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Solid-State Properties of TCNQ, Perchlorate, and Bromide Salts of a Phenothiazine Derivative

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Three different salts, perchlorate, bromide, and TCNQ simple salts of the phenothiazine derivative, were prepared. Magnetic susceptibility, diffuse reflectance, and EPR were used to study the electronic properties of these compounds in the solid state. The most paramagnetic is the perchlorate, and bromide is less paramagnetic; this is attributed to the minor steric effect produced by the Br^- within a column formed by stacked radicals of promazine$^+$. CT bands of the ClO_4^- are those of a CT between ion radicals stacked flat upon each other where the unpaired π electrons form an overlap which produces a more than pairwise interaction. The stronger interaction among Br^- radicals is made evident mainly by a splitting of the CT band. From the ir spectra it can be concluded that the TCNQ–promazine salt is mainly ionic: $\mathrm{TCNQ}^{\overline{\cdot}}$ $\mathrm{Pro}^{\dot{+}}$ is diamagnetic as expected in compounds where an almost complete electron transfer is produced as shown by the EPR. TCNQ–promazine shows an absorption spectrum in the solid state with at least three maxima, which can be attributed to three transitions:

(a) the lowest-energy transition to $\mathrm{TCNQ}^{\overline{\cdot}}$: promazine$^{\dot{+}}$,

(b) the highest-energy transition to a CT among the cation radicals $\mathrm{Pr}^{\dot{+}}:\mathrm{P}\text{-}^{\dot{+}}$, and

(c) the intermediate energy band to a CT between the anion radicals $\mathrm{TCNQ}^{\overline{\cdot}}:\mathrm{TCNQ}^{\overline{\cdot}}$.

Introduction

Phenothiazine and its derivatives are diamagnetic molecules. The oxidation of these products gives cation radicals with an unpaired electron: many azo dyestuffs, such as methylene blue, are oxidation products of substituted phenothiazines. However, though there has been plenty of work done on the radical cation of phenothiazine and its derivatives in solution (*1, 2*), not much work has been produced on the solid state of these radicals.

In general, solid ion-radical salts have been of great interest because the ion-radical molecules form a plane to plane stacking into columns to give a large overlap between the half-filled π orbitals of each radical forming energy bands belonging to the crystalline complex (*3*).

The type of compounds in the solid state produces absorption bands, of which the longest-wavelength band has been definitely determined to be an intermolecular charge transfer between the stacked radicals, due to the interaction between the unpaired electron of each radical. Therefore, the appearance of the CT band is correlated with the magnitude of the intermolecular electron exchange interaction and this de-

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pends on the relative interatomic distances and orientation of the stacked radicals in the solid state.

Electronic absorption spectra and the magnitude susceptibility should be able to yield information concerning the interaction among solid radical salts (*4*).

We report here the preparation and solid-state properties of three salts of the phenothiazine derivative promazine: perchlorate, bromide, and TCNQ salts.

The magnetic susceptibility of these radicals based on the phenothiazine cation radicals and closed-shell diamagnetic counter ions such as ClO_4^- and Br^- is clearly associated with the phenothiazine nucleus. Therefore, they provide us with a simple case to study CT complexes where the magnetic properties are associated with only one stack. However, the TCNQ-promazine presents more difficulty in ascertaining the respective contribution of each stack to the magnetic susceptibility.

Experimental

(*A*) *Compounds*

The formulas of promazine and TCNQ are given in Fig. 1. Promazine was supplied by a pharmaceutical laboratory and TCNQ by Aldrich. Both compounds were purified before use. ClO_4H and all other solvents employed are from Merck.

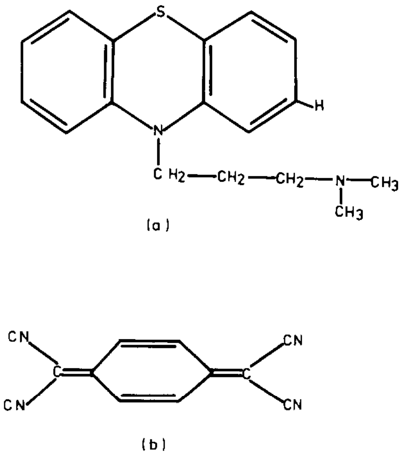

FIG. 1. (a) Promazine. (b) 7,7,8,8-Tetracyano-*p*-quinodimethano.

(*a*) *Perchlorate*. In order to obtain the cation radical in the solid state the Merkle method was used (*5*). The melting point of this salt is 223°C. This cation is stable in the presence of air indefinitely and no change is experienced in the composition or properties even after a considerable length of time. The elemental analysis is $C = 41.15\%$, $S = 6.38\%$, $N = 5.58\%$, $H = 4.82\%$, and $Cl = 14.12\%$. These values agree with the proposed formula given by Merkle for chlorpromazine perchlorate (*5*).

(*b*) *Bromide*. The bromide cation radical was prepared by the oxidation of the organic compound dissolved in acetic acid with bromide, as was described by Kerhmand and Diserens (*6*). The elemental analysis for this compound is $C = 33.80\%$, $H = 3.34\%$, $S = 5.31\%$, $N = 2.98\%$, and $Br = 52.91\%$. From this analysis the bromide content is as high as 4 Br for each promazine molecule. The melting point of this compound is 152°C.

(*c*) *TCNQ-promazine*. This salt was obtained by dissolving equimolecular quantities of both compounds in acetonitrile and letting the mixture evaporate at room temperature. The salt crystallizes as very brittle dark-green needles of varying size. The melting point of this radical salt is 162°C. The elemental analysis indicates that the composition of this salt is 1 : 1.

(*B*) *Equipment*

A CARY-17 was used to obtain the visible spectra of the radicals in solution. Solutions of 9 *N* H_2SO_4 and acetonitrile were employed as solvent for the salts. A Beckmann IR-20 was used to obtain the ir spectra of these salts in the solid state. The spectra were recorded as usually, employing KBr as an inert matrix at a 200 : 1 ratio.

(*C*) χ *Measurements*

Magnetic susceptibilities were obtained by the Faraday method. Samples in powder form were tightly packed in quartz tubes 4 mm in diameter and 8 mm in height. The tubes were placed in a double cylinder of glass in which a thermostated liquid was circulated between the constant $B\, \partial\, B/\partial x$ pole caps of a F-M6 Bruker electromagnet. The force acting on each sample, which weighed approximately 0.06 and 0.07 g, was of the order of 10^{-2}–10^{-3} μG depending on the magnetic field H in a 3-cm gap with pole pieces $H\, \partial\, H/\partial x$ 21.54 kG · cm^{-1} for 30 A and $H\, \partial\, H/\partial x = 12.21$ kG · cm^{-1} for 20 A. For the elimination of ferromagnetic impurities X was obtained from (χ, $1/H$) plot by extrapolation of χ to $1/H = \infty$. Slopes of the order of 10^{-4}–10^{-5} G were obtained, i.e., the samples contained very low concentrations of ferromagnetic impurities with reference to the standard used, which was $C_{10}H_{22}$ (Merck), for which a value of $\chi = 0.8523 \times 10^{-6}$ cgs was taken (*7*).

Each sample was measured ten times at two different field strengths (13.35 and 10.33 kG) in a vacuum of 10^{-2} Torr. The accuracy of the measurements of χ is $\pm 0.5\%$.

(*D*) *EPR Spectra*

EPR spectra were recorded working in χ band with a Varian E-12 spectrometer. All recordings were carried out at room temperature. Samples were placed inside a quartz capillary and measured in the presence of air. The spectra are derivative spectra. The microwave power was 5 mW, enough not to saturate the resonance and the field modulation was 0.4 G. The accuracy is of 0.001%. The standard taken is peroxilamine disulfonate potassium with a $g = 2.0053$.

(*E*) *RD Spectra*

A Beckmann DK-2A with the corresponding attachment was used. Wavelength ranged from 400 to 2500 nm. The radiation source was a tungsten lamp and the detector was lead sulfide. Pure samples were used as well as samples where the salt under analysis was dissolved in an optically inert KBr matrix. The ratio between the cation radical and solvent was 1 : 200, and the spectra were recorded as the difference of absorbance between the mixture and pure KBr.

Results

In order to study the solid-state properties of these compounds one must consider that the principal difference between the three salts is that TCNQ : Pro is formed by two organic open-shell ions, $TCNQ^{\bar{\cdot}}$ and $Prom^+$, both being responsible for such properties. However, the other two salts are formed by closed-shell anions ClO_4^- and Br^- and the cation $Prom^+$, this latter being responsible for the solid-state properties.

(*a*) *Infrared Spectra*

To characterize the TCNQ salt we proceeded as follows: if the vibrational spectrum resembled those of the component compounds then the salt would be a molecular type D : A, but if the vibrational spectrum of the salt consists of the ionized components then the association is mainly ionic $D^{\dot{+}} : A^{\dot{-}}$ (*8*). Thus Fig. 2a shows the spectrum of the neutral promazine. The Fig. 2b spectrum is that of the ClO_4^- promazine, which is completely different from (a), being characterized as the ionic form corresponding to Pr^+. The (c) spectrum corresponds to the salt $TCNQ^- : Pro^+$ and this is similar to the (b) spectrum though the electronic absorption of this compound yields smaller signal-to-noise for the vibrational features than does the ClO_4^- salt.

(*b*) *Solution Spectra*

In order to characterize the solid-state spectra of the promazine cation radical

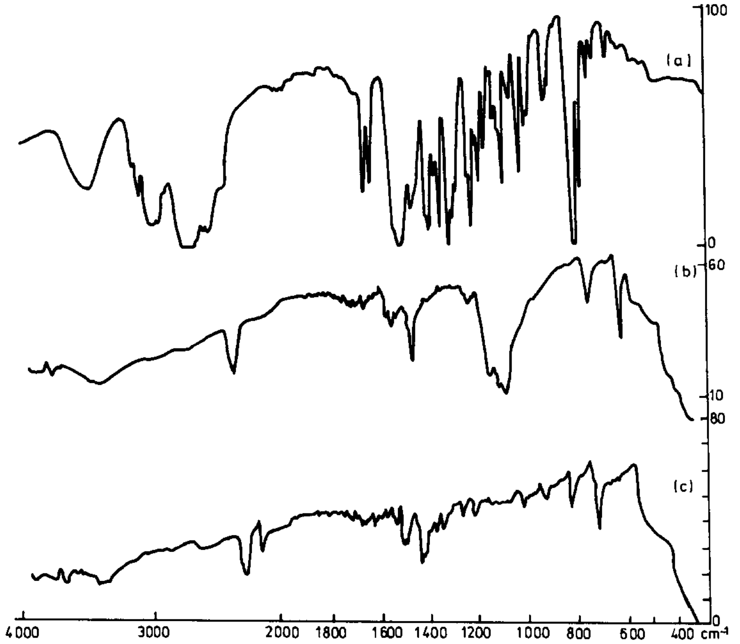

FIG. 2. Infrared spectra of (a) neutral promazine, (b) ClO_4^- promazine, and (c) TCNQ–Pro.

salts, the absorption spectra of the three compounds in solution are presented.

—ClO_4^- promazine: This cation radical salt was dissolved in 9 *N* H_2SO_4, which provides an acid-stabilized solution, because in a less acid solution the radical rapidly decays (*8*). The intense coloration of the solution indicates the existence of the semiquinone in solution, as the sulfoxide or neutral form is uncolored (*9*). The ClO_4^- ion gives no signal in the visible region, therefore the absorption spectrum of this salt seems to be due to the phenothiazine derivative cation radical monomer (*10*). The spectrum shows a weak band composed of several vibrational structures from 775 to 865 nm and a very strong band at 518 nm.

—Bromide promazine: The solution of this radical is similar to the above, however, the maxima are strongly displaced to the red. The major maximum is found at 560 nm and vibrational structure at 680 and 740 nm. Therefore the maximum is displaced 42 nm. This seems to be caused by a substitution of a Br^- in the phenothiazine nucleus (*11*).

—Crystals of TCNQ–promazine in acetonitrile produced an intense green color, characteristic of $TCNQ^-$ ion (*12*). The spectroscopic study of this solution presents maxima corresponding to the $TCNQ^-$ anion. Thus 240 and 842 nm are the major maxima and 744, 760, 680, and 665 are minor bands. However, no maximum corresponding to the cation radical of promazine was found. Also, no other transition was found in the near-ir range which could correspond to a CT band.

The ir spectrum of TCNQ–Pro, together with the lack of a CT band in the solution spectra, clearly indicates that this salt is not molecular but ionic as $TCNQ^{\overline{\cdot}}$: Pro^{+}.

(*c*) *Solid-State Spectra*

Promazine perchlorate. The diffuse reflectance of this compound shows two bands, one at 50 nm and another at approximately 850 nm, and no other transition was obtained up to 2500 nm. The characteristics of these bands are different from those of the same radical in solution. Thus the position of the first band matches the spectrum of the same radical in solution, although it is slightly displaced toward the blue zone. These transitions of the monomer are supposed to be affected by the field of the other cations and cause a shift in the $\pi \rightarrow \pi^*$ band (*3*).

The second band exhibits typical characteristics of charge transfer, for it is wide without very well defined maxima. Therefore, this transition can be considered a CT band produced by the interaction between the unpaired electron of the half-filled π orbital or each radical within a column in the solid:

$$(\mathrm{Pr}^+ \;.\;.\;.\;.\; \mathrm{Pr}^+ \;.\;.\;.\;.\; \mathrm{Pr}^+ \;.\;.\;.\;.\; \mathrm{Pr}^+ \;.\;.\;.\;.)$$

$$(\mathrm{Pr}^0 \;.\;.\;.\;.\; \mathrm{Pr}^{2+} \;.\;.\;.\;.\; \mathrm{Pr}^0 \;.\;.\;.\;.\; \mathrm{Pr}^-).$$

This CT band (Fig. 3a) appears to superpose upon the vibrational structure of the radical cation in solution, which is observed at 775–865 nm, since the intensity of the CT band is considerably stronger than the vibrational structure of the monomer in solution.

Promazine bromide. In this spectrum two bands can also be appreciated (Fig. 3b). There is one at about 500–600 nm and an-

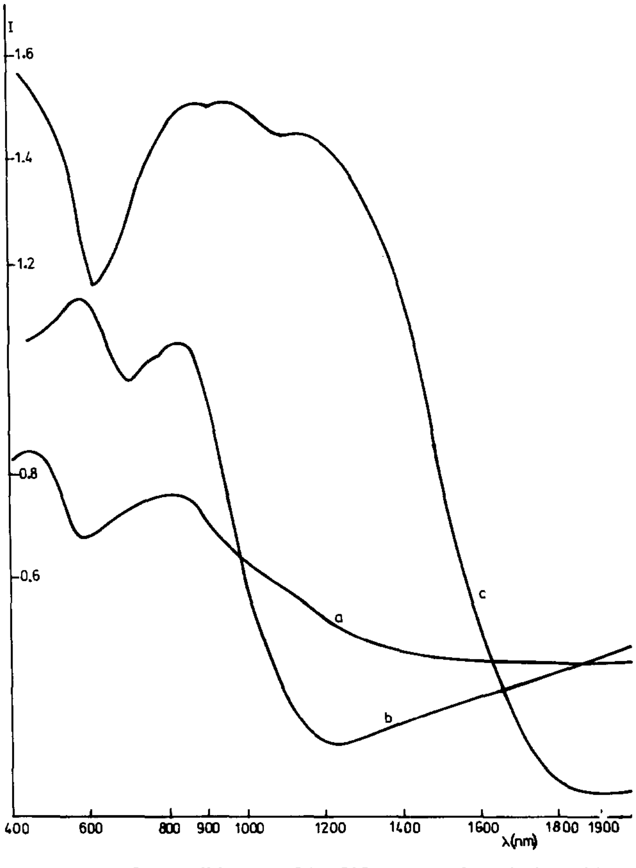

FIG. 3. Absorption spectra of the solid state of (a) ClO_4^- promazine, (b) bromide promazine, and (c) TCNQ : Pro.

other at 800–900 nm, and no other transition was obtained up to 2500 nm. The first seems to correspond to that of the cation radical in solution, and the second corresponds to the CT band of the perchlorate radical cation at approximately the same wavelength. However, there is a splitting of this band and although it is not completely resolved it seems to consist of two prominent peaks (*13*).

TCNQ–promazine. In the absorption spectrum of this solid there can be distinguished three bands which do not appear in the spectrum of the salt in solution (Fig. 3c).

The band at 1200 nm is supposed to be the charge transfer band produced between TCNQ$^-$ and Pro$^+$ (*14*). In the 800- to 100-nm range, there appear to be two bands very close to each other, and the one at 800 nm must be considered to be the same as that obtained for ClO$_4^-$ and Br$^-$ salts since it comes at the same wavelength; however, the one at 1000 nm can be considered to be an anion–anion transition.

(*d*) *Magnetic Susceptibility*

Charge transfer interaction between ion radicals produces a marked decrease in the magnetic susceptibility of these salts (*15*).

Table I gives the values of the magnetic susceptibilities for the three compounds. The diamagnetic contribution was estimated from the values of diamagnetic susceptibilities of the components on the assumption that the value for a neutral organic molecule may be used in place of the molecule ion. (However, when the neutral organic molecule is changed into an ion, it may become coplanar and this would result in a small increase in diamagnetic susceptibility.) The values for the phenothiazine derivative and TCNQ were taken from Pascal's constants and for ClO$_4^-$ and Br$^-$ from Mulary (*16*).

The value of the magnetic susceptibilities given in Table I must be necessarily related to the interaction degree of the radicals in the solid state.

For the first two compounds, the difference in the χ_m could be attributed to the steric effect to the counter anions ClO$_4^-$, and the distance between the cation radicals will be shorter and consequently the interaction between them stronger, with its χ_m value lower than the corresponding perchlorate value.

TCNQ–promazine is a diamagnetic compound and temperature independent (from room temperature to 80°C). This salt seems to exist as $D^{\dot{+}} : A^{\dot{-}}$ with an almost complete electron transfer, in a diamagnetic singlet ground state with a corresponding paramagnetic triplet excited state (*12*). The degree of electron transfer is indicated by the EPR measurements (*17*).

The CT band of this compound is the strongest of the three and this agrees with the fact that diamagnetic or very slightly paramagnetic compounds apparently produce very strong CT (*17*).

TABLE I

MAGNETIC SUSCEPTIBILITIES OF THE SALTS

Promazine	MW	Observed suscept. at 294°K (cgs/mole) 10^{-6}	Ass. diamagnetism (cgs/mole) χ_d (-10^{-6})	Magnetic suscept. $\chi_m 10^{-6}$ (cgs/mole)
ClO$_4^-$	502.25	+1.340	257.50	+930.45
Br$^-$	603.91	+0.352	302.30	+514.67
TCNQ$^-$	488.6	−0.531	269.46	(+6.45

(*e*) *EPR Spectra*

In order to obtain information on the origin of the unpaired electron, g values were determined for powder samples by EPR measurements at room temperature. The spectra of the three compounds are displayed in Fig. 4.

The spectra of ClO_4^- and Br^- indicate that the unpaired electron is situated in an axial symmetry field. ClO_4^- shows existence of hyperfine structure with an asymmetrical pattern, due to the g factor asymmetry, and its values are $g_1 = 2.009$, $g_2 = 2.007$, $g_3 = 2.004$, and the g average will be $g_{av} = 2.0065$ (Fig. 4a).

The bromide lacks hyperfine structure with a g value of 2.0072.

The variation in these two compounds is mainly in the steric effect of the counter anions, which is very important because the repulsion and interaction between the charges depend on the separation between two adjacent radicals and this distance is a consequence of the size of the counter anions.

Therefore the difference in the two EPR spectra must be due to the different steric effect produced by the two counter anions. As the steric effect of Br^- is reduced compared to that of ClO_4^-, the interaction among the radicals will be stronger and consequently a larger linewidth of the spectrum appears (Fig. 4b) in the bromide.

For TCNQ–promazine a single exchange-narrowed absorption line was observed with only a g value of 2.0032 (Fig. 4c). This value must be the average contribution to the magnetic susceptibility of the cation Pr^+ and the anion $TCNQ^{\overline{\cdot}}$.

The spectrum of this salt in dimethylphormamide solution gives only an EPR signal with hyperfine structure. It was not possible to find another EPR signal which could correspond to the other ion component of the compound.

Conclusions

Ion radical salts are assumed to exist in the solid state as columns in which each radical is stacked upon an other radical. The overlap of the half-filled π orbital of each radical produces a charge transfer which shows up in the absorption spectra in the visible and near-ir range. The appearance of the CT band is correlated with the degree of magnetic susceptibility.

As the properties studied in the perchlorate and bromide salts are a consequence of the contribution of the stack formed by the

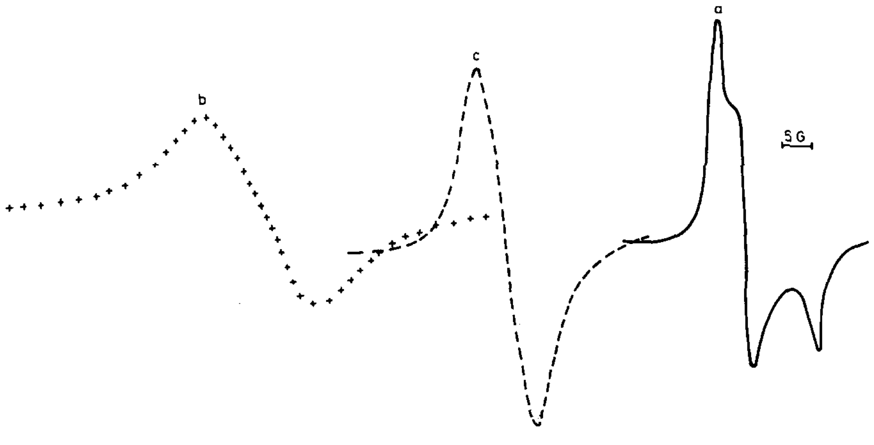

FIG. 4. EPR spectra of (a) ClO_4^- promazine, (b) bromide promazine, and (c) TCNQ–Pro.

cation radical promazine, they provide us with a method to identify the contribution of the other type of stack formed by the anion in the TCNQ : promazine salt.

Thus the most paramagnetic salt produces the weaker band, the variation of the χ_m in the ClO_4^- and Br^- salts must be a consequence of the different steric effect produced by the two counter anions, the minor steric effect produced by the Br^- gives rise to a stronger interaction between the radicals, which shows in a lower χ_m and a splitting of the CT band, and also the bandwidth of the EPR signal indicates stronger interaction in the bromide salt. As the CT band appears at the same position as that of the dimer CT in solution (*3*), it could be thought that this transition could be of only a dimer type in the solid. However, the radicals are closer to each other in the solid than in solution. The CT transitions must be related more than pairwise.

The simple salt TCNQ–promazine is diamagnetic, which agrees with a model of $D^+ : A^{\dot{-}}$ with a diamagnetic singlet ground state and a triplet excited state. The EPR measurements give an idea of the degree of charge transfer produced in the salt, practically one electron. Also, from the ir spectra an ionic pattern can be appreciated.

Reflectance diffuse spectrum of the solid indicates that three different transitions occur in this salt:

(a) There is a $TCNQ^- : Pro^+$ transition at longest wavelength.

(b) The shortest-wavelength transition must be the CT band produced between the cations $Pr^+ \ldots Pr^+ \ldots Pr^+$.

(c) The intermediate band probably corresponds to the transition between the anions $TCNQ^- : TCNQ^- : TCNQ^-$ (*19*). The overlapping of the band c bands can be attributed to the equivalent energy of both transitions. The fact that the intensity of the intermolecular transition of TCNQ and promazine is comparable to the intensity of the absorption bands of the intramolecular transitions of the component ions indicates that the CT is quite strong.

For comparison with other similar compounds the most probable structure of TCNQ : promazine is similar to the NMP–TCNQ structure (*4*) formed by two parallel columns of both TCNQ and Pro^+.

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