipitating the crystals out by slow evaporation of acetone under reduced pressure. After two recrystallizations the yield was 4.2697 g or 87.9%. The ir spectrum shows the presence of water despite prolonged drying under vacuum. The element analysis indicates that the salt exists as a hydrate rather than as a simple salt.

Anal. Calcd for a 1:1 salt hydrated by one water molecule, $C_{13}H_{11}NSClO_4 \cdot H_2O$: C, 47.10; H, 3.92; N, 4.22; S, 9.67; Cl, 10.69. Found: C, 48.48; H, 3.96; N, 4.08; S, 9.58; Cl, 10.08.

The nonhydrated salt decomposes in several hours. This was seen when the synthesis was attempted using a solvent such as acetone. The compound starts decomposing above 120°.

10-Methylphenothiazine Tetrafluoroborate (10-MPBF$_4$). The salt was prepared in the same way as 10-MPClO$_4$. The respective quantities of reactants were 3.3220 g of 10-MP (0.0156 mol), 1.9760 g of I_2 (0.0077 mol), and 4.6668 g of $AgBF_4$ (0.0156 mol). The yield after recrystallization was 4.3048 g or 80.0%.

Anal. Calcd for a 1:1 salt, $C_{13}H_{11}NSBF_4$: C, 52.04; H, 3.66; F, 25.30; S, 10.68. Found: C, 53.40; H, 4.31; F, 23.74; S, 11.04.

Anal. Calcd for the 1:1 salt (+0.10 10-MP): C, 54.1; H, 3.85; F, 23.95; S, 11.10.

The compound decomposes above 120°.

10-Methylphenothiazine Hexafluoroantimonate (10-MPSbF$_6$). This was prepared as the salts above. The respective amounts of reagents were 3.3220 g of 10-MP, 1.9760 g of I_2, and 5.295 g of $AgSbF_6$. After recrystallization the yield was 4.456 g or 64.4%.

Anal. Calcd for a 1:1 salt, $C_{13}H_{11}NSSbF_6$: C, 34.77; H, 2.47; S, 7.14; F, 25.39. Found: C, 36.54; H, 2.46; S, 6.82; F, 24.86.

The compound decomposes above 145°.

Dibenzo-N-methylphenothiazine (DiB-N-MP). Dibenzophenothiazine was prepared from 2,2′-dinaphthylamine,[7] and subsequently methylated by the same procedure as phenothiazine. The melting point of dibenzophenothiazine was 230° (lit.[7] 232°). The yield was 77%. The melting point of the methylated compound was 287° and the yield was 85.1%. It was recrystallized from pyridine.

TABLE I: Optical Spectra of Cation Radicals in Acetonitrile Showing Band Maxima Positions and Extinction Coefficients

Compound	Band maximum mμ	Band maximum eV	Extinction coefficient
10-MPClO$_4$	850	1.46	1320
	760	1.63	1320
	512	2.42	7830
	480	2.58	6480
	312	3.98	2400
10-MPSbF$_6$	Same as above		
DiB-N-MPClO$_4$	720	1.72	9050
	568	2.18	2830
	500	2.48	3580

Anal. Calcd for $C_{21}H_{15}NS$: C, 80.43; H, 4.79; N, 4.47; S, 10.24. Found: C, 79.43; H, 5.00; N, 4.45; S, 10.39.

Dibenzo-N-methylphenothiazine Perchlorate (DiB-N-MPClO$_4$). DiB-N-MP being poorly soluble in ethanol, only 0.4690 g was dissolved in 750 ml at ~60° and 0.1889 g of I_2 in 30 ml of ethanol was added. After stirring the solution for 5 min, 0.3086 g of $AgClO_4$ in 5 ml of ethanol was poured in. The solution turned blue-black and a precipitate of AgI settled slowly to the bottom. Unfortunately DiB-N-MPClO$_4$ partly precipitated too; many extractions with ethanol were required to dissolve it from the silver iodide. After filtration and evaporation of the solvent, the salt was a black crystalline powder similar to the 10-MP salts. The yield was only 0.2764 g (44.8%). The salt was recrystallized from the same solvent–nonsolvent mixture as the 10-MP salts. It decomposes above 125°. The ir spectrum shows the presence of water not removed after several days of drying *in vacuo*.

Anal. Calcd for a hydrated 1:1 salt, $C_{21}H_{15}NS \cdot ClO_4 \cdot H_2O$: C, 58.53; H, 3.94; N, 3.25; S, 7.44; Cl, 8.23. Found: C, 59.15; H, 3.81; N, 3.11; S, 7.16; Cl, 8.20.

All synthesized compounds were stable in air for months.

Characterization. Optical Spectra. The uv and visible spectra of the salts in acetonitrile solution were taken on a Cary 14 spectrophotometer at concentrations of 2×10^{-5} to 10^{-4} *M*. Transmission spectra on the solids were taken in Nujol mulls on the same instrument.

Table I shows the band positions and extinction coefficients for 10-methylphenothiazine perchlorate and dibenzo-*N*-methylphenothiazine perchlorate. Beer's law is obeyed.

Esr Spectra. The solid salts were diluted with NaCl (1% of the salt). The concentration of the solutions was 8×10^{-4} *M*. The measurements were made at room temperature on a Varian E-3 spectrometer.

Electrical resistances were measured on pellets of compressed powder. The ac resistance was measured on a Tektronix curve tracer, Type 576, at 60 Hz. The higher resistances were measured in dc using a Keithley 610C electrometer. The oscilloscope display was a simple straight line indicating that the compounds obey Ohm's law.

Magnetic susceptibility measurements were made by Mr. Lever, Department of Chemistry, York University, Downview, Ontario. He used the Faraday method.

X-Ray spectra were run on powders using the General Electric XRD-6 wide angle diffractometer.

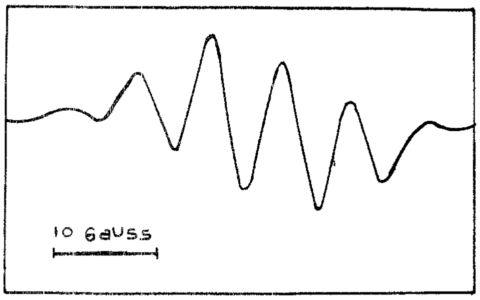


Figure 1. Esr spectrum of 10-MPClO$_4$ in acetonitrile: concentration 8 × 10^{-4} *M*.

Results

Esr Spectra. The esr spectrum of 10-MPClO$_4$ in acetonitrile is shown in Figure 1. The spectrum is exactly the same as obtained by other workers who oxidized the compound in sulfuric acid[8,9] or electrochemically.[10] The relative intensities of the lines are 1:4:7:7:4:1. The coupling constants of the electron with the nitrogen nucleus and the protons are A_N = 8.5 G and A_H = 7.4 G. DiB-N-MPClO$_4$ exhibits exactly the same solution spectrum.

The solid state spectra reduce to single lines of 4.95 and 5.3 G width respectively, indicating a large exchange effect.

X-Ray Data. Powder diagrams of the neutral 10-MP and its perchlorate salt are compared in Table II. The relative intensities of the strongest reflections are given.

Conductivity. All salts obey an exponential temperature dependence characteristic of semiconductors (Figure 2). The 10-MP salts exhibit very high σ_0 values and high activation energies. Many, Harnik, and Gerlich[11] postulated the relation

$$\sigma = \epsilon \mu N_0 \exp(-E/kT)$$

where μ is the drift mobility, ϵ the electron charge, and N_0 the effective density of states in the conducting levels of the crystal. N_0 was taken as 10^{21} from the number of molecules per cm^3 and the multiplicity of the first excited electronic level of each molecule. We used this relation to estimate maximum possible intrinsic drift mobilities. Table III summarizes the data obtained from conductance measurements.

Magnetic Susceptibility. The magnetic susceptibility of 10-MPClO$_4$ follows the Curie–Weiss law, as shown in Figure 3. The concentration of spins calculated from the Curie constant indicates one unpaired electron per cation radical. The constant Θ was −175°K showing antiferromagnetic interactions. In order to determine the energy of the interaction we applied the linear Ising model[12] which has been shown to fit similar crystalline organic free-radical systems reasonably well.[13] (The singlet–triplet model was also tested but proved unsatisfactory.) The susceptibility is given by

$$\chi_M = \frac{Ng^2 \mu_B{}^2}{4kT} \exp \frac{-J}{kT}$$

where N is the total number of spins, μ_B is the Bohr magneton, g the usual g factor, and J is the energy of interaction, often called exchange energy. The plot of log ($\chi_M T$) *vs.* $1/T$ gave a straight line (Figure 4), from the slope of which J was calculated to be 0.011 eV. Figure 5 shows the agreement between the experimental values of susceptibility and those calculated from the above equation using J = 0.011 eV. The low temperature divergence of the experimental points is attributed to a small amount of paramagnetic impurity. The overall behavior of the salt is, therefore, one of an antiferromagnetic substance in the ground state, which becomes progressively paramagnetic with increasing temperature.

DiB-N-MPClO$_4$, however, gave the susceptibility temperature dependence shown in Figure 6 (points). The curve can be reproduced to a large extent if we assume the material to act as an Ising solid with J = 0.036 eV, which contains about 15% of a paramagnetic impurity (Figure 6, solid line). The calculated higher temperature

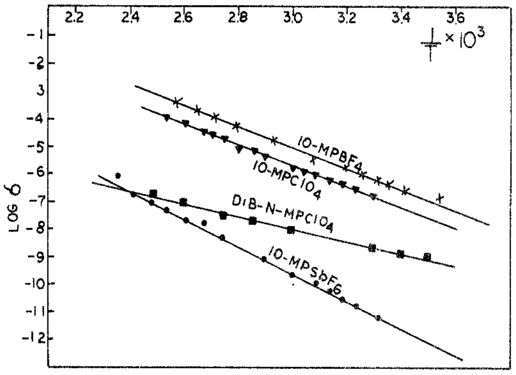


Figure 2. Temperature dependence of conductivity for the cation radical salts.

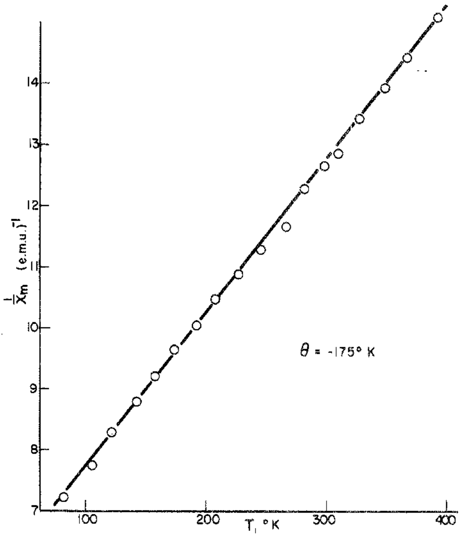


Figure 3. Reciprocal magnetic susceptibility *vs.* temperature for 10-MPClO$_4$.

TABLE II: Relative Intensities of Strongest X-Ray Reflections of 10-MP and 10-MPClO$_4$

Compound	*d* spacings of strongest reflections	Relative[a] intensity
10-MP	8.92	0.066
	4.97	0.056
10-MP	4.45	0.116
	3.72	0.200
10-MPClO$_4$	5.33	0.027
	4.97	0.048
	4.45	0.065
	3.54	0.110

[a] The intensities were corrected for Lorentz and polarization factors.

TABLE III: Data Obtained from Conductance Measurements

Compound	Conductivity at 25°, ohm^{-1} cm^{-1}	Activation energy, E, eV	σ_0, ohm^{-1} cm^{-1}	N_0	Estimated maximum drift mobility, μ, cm^2 sec^{-1} V^{-1}	Interaction energy, J, eV
10-MPClO$_4$	1.8×10^{-7}	0.73	1.8×10^{5}	1.9×10^{21}	5.8×10^{2}	0.011
10-MPSbF$_6$	1.6×10^{-11}	0.98	2.5×10^{5}	1.3×10^{21}	1.2×10^{3}	
10-MPBF$_4$	7.0×10^{-7}	0.75	1.8×10^{6}	2.0×10^{21}	5.5×10^{3}	
DiB-N-MPClO$_4$	2.5×10^{-9}	0.43	0.035	1.4×10^{21}	1.5×10^{-4}	0.036

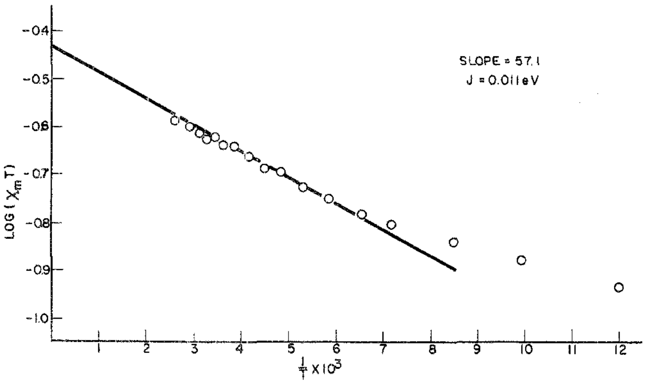


Figure 4. Ising model plot for 10-MPClO$_4$.

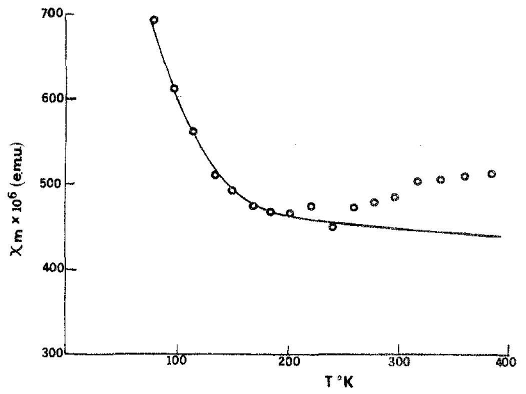


Figure 6. Magnetic susceptibility *vs.* temperature for DiB-N-MPClO$_4$: points, experimental; line, calculated from Ising model for J = 0.036 eV, assuming 15% of a paramagnetic impurity.

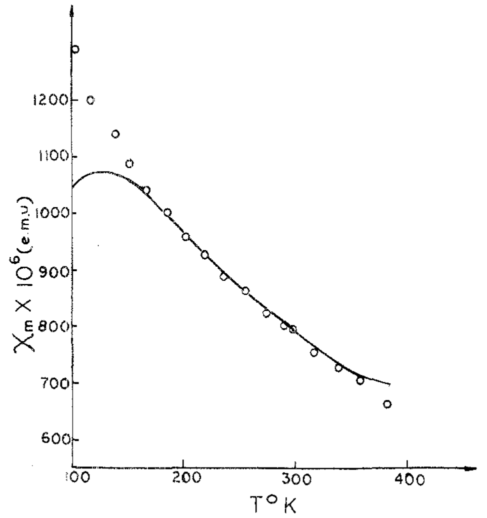


Figure 5. Magnetic susceptibility *vs.* temperature for 10-MPClO$_4$: solid line, calculated from Ising model equation using J = 0.011 eV; points, experimental.

susceptibilities deviate from the experimental curve. This may be due to a change in J with temperature caused by lattice expansion. Other workers have also reported that the interaction energy is a function of temperature.[1,14]

Discussion and Conclusions

Although the crystal structure of these salts has not been elucidated, the strongest reflection in the X-ray spectrum of 10-MPClO$_4$ was at 3.54 Å. This value is only slightly smaller than the strongest reflection for 10-MP itself (3.72 Å) the latter being the distance between parallel 10-MP molecules.

It has been recently shown that *N*-methylphenazinium tetracyanoquinodimethane, as well as TCNQ salts with inorganic cations, consist of linear chains of TCNQ$^-$ anions stacked essentially face to face, the interplanar distance between TCNQ molecules within a given chain being 3.26 Å.[3,15] It is worthwhile pointing out that *N*-methylphenazinium cations also formed linear arrays between TCNQ$^-$ chains.

Therefore it seems very likely that 10-MP and DiB-N-MP cation radical salts are also built up of alternating columns of cations and anions. The electronic structure becomes pseudo one dimensional with maximum π-electron interaction along the 10-MP$^+$ chains.

It follows that the state of the solid is largely paramagnetic at room temperature. However, the salts exhibit moderate electrical conductivities. Obviously not all the paramagnetic electrons are participating in conduction. Only those that can be excited to conduction levels behave as carriers. The paramagnetism is, therefore, due to the uncoupled electrons in the lowest antibonding π orbitals. The population of the conduction band is very small at room temperature or slightly above. The activation energy for conduction can probably be related to the Coulomb repulsion energy for the double cation as elucidated in the modified Hubbard model for one-dimensional conductors.[16] As would be expected, the conduction activation energy is lower for DiB-N-MP than for the smaller molecules since a double positive charge can be accommodated more easily in the larger molecule.

Under our conditions, the solid state spectra of 10-MCPlO$_4$ did not show evidence of an absorption edge at 0.73 eV. The solution absorption at 1.46 eV is reproduced in the solid state spectrum. However, we feel that though it is twice the conduction activation energy, they are probably not related.

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Structure of Aqueous Solutions. Structure Making and Structure Breaking in Solutions of Sucrose and Urea

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The effect of sucrose and urea on the librational band of water has been studied by infrared spectroscopy. Sucrose is found to produce little change in the band while all band characteristics are changed by the addition of urea. Comparison with changes produced by electrolytes indicates that the structural change produced by urea is different from that observed in electrolyte solutions.

The terms structure making and structure breaking have been used to describe aqueous solutions containing various solutes. From various measurements it was concluded that urea was a structure breaker while sucrose was a structure maker.[1,2] The region of the vibrational spectrum which corresponds to the librational energy of water molecules has been little studied although it may be expected to yield significant information on the hydrogen bonded structure in solutions. We present here a preliminary report of a study of the librational spectrum of water in solutions of sucrose and urea using a thin film infrared technique.

The spectra were obtained using a Perkin-Elmer 457 spectrometer and a thin film transmission technique in which a film of $\sim 7\ \mu$ thickness was held between KRS-5 plates. Appropriate corrections were made for reflection losses and variations in film thickness and reproducibility of better than 1% in band intensity could be maintained from run to run. Band intensities are adjusted to unit concentration of water and all intensities are quoted relative to that of pure water at 20°. The technique is reported in detail elsewhere.[3] The collected results for urea and sucrose at various concentrations and temperatures are collected in Table I. Also shown, for comparison, are results for selected ionic salts.[3,4]

Three of the four band characteristics reported in Table I show different behavior for urea and sucrose. The shift in band maximum with added solute shows a small decrease in energy with either sucrose or urea. This decrease is similar to that noted for a number of ionic salts. The band intensity increases much faster with added urea than it does for added sucrose. In this respect urea is similar to tetraethylammonium nitrate and potassium iodide; sucrose on the other hand resembles potassium nitrate. The decrease of intensity with temperature rise noted for urea is unique among the solutes studied; pure water and all other solutions examined show an intensity increase. The band asymmetry as measured by the asymmetry index[5] is markedly different for urea for which the asymmetry goes from negative for pure water to appreciably positive. The only other solutes for which positive asymmetry indices have been measured are $LiNO_3$, $NaClO_4$, LiCl, $BaBr_2$, NaI, and KI at very high salt concentrations (*e.g.*, for $LiNO_3$ concentration of 10 *m* the asymmetry index is +8).

Examination of the spectrum of water as the temperature is raised indicates that a gradual disruption of the water structure produces a small increase in band intensity, a marked decrease in the band maximum, and little effect on the band asymmetry. The salts NH_4Cl, NH_4Br, and to a lesser extent NH_4NO_3 and NH_4ClO_4 show concentration-dependent behavior which resembles this. The behavior of all other solutes is more complex.

Intensity increase with added solute is frequently large; the largest increases are noted when there is a great size difference between anion and cation (*e.g.*, LiI) or when the cation has aliphatic side chains (tetraalkylammonium cation). The former may be ascribed to the structure disruption produced by the dissimilar ion sizes while the latter may generally be ascribed to hydrophobic bonding. In