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A Correlation between the Magnetic and Optical Properties of Some Cation Radical Salts

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The paramagnetic susceptibilities of the cation radical salts formed by the oxidation of phenothiazine (PT), *N*-methylphenothiazine (MPT), and thianthrene (TA) with antimony pentachloride have been reported in a previous paper.1) The variation in the susceptibilities for PT·$SbCl_4$ and PT·$SbCl_5$ with temperature has been explained in terms of the linear Ising model; thus, the spin-exchange coupling parameters (J) have been determined to be 0.034 and 0.0042 eV respectively. The susceptibilities for MPT·$SbCl_5$ and TA·$SbCl_5$, on the other hand, obeyed the Curie-Weiss law above 100°K. The Weiss constants (θ) for these salts were found to be -5 ± 10°K and 0 ± 4°K respectively.

In this paper we will report a finding of correlation between the values of the spin-exchange coupling parameter and the intensities of the absorption band in the near-infrared region of the solid cation radical salts. The static susceptibility of phenothiazine bromide (PT·Br), which was prepared by the procedure of Kehrmann and Diserens,2) was also measured as a function of temperature with a Faraday-type magnetic balance. The absorption spectrum of a solid radical salt was obtained with a powder sample suspended in liquid paraffin.

Results and Discussion

Solid phenothiazine bromide was found to be diamagnetic at room temperature (-14.3×10^{-5} emu/mol). After corrections had been made for the diamagnetism and for a small paramagnetism due to impurities, the intrinsic paramagnetic susceptibility for the bromide was found to be 1.2×10^{-5} emu/mol at 296°K, and to decrease with a decrease in temperature. The change in the paramagnetic susceptibility with temperature was found to fit well the curve calculated from the linear Ising model, for which J was taken to be 0.12 eV.

The values of the spin-exchange coupling parameter for MPT·$SbCl_5$ and TA·$SbCl_5$ were not given explicitly in the previous paper. If we assume that the linear Ising model for which the relation

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$J = -k\theta$ holds in the temperature region $T \gg J/k$, is applicable to the paramagnetism of the salts, the parameter can be estimated from the observed value of a Weiss constant. The values thus calculated are listed in Table 1.

TABLE 1. EXCHANGE COUPLING PARAMETER FOR THE SALTS STUDIED

Compound	J (eV)
TA·SbCl$_5$*	$\sim$ 0
MPT·SbCl$_5$*	$\sim 4.3 \times 10^{-4}$
PT·SbCl$_5$*	4.2×10^{-3}
PT·SbCl$_4$*	3.4×10^{-2}
PT·Br	$\sim 1.2 \times 10^{-1}$

* The paramagnetism of these salts originates entirely from the respective mono-positive organic molecules and antimony pentachloride is thought to be forming closed shell negative ions.[1]

The absorption spectra for solid TA·SbCl$_5$ and MPT·SbCl$_5$ were found to correspond well to the spectra of the respective solutions in dichloromethane, and no extra band could be observed in the spectra of the solids, as is shown in Fig. 1. This result reveals that the cation radicals in a solid are nearly as free as in a solution. The same conclusion has been derived from the magnetic susceptibility measurements, which have shown negligible values of the spin-exchange coupling parameter for these salts.

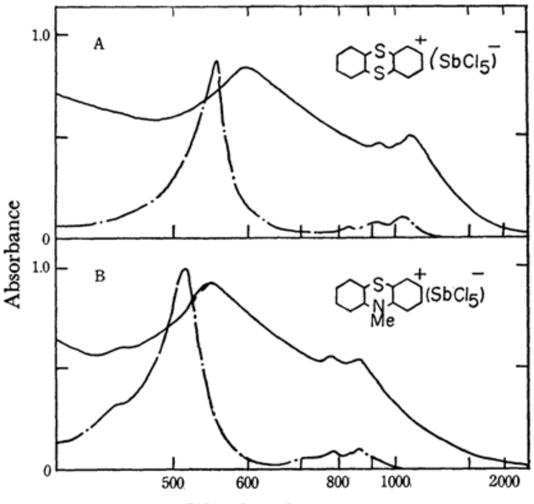

Fig. 1. A, The absorption spectra of thianthrene mono-positive ion. ——— Solid TA·SbCl$_5$, —·—·—·— dichloromethane solution; B, The absorption spectra of *N*-methylphenothiazine mono-positive ion. ——— Solid MPT·SbCl$_5$, ——·——·——·— dichloromethane solution.

The spin-exchange coupling parameters for the three kinds of radical salts of phenothiazine, PT·Br, PT·SbCl$_4$, and PT·SbCl$_5$, were larger in value than those for MPT·SbCl$_5$ and TA·SbCl$_5$, and their values decreased in this sequence, as Table 1 shows. The solution spectra of all these phenothiazine salts showed the same pattern, a pattern which was also in agreement with that reported for a phenothiazine mono-positive ion by Shine and Mach.[3] When the salts were formed into a solid, they showed extra absorption bands in the near-infrared region, where no absorption was found in the solution spectra. As is shown in Fig. 2, PT·Br, PT·SbCl$_4$, and PT·SbCl$_5$ exhibited new absorption bands at 900, 1070, and 1000 mμ (shoulder) respectively. The band for PT·Br was found to be the strongest in intensity among the salts; this fact is consistent with the fact that the spin exchange coupling parameter for the salt is the largest in value. The absorption bands for the phenothiazine salts decreased in intensity in the same sequence as the spin-exchange coupling parameters, though little difference was found with respect to the position of the absorption band.

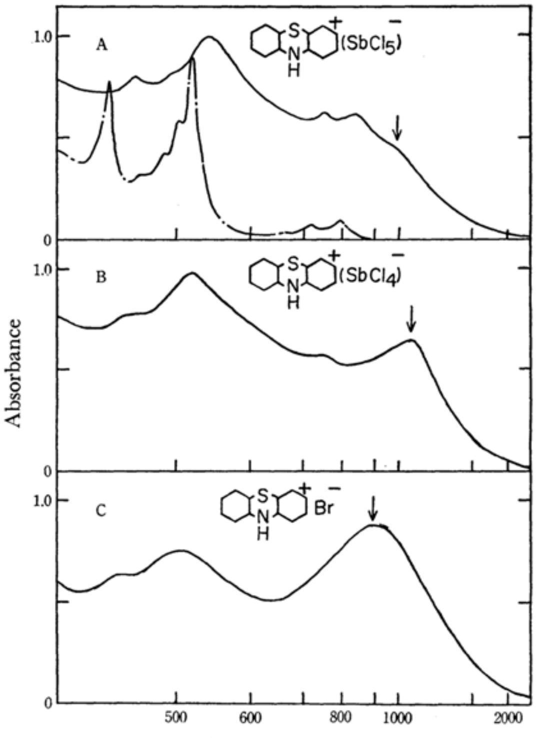

Fig. 2. The absorption spectra of phenothiazine mono-positive ion. A, ——— Solid PT·SbCl$_5$, —·—·—·— dichloromethane solution; B, Solid PT·SbCl$_4$; C, Solid PT·Br. The position of the charge-transfer absorption band for the respective salt is indicated by an arrow.

The new absorption band is regarded as arising

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3) H. J. Shine and E. E. Mach, *J. Org. Chem.*, **30**, 2130 (1965).

from charge-transfer interaction between phenothiazine cation radicals in the solid. When phenothiazine radicals are stacked in a face-to-face manner, forming chain-like arrays of molecules, as is known in the structure of some radical salts,[4)] the charge-transfer absorption may be expressed as a transition of the type $<\cdots D^+D^+D^+D^+\cdots> \rightarrow <\cdots D^+D^{2+}D^0D^+\cdots>$, where D denotes a phenothiazine molecule. The excitation energy of the transition is not greatly influenced by a small change in the intermolecular distance or mutual orientation, for it is essentially determined by the difference between the ionization potential and the electron affinity of the phenothiazine *mono-positive ion* radical (D^+). This is in agreement with the observed insensitivity of the band positions in the three phenothiazine radical salts.

The spin-exchange coupling parameter and the intensity of a charge-transfer band are both thought to be approximately proportional to the square of an overlap integral between neighboring radicals. A relatively small change in the intermolecular distance or mutual orientation may cause a somewhat large change in the overlap integral; this change, in turn, results in the different intensity of the charge-transfer absorption and in the different value of the spin-exchange coupling parameter. This may be what has been observed with the three kinds of phenothiazine radical salts. The same interpretation can be given to the appearance of intense charge-transfer absorption bands with the radical salts, such as *p*-phenylenediamine bromide,[5)] Würster's blue perchlorate at 77°K,[5-9)] and alkali metal salts of 7,7,8,8-tetracyano-*p*-quinodimethan,[10,11)] which exhibit strong antiferromagnetic spin-exchange coupling.

From the observed correlation between the magnetic and optical properties, it may be inferred that the spin-exchange coupling parameter, J, is determined mainly by the charge-transfer interaction in these salts. A qualitative explanation may be made by considering, for the sake of brevity, a particular pair of adjacent radicals in a chain. The pair of identical radicals gives rise to a singlet (non-magnetic) state and a triplet (magnetic) state, for which the relative positions are determined, to a first approximation, by an exchange integral between the paired radicals. The excited charge-transfer configuration specified above, which is usually singlet, will then interact with the ground state and stabilize its energy, while the triplet state remains unaffected, thus leading to a further separation of the singlet-triplet energy gap. This view of the situation, when extended to a linear array of radicals, implies that the charge-transfer configurational interactions also contribute to the determination of the relative energy levels of the magnetic and non-magnetic states. Therefore, it appears that the sign and magnitude of a spin-exchange coupling parameter are sensitively dependent on the relative energies of the exchange interaction and the charge-transfer configurational interaction effects. For the cation radical salts studied here, it is likely that the stabilization energy due to the latter effect is of primary importance rather than that due to the former.

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