

Magnetic and Optical Properties of Aromatic Hydrocarbon Cation Radical Salts

Yoichiro SATO, Minoru KINOSHITA, Mizuka SANO*¹ and Hideo AKAMATU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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Stable cation radical salts were prepared by oxidation of perylene, 9,10-diphenylanthracene, 9,10-dimethylantracene, and 9,10-dichloranthracene with antimony pentachloride. Perylene perchlorate was also obtained in a stable form. From the temperature variations of their paramagnetic susceptibilities, the exchange coupling constants for these salts were found to increase in the sequence of above listing ranging from ~ 0 to 8.5×10^{-2} eV. The absorption spectra of these solid compounds were compared with those observed with solutions. While the absorption bands of each salt in the visible region were found to correspond to those of the solution spectrum of the respective compound, an extra absorption band was observed in the near-infrared region for compounds with larger exchange coupling constants. The appearance of the new absorption band was reasonably ascribed to charge-transfer interaction between the radicals. These observations are considered to support further our previous suggestion that the magnitude of the exchange coupling constant obtained through magnetic measurements is basically determined by the stabilization energy due to the charge-transfer configurational interaction.

In the magnetic behaviors of organic radicals, when they are formed into solid, a deviation from the Curie or Curie-Weiss law has often been found in a commonly available temperature range. The anomaly of paramagnetism is caused by the interaction between radicals, and has been interpreted in terms of an exchange-coupled linear chain model.¹⁻⁶ The model has been applied to various organic radical crystals and their magnetic behaviors have been characterized by an empirical parameter, that is by the exchange coupling constant (J). It should be noted that, if the parameter could be explained on the basis of molecular wavefunctions, the interaction in organic radical crystals would be better understood through such a parameter.

We have suggested the importance of charge-transfer interaction in the observed exchange coupling constant, based on the correlation found between the exchange coupling constants and the charge-transfer absorption bands for phenothiazine, *N*-methylphenothiazine and thianthrene cation radical

salts.⁷ The present work is intended to confirm the contribution of charge-transfer interaction to magnetic behaviors of organic radical crystals by the measurements of paramagnetic susceptibilities and charge-transfer absorption bands for aromatic hydrocarbon radical salts.

Lewis and Singer⁸ have prepared a number of aromatic hydrocarbon cations in solution with a skillful technique, and observed their ESR hyperfine structures. We have tried extensively to obtain crystalline radical salts from a variety of aromatic hydrocarbons treated with antimony pentachloride. So far tested, perylene (P) and anthracene derivatives substituted at 9 and 10 positions, *i. e.*, 9,10-diphenylanthracene (DPA), 9,10-dimethylantracene (DMA) and 9,10-dichloranthracene (DCA) have formed stable monopositive ion radical salts at room temperature. Another stable cation radical salt has been prepared from perylene as perchlorate.

Experimental

Preparation. Stable cation radical salts were prepared by the following procedures and the compositions of the solid salts were determined by elementary analysis of carbon, hydrogen and chlorine. No appreciable chlorination of the hydrocarbons was observed,

*¹ Present address: Department of Materials Science, The University of Electro-Communications, Chofu, Tokyo.

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which was checked by elementary analysis of the hydrocarbons recovered from the salts by hydrolysis. X-Ray diffraction of the powdered samples of all the salts gave distinct, crystalline patterns.

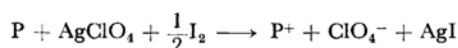
DPA·SbCl₅: To a solution of 9,10-diphenylanthracene in dichloromethane was added a dichloromethane solution of SbCl₅ in an excess amount (2 to 3 equivs.). Dark blue crystalline powder precipitated, the composition of which was determined to be C₂₆H₁₈·SbCl₅. This salt was found to be the most stable among the salts of aromatic hydrocarbons prepared here.

P·SbCl₅: Dark green powder with the composition of C₂₀H₁₂·SbCl₅ was obtained by adding a dichloromethane solution of SbCl₅ to a solution of perylene.

DMA·SbCl₅: The greenish product of C₁₆H₁₄·SbCl₅ was obtained from 9,10-dimethylantracene by a similar procedure. The addition of a nearly equivalent amount of SbCl₅ seemed preferable for the preparation.

DCA·SbCl₅: The greenish product of C₁₄H₈Cl₂·SbCl₅ was obtained when 9,10-dichloranthracene was used in place of 9,10-dimethylantracene.

P·ClO₄: To a nearly saturated solution of 1 mmol perylene in dichloromethane, 1 mmol AgClO₄ dissolved in a very small amount of acetonitrile was added, and then mixed thoroughly. When a dichloromethane solution of 0.4 mmol iodine was poured into the solution with stirring, color characteristic of perylene monocation appeared immediately, and then dark green powder precipitated. No noticeable oxidation of perylene occurred by the addition of either AgClO₄ or iodine only. An elementary analysis indicated the composition to be C₂₀H₁₂ClO₄·AgI with high reproducibility. An X-ray diffraction pattern of the product revealed the inclusion of silver and iodine in the form of AgI. From these observations, the product was found to be a homogeneous mixture of P·ClO₄ and AgI in an equivalent amount, which was formed as follows,



Measurements. In the same manner as described in a previous paper,¹⁾ the static susceptibilities of the salts were measured with a Faraday-type susceptibility microbalance in the temperature range from 77 to 296°K. The measurement was made at three different field strengths up to 15 k gauss in order to check ferromagnetic impurities. The susceptibility balance was calibrated

by referring to distilled oxygen-free water, for which the susceptibility was taken to be -0.720×10^{-6} emu/g at room temperature.

The absorption spectra of solid radical salts dispersed in liquid paraffin were measured in the range from 340 to 2500 mμ at room temperature. The solution spectra were observed by using dichloromethane as a solvent.

Results

Magnetic Susceptibilities. The salts formed by the reaction with SbCl₅ were found to be strongly paramagnetic at room temperature. As the temperature was lowered, the paramagnetic susceptibilities of DPA·SbCl₅ and P·SbCl₅ continued to increase, while those of DMA·SbCl₅ and DCA·SbCl₅ reached a maximum at about 80°K. Perylene perchlorate was found to be diamagnetic and showed a little change in susceptibility with temperature.

Diamagnetic contribution was estimated from the value of diamagnetic susceptibility of each component. The experimentally determined value of diamagnetic susceptibility for a neutral organic molecule was used in place of the value for the molecular ion, *i. e.*, -167×10^{-6} for perylene, -234×10^{-6} for 9,10-diphenylanthracene, -146×10^{-6} for 9,10-dimethylantracene, and -167×10^{-6} emu/mol for 9,10-dichloranthracene. The values for SbCl₅⁻ and SbCl₆⁻ were taken to be -124×10^{-6} , and -139×10^{-6} emu/mol, respectively, following Kainer and Hausser.⁹⁾ The diamagnetic susceptibilities calculated from these values are given in Table 1, together with the observed susceptibilities at 296°K and the paramagnetic susceptibilities χ_p estimated by subtracting the diamagnetic contribution.

The paramagnetic susceptibility of P·SbCl₅ was found to obey the Curie-Weiss law, while that of DPA·SbCl₅ obeyed the Curie law. The values of the Curie constant and the Weiss constant were determined by plotting the inverse paramagnetic susceptibility $1/\chi_p$ against temperature, as shown

TABLE 1. MAGNETIC SUSCEPTIBILITIES AND EXCHANGE COUPLING CONSTANTS

Substance	Observed susceptibility at 296°K $\times 10^6$ (emu/mol)	Diamagnetic susceptibility $\times 10^6$ (emu/mol)	Paramagnetic susceptibility at 296°K $\times 10^6$ (emu/mol)	Weiss constant θ (°K)	Radical concentration (%)	Exchange coupling constant J (eV)
DPA·SbCl ₅	752	-373	1125	0 ± 4	89	~0
P·SbCl ₅	707	-291	998	-4 ± 4	80	3.4×10^{-4} *
DMA·SbCl ₅	467	-270	737		(74-89)	6.9×10^{-3} *
DCA·SbCl ₅	234	-291	525		(52-63)	6.9×10^{-3} *
P·ClO ₄	-195	-209	14			8.5×10^{-2} **

* The value calculated according to the linear Ising model.

** The value calculated according to the singlet-triplet model.

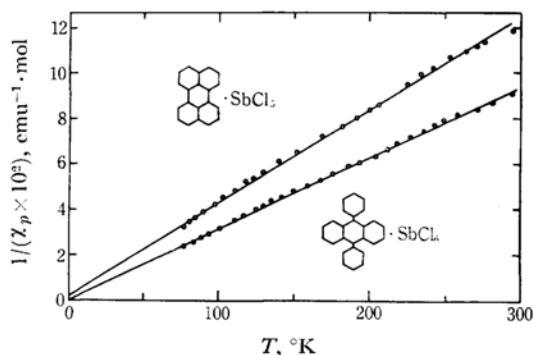


Fig. 1. The inverse paramagnetic susceptibilities of $\text{DPA} \cdot \text{SbCl}_6$ and $\text{P} \cdot \text{SbCl}_5$ as a function of temperature.

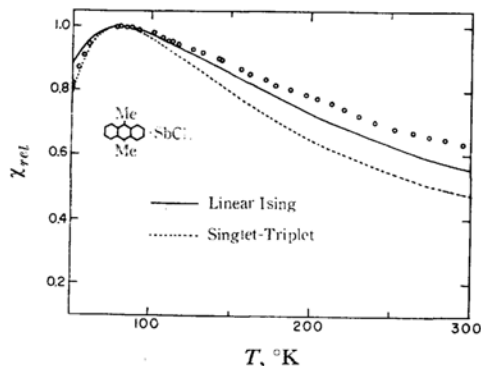


Fig. 2. The relative paramagnetic susceptibility of $\text{DMA} \cdot \text{SbCl}_5$ as a function of temperature. The experimental plot and the theoretical curves are normalized at $T_{\text{max}} = 80^\circ\text{K}$.

in Fig. 1, and then the radical concentration was estimated from the Curie constant. $\text{DPA} \cdot \text{SbCl}_6$ exhibited the highest radical concentration, which was consistent with its remarkable stability.

The paramagnetic susceptibility of $\text{DMA} \cdot \text{SbCl}_5$ showed a broad maximum at approximately 80°K , when the measurement was made down to 50°K , as shown in Fig. 2. The reliable determination of both the Curie constant and the Weiss constant was not feasible, since the deviation from the Curie-Weiss law was appreciable even at high temperatures. $\text{DCA} \cdot \text{SbCl}_5$ showed a quite similar behavior in susceptibility, though its radical concentration was lower. The relative paramagnetic susceptibilities for these two salts were found to coincide fairly closely with each other in a wide temperature range.

The apparent susceptibility of perylene perchlorate was found to be diamagnetic, after the correction was made for the susceptibility for AgI , which was taken to be $-87 \times 10^{-6} \text{ emu/mol}$. As shown in Fig. 3a, the apparent susceptibility showed a minimum around 200°K . The rise in susceptibility in the lower temperature region seems to

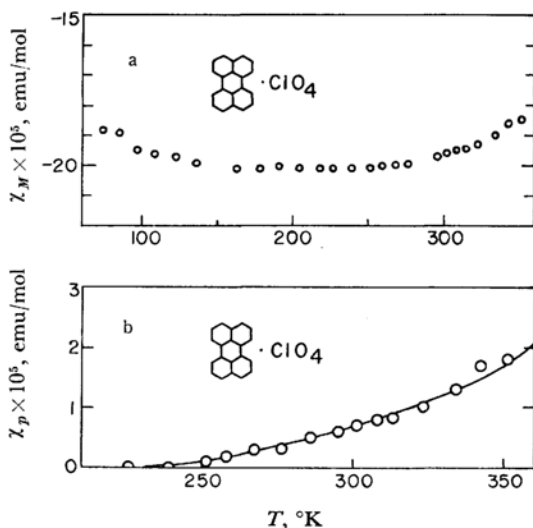


Fig. 3. The susceptibility of $\text{P} \cdot \text{ClO}_4$ as a function of temperature. a, The observed susceptibility. b, The intrinsic paramagnetic susceptibility. The solid curve indicates the susceptibility calculated according to the singlet-triplet model for $J = 0.085 \text{ eV}$.

indicate the presence of a small amount of paramagnetic impurities. Assuming that the susceptibility variation in the lower temperature region was dominated by the impurity paramagnetism which obeyed the Curie law, the diamagnetic susceptibility of the salt was estimated to be $-209 \times 10^{-6} \text{ emu/mol}$. After the correction was made for the diamagnetism and the impurity paramagnetism thus evaluated, the intrinsic paramagnetic susceptibility for the salt was obtained as a function of temperature. It increased with the increase in temperature, as shown in Fig. 3b.

Determination of Exchange Coupling Constant. The exchange coupling constant (J) was determined by the comparison between experimental and theoretical values. The paramagnetic susceptibility is expressed analytically as a function of temperature for two extreme cases of an exchange-coupled linear chain model. As it was discussed in a previous paper,¹⁾ we will summarize the results only, for convenience of discussion. For the singlet-triplet case, the paramagnetic susceptibility is given by

$$\chi_p = (2N'g^2\beta^2/kT)[3 + \exp(2J/kT)]^{-1} \quad (1)$$

where $2J$ corresponds to the singlet-triplet energy separation, and N' is the number of spin pairs. In a low temperature region, i. e., $T \ll 2J/k$, Eq. (1) reduces to a simple form,

$$\chi_p = (2N'g^2\beta^2/kT) \exp(-2J/kT) \quad (2)$$

For the linear Ising case, the paramagnetic susceptibility is expressed by

$$\chi_p = (N'g^2\beta^2/4kT) \exp(-J/kT) \quad (3)$$

in the temperature range discussed.

We could find a relation between the exchange coupling constant J and the temperature T_{\max} at which the susceptibility reaches its maximum value. The ratio, kT_{\max}/J is 1.25 for the singlet-triplet model, 1.00 for the linear Ising model, and 1.28 for the regular chain Heisenberg model.¹⁰⁾

In a high temperature region, *i. e.*, $T \gg J/k$, however, the paramagnetic susceptibility obeys the Curie-Weiss law,

$$\chi_p = C/(T - \theta) \quad (4)$$

where C is the Curie constant, and θ is the Weiss constant. The exchange coupling constant could also be evaluated from the Weiss constant. The relation, $J = -2k\theta$ holds for the singlet-triplet model, and $J = -k\theta$ for the linear Ising model.

The exchange coupling constant for $P \cdot SbCl_5$ was estimated from the Weiss constant of $-4^\circ K$ to be 6.9×10^{-4} eV in the case of the singlet-triplet model, or 3.4×10^{-4} eV in the case of the linear Ising model. The coupling constant for $DMA \cdot SbCl_5$ was evaluated from the temperature T_{\max} of $80^\circ K$ to be 6.9×10^{-3} eV according to the linear Ising model. The radical concentration for this salt was not known accurately, so that the relative paramagnetic susceptibility is shown in Fig. 2. It is compared with the theoretical curves for the singlet-triplet and the linear Ising models, which are normalized at the temperature T_{\max} .

The exchange coupling constant for $P \cdot ClO_4$ could be evaluated either from Eq. (1) or (2). As shown in Fig. 3b, the observed values fitted closely to the curve calculated from the singlet-triplet model with the exchange coupling constant of 0.085 eV. According to Eq. (2), a plot of $\log \chi_p \cdot T$ against $1/T$ gives a straight line, the slope of which corresponds to $-2J/k$. The slope is not affected by the change in radical concentration, so that this analytical method is useful in the case that radical concentration is unknown. The exchange coupling constant thus estimated was 0.09 eV for $P \cdot ClO_4$.

Absorption Spectra. The absorption spectrum of solid $DPA \cdot SbCl_5$ was found to greatly resemble the spectrum of the salt in solution, as shown in Fig. 4a. The spectrum was in agreement with that reported for 9,10-diphenylanthracene monocation by Shida and Hamill.¹¹⁾ The spectrum of solid $P \cdot SbCl_5$ was also found to correspond with that of the salt in dichloromethane, as shown in Fig. 5a. No extra absorption band could be detected in the near-infrared region. These solution and solid spectra of perylene ion are in good agree-

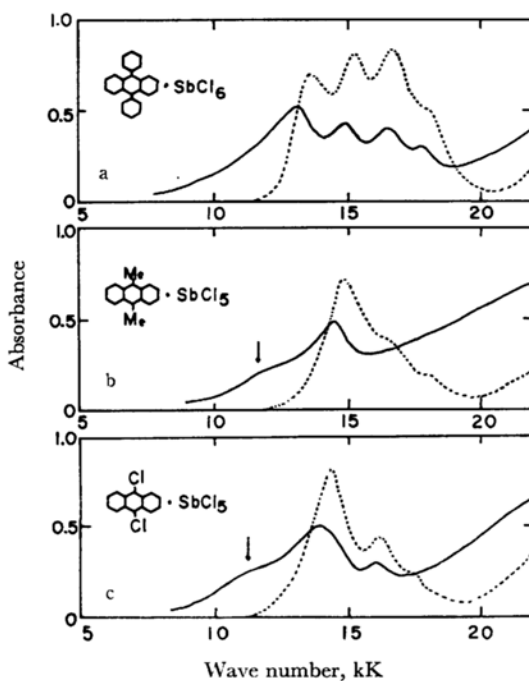


Fig. 4. The absorption spectra of the mono-positive ion radical salts of the anthracene derivatives: a, $DPA \cdot SbCl_5$; b, $DMA \cdot SbCl_5$; c, $DCA \cdot SbCl_5$. The full lines indicate the solid spectra and the broken lines indicate the spectra of the salts in dichloromethane solution. The arrows indicate the charge-transfer bands.

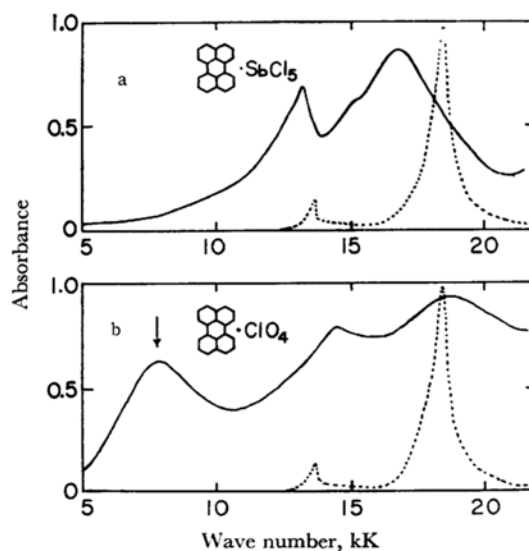


Fig. 5. The absorption spectra of the mono-positive ion radical salts of perylene: a, $P \cdot SbCl_5$; b, $P \cdot ClO_4$. The full lines indicate the solid spectra and the broken lines indicate the spectra of the salts in dichloromethane solution. The arrow indicates the charge-transfer band.

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ment with those observed by other investigators.^{12,13)}

In contrast with $P \cdot SbCl_5$, solid $P \cdot ClO_4$ showed broad absorption bands, and in addition, a new absorption band was observed at approximately 7700 cm^{-1} as shown in Fig. 5b. The spectra for solid $DMA \cdot SbCl_5$ and $DCA \cdot SbCl_5$ showed a shoulder at longer wavelengths, besides the absorption bands which corresponded to those in the solution spectrum, as shown in Figs. 4b and 4c.

Discussion

The high radical concentration in the salts studied here indicates that one unpaired electron is associated with each formula unit. An ESR measurement revealed that the aromatic hydrocarbon radical salts showed a single exchange-narrowed line with a g -value between 2.002 and 2.003, which was characteristic of aromatic hydrocarbon radicals.¹⁴⁾ It is, therefore, reasonable to ascribe the unpaired electron to the mono-positive ion radicals produced by oxidation of the aromatic hydrocarbons with $SbCl_5$.

The new absorption bands in the near-infrared region observed for solid $P \cdot ClO_4$, $DMA \cdot SbCl_5$ and $DCA \cdot SbCl_5$ is reasonably explained by the charge-transfer interaction between aromatic ion radicals caused upon the formation of an aggregate state. An appearance of a similar absorption band for a number of organic radicals has been ascribed to the charge-transfer interaction between radicals. For example, a quite similar spectrum to that observed with solid $P \cdot ClO_4$ has been reported in a previous paper for a solution of perylene mono-positive ions in a solvent of low dielectric constant.¹⁵⁾ We have attributed it to perylene ions in an associated state, and the absorption band in the near-infrared region has been suggested to originate from the charge-transfer interaction be-

tween perylene ions. Hausser and Murrell have also suggested charge-transfer between radical molecules for the appearance of a new absorption band in the solution spectra of Wurster's blue perchlorate and *N*-ethylphenazyl at low temperatures.¹⁶⁾

The appearance of a charge-transfer band in a solid spectrum is noted to correlate to the deviation of paramagnetism from the Curie law or, equivalently, the magnitude of an exchange coupling constant. Solid $P \cdot ClO_4$ shows the large values both in an exchange coupling constant and an intensity of a charge-transfer band, which indicates the presence of strong interaction between perylene ions. Solid $DPA \cdot SbCl_5$ and $P \cdot SbCl_5$, on the other hand, exhibit nearly free nature of their aromatic ions, which is reflected on the negligible value of exchange coupling constant and the absence of charge-transfer band. $DMA \cdot SbCl_5$ and $DCA \cdot SbCl_5$ are an intermediate case with respect to the intermolecular interaction.

It is likely that the correlation between the magnetic and optical properties holds generally for a variety of crystalline radicals. From the observations so far made, the following qualitative features have been derived: 1) The apparent susceptibility of a radical solid which shows an intense charge-transfer band is diamagnetic, or at most weakly paramagnetic at room temperature. The exchange coupling constant for such a solid is usually found to be larger than 0.05 eV. 2) The crystalline radicals with the exchange coupling constant $J \leq 0.02\text{ eV}$ exhibit a fairly weak charge-transfer band, which is thus usually observed as a shoulder. 3) The charge-transfer band for the solid with $J < 10^{-3}\text{ eV}$ is usually undetectable.

The parallelism found between the exchange coupling constant and the charge-transfer band is, therefore, considered to support strongly our previous suggestion that the value of exchange coupling constant obtained through magnetic measurements is basically determined by the stabilization energy due to the charge-transfer configurational interaction associated with the crystalline state of radical molecules.

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