Proton Magnetic Resonance in Some Triarylaminium Salt Free Radicals

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The static magnetic susceptibilities from 77 to 300 K and the proton NMR spectra from 1.5 to 77 K have been measured on powder samples of tris-*p*-chlorophenylaminium perchlorate and chloroantimonate, and tris-*p*-tolylaminium perchlorate and chloroantimonate. The Weiss constants have been determined to be −2.0, −40, −0.5, and −10 K respectively. A broad maximum which indicates an antiferromagnetic interaction has been observed in the electron susceptibilities of the chloroantimonates obtained from the paramagnetic shift. The magnetic behavior is interpreted assuming the linear-chain model. On the other hand, the perchlorates obeyed the Curie-Weiss law down to 1.5 K. The isotropic hyperfine coupling constants of these four aminium salts have been estimated from the proton NMR spectra, from which the cations of these crystalline aminium salts can be expected to have similar configurations.

The magnetic properties of the stable organic free radicals have been intensively investigated. A deviation from the Curie-Weiss law and a broad maximum in the susceptibilities of some ion-radical salts have been observed above the temperature of liquid nitrogen.[1] The anomalous behavior arises from the strong interaction between adjacent radicals and has been interpreted in terms of an exchange-coupled pair model or a linear-chain model. The mechanism of such a strong interaction is considered to be the charge-transfer stabilization. In the case of neutral organic radicals, an anomalous paramagnetism has often been found in the sufficiently low-temperature region and explained on the basis of a regular or alternating Heisenberg linear-chain model.[2,3] The mechanism of such a weak interaction is attributable to the overlap of $p_z\pi$-orbitals occupied by the unpaired electrons.

The series of *para*-substituted triarylaminium salts is reasonably stable in air and can be kept in the solid state for some time. Paramagnetic resonance absorption has been observed in these salts, and linewidth measurements have been reported for powder samples, together with the *g*-values.[4] However, the magnetic properties of these salts have never been studied except for the preliminary susceptibility measurements of three salts.[5] We would like to report on the magnetic behavior of four aminium salts, tris-*p*-chlorophenylaminium perchlorate and chloroantimonate ($TCA\cdot ClO_4$ and $TCA\cdot SbCl_5$), and tris-*p*-tolylaminium perchlorate and chloroantimonate ($TTA\cdot ClO_4$ and $TTA\cdot SbCl_5$), in the wide temperature range from 1.7 to 300 K. The two aminium cations, TCA and TTA, have the molecular structures shown in Fig. 1. A comparison of the infrared spectra of several tris-*p*-tolylaminium salts with those of triarylmethyl salts indicates that their cations have similar propeller-like configurations.[6] The triarylaminium radical cations are stabilized by the delocalization of the unpaired electron on the three rings.[7] Therefore, a large paramagnetic shift can be expected in the proton NMR of these salts. The proton NMR spectrum with two partially resolved lines for the $TCA\cdot ClO_4$ salt have been studied at 77 K by Brown *et al.*[8] Since the paramagnetic shift is proportional to the product of the static magnetic susceptibility of the unpaired electron times the hyperfine constant, information concerning the electron susceptibility from the microscopic point of view, as well as the sign and magnitude of the hyperfine constant in the solid state, can be obtained from the nuclear magnetic resonance. The static susceptibility measurements of the four triarylaminium salts have been carried out in the high-temperature range from 77 to 300 K. The proton resonance spectra of these salts have been measured in the low-temperature range from 1.5 to 77 K in order to obtain the temperature dependence of the electron susceptibility and the hyperfine constants in the solid state. This is because some impurity effects at low temperatures encountered often in the static susceptibilities can be excluded in the case of the electron susceptibilities.

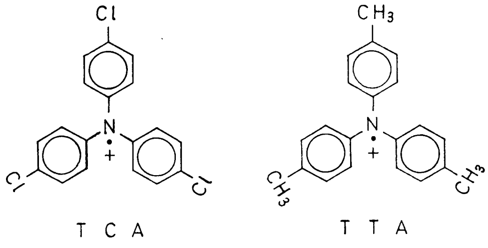

Fig. 1. The molecular structures of the triarylaminium cations, TCA and TTA.

Experimental

The tris-*p*-chlorophenylamine and tris-*p*-tolylamine were prepared by the method of Walter and were purified a few times through recrystallization. The $TCA\cdot ClO_4$ and $TTA\cdot ClO_4$ were prepared by the oxidation of the corresponding amine with silver perchlorate and iodine in ether by following the procedure of Walter.[9] The melting points were found to agree well with the values in the literature, and the results of the elementary analysis of the carbon, hydrogen, and nitrogen of each sample corresponded closely to the calculated values. The $TCA\cdot SbCl_5$ was prepared by the following procedure. To a solution of the corresponding amine in chloroform, we added a chloroform solution of $SbCl_5$. A deep blue crystalline product with a metallic luster was obtained from the solution by cooling; it was then washed with chloroform and ether. This salt was found to be the most stable of the four salts. It melts sharply with decomposition at 195—196 °C. Found: C, 32.59; H, 2.09; N, 2.19; Cl, 44.35%. Calcd for $C_{18}H_{12}NCl_8Sb$: C, 33.38; H, 1.89; N, 2.16; Cl, 43.79%. The $TTA\cdot SbCl_5$ was obtained according to the method of Wieland,[10] mp 114—115 °C. Found: C, 42.79; H, 3.60; N, 2.29; Cl, 30.28%. Calcd for $C_{21}H_{21}NCl_5Sb$: C, 43.01; H, 3.61; N, 2.39; Cl, 30.23%.

The magnetic susceptibility measurements from 77 to 300 K were done, by means of a magnetic torsion balance described elsewhere,[11] on powder samples of about 50—100 mg in a field of 8.8 KG. The temperature was determined using a calibrated AuCo-Cu thermocouple. Manganese Tutton salt was used for the calibration of the thermometer as well as the product of the magnitude times the gradient of the magnetic field. The ESR spectra were observed at room temperature by using an X-band spectrometer PE3X of JEOLCO. The magnetic field was calibrated by the hyperfine splittings of Mn^{2+} doped in MgO. The proton NMR measurements were carried out using a Pound-Watkins-type spectrometer and a Robinson-type spectrometer at 20.0 and 35.0 MHz respectively, with an 80 Hz field modulation and a field sweep. The magnetic field was calibrated by means of the proton absorption of H_2O. A conventional cryostat was used, and the temperatures were determined using an Allen-Bradly carbon resistor calibrated against the vapor pressures of liquid helium, hydrogen, and nitrogen.

Results and Discussion

The diamagnetic correction was made using Pascal's constants. The value of the diamagnetic susceptibility for $SbCl_5^-$ was taken to be -1.24×10^{-4} cgs emu/mol, following Kainer and Hausser.[12] The paramagnetic susceptibilities of the four salts follow the Curie-Weiss law in the high-temperature range from 77 to 300 K. The values of the Curie constant and the Weiss constant were determined by plotting the inverse paramagnetic susceptibility against the temperature, and then the radical concentration was estimated from the Curie constant. The chloroantimonates have relatively large negative Weiss constants, indicating the presence of an antiferromagnetic exchange interaction between the unpaired electrons, while the perchlorates have small negative Weiss constants. The diamagnetic susceptibility, the Curie constant, the Weiss constant, and the radical concentration for each salt are summarized in Table 1.

Table 1. Results from susceptibility measurements

Compound	Diamagnetic susceptibility 10^{-6} (cgs emu/mol)	Curie constant (K·cgs emu/mol)	Weiss constant (K)	Radical concentration (%)
TCA·ClO_4	−246	0.358	-2.0 ± 0.5[a]	95
TCA·$SbCl_5$	−336	0.329	-40 ± 10	87
TTA·ClO_4	−230	0.281	-0.5 ± 0.2[a]	75
TTA·$SbCl_5$	−320	0.354	-10 ± 2	94

a) The values estimated from the paramagnetic shift in the low-temperature region.

The ESR absorption spectrum for each sample, as measured at room temperature, show a symmetrical single line. The linewidth, which was taken to be the peak-to-peak linewidth of the first derivative of the absorption spectrum, and the g-value are shown in Table 2. The ESR data indicate that each aminium salt is a monopositive cation radical salt.

Table 2. Results from ESR measurements

Compound	Linewidth (Gauss)	g-value
TCA·ClO_4[a]	4.6	2.0045
TCA·$SbCl_5$	4.0	2.0042
TTA·ClO_4[a]	2.3	2.0029
TTA·$SbCl_5$	1.4	2.0029

a) Ref. 4.

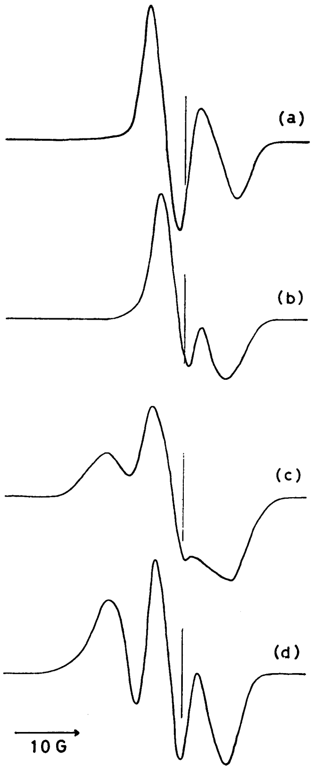

Fig. 2. Proton magnetic resonance absorption derivative curves (a) of TCA·ClO_4, (b) of TCA·$SbCl_5$, (c) TTA·ClO_4, (d) of TTA·$SbCl_5$, measured at 35.0 MHz, 77 K. The vertical lines show the free-proton position.

The 77 K proton resonance spectra of powder samples of the four salts measured at 35.0 MHz are shown in Fig. 2. The spectrum for TCA·ClO_4 agrees well with the results reported by Brown *et al.*[8] The spin Hamiltonian for a free radical in which one proton interacts with one unpaired electron can be described by the following equation:

$$\mathscr{H} = -g_N\beta_N\boldsymbol{H}\cdot\boldsymbol{I} + a_H\boldsymbol{S}\cdot\boldsymbol{I} + \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{I} \qquad (1)$$

The meanings of the symbols have been described in a previous paper.[13] In the paramagnetic state, the proton sees only a time-averaged local field proportional to the mean value, $\langle S_z\rangle$, of the electron spin component because of the exchange interaction between the unpaired electrons. In polycrystalline samples, the third term of Eq. (1), which is due to the electron-nuclear dipolar interaction, produces a distribution of the proton resonance shift and broadens the proton resonance, but it does not shift the resonance center of gravity significantly.[8,13] In polycrystalline samples, therefore, the proton-resonance-signal shift from the free-proton position to a higher field can be approximately described by the following equation:

$$\Delta H = -a_{\mathrm{H}}\chi H / g\beta g_{\mathrm{N}}\beta_{\mathrm{N}} \qquad (2)$$

Thus, ΔH is proportional to the isotropic hyperfine coupling constant, the static susceptibility, χ, and the resonance frequency. Further, the more the resonance line is shifted, the broader the linewidth becomes because of the third term of Eq. (1). The isotropic hyperfine constant, a_{H}, of a proton attached to a carbon atom is related to the π-electron spin density on the carbon atom by the so-called McConnell relation, $a_{\mathrm{H}} = Q\rho$.[14,15] The Q value for aromatic C–H fragment has been semiempirically determined as $Q(\mathrm{CH}) = -22.5$ G. In the proton resonance of TCA·ClO_4 and TCA·$SbCl_5$ measured at 77 K, the upper-field line and the lower-field line are attributable to the *ortho* protons attached to the carbon atoms with positive spin densities, and to the *meta* protons attached to the carbon atoms with negative spin densities, respectively, following the results of Brown *et al.*[8] The fact that the two lines for TCA·ClO_4 are shifted from the free-proton position more than those for TCA·$SbCl_5$ can be ascribed to the difference in the magnitude of the magnetic susceptibility, for TCA·$SbCl_5$ has a much larger negative Weiss constant than TCA·ClO_4. One upper-field line and two lower-field lines have been observed in the spectra of TTA·ClO_4 and TTA·$SbCl_5$. The proton hyperfine coupling constant of a methyl group attached to an aromatic carbon atom is related to the π-electron spin density of the carbon atom. In this case, the Q value has been empirically estimated to be +27.2 G. Therfore, the line with the largest lower-field shift is attributable to the protons of the methyl groups attached to the carbon atoms with positive spin densities situated at the *para* positions. The upper-field line and the other lower-field line can be assigned to the *ortho* protons and to the *meta* protons respectively. The spectrum for TTA·ClO_4 apparently includes an unshifted line arising from the diamagnetic impurities due to the radical decomposition, as will be shown below.

On the basis of the assignment of the polycrystalline NMR spectra, the isotropic hyperfine constants in the crystalline state have been evaluated by using the susceptibility results. The results are tabulated in Table 3, together with the ESR results in solution.[7] The a_{H} values of TCA radical salts do not agree with those in solution. The disagreement may be due to the inadequacy of the ESR simulation or to some other effect. From the results, the unpaired electron distribution on the three aryl groups can be expected to be equal to each other, even in the crystalline state. Probably, the crystalline aminium salts have similar D_3 propeller-like configurations, as is to be expected from the infrared spectra.[6] The three protons of the methyl group have identical isotropic hyperfine constants; this suggests that the methyl group rotates freely about the C–C bond in solution and even in the crystalline state at 77 K. Further, the proton NMR data indicate that the paramagnetism of the chloroantimonates observed in the susceptibility measurements arises from the aminium cation, and that the antimony pentachloride in the salts has a diamagnetic formula. Kainer and Hausser have suggested the formula of $(SbCl_4^- + SbCl_6^-)/2$ for the complexes of diphenylamine derivatives.[12]

When the temperature was lowered from 77 K, the paramagnetic shift of the perchlorates increased con-

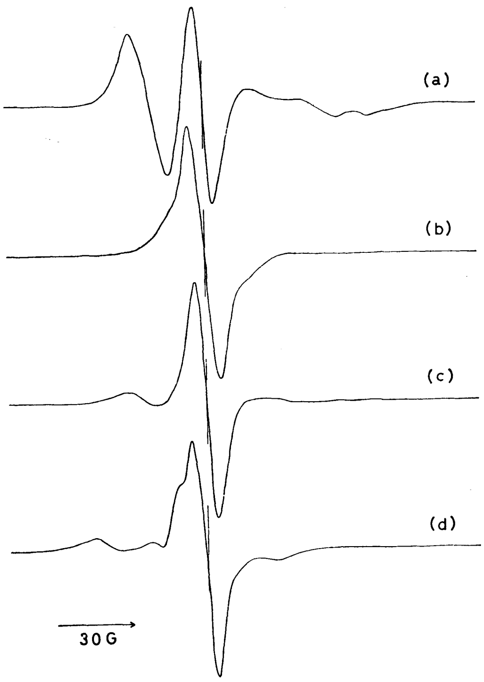

Fig. 3. Proton magnetic resonance absorption derivative curves (a) of TCA·ClO_4, (c) of TTA·ClO_4, measured at 20.0 MHz, 4.2 K, and (b) of TCA·$SbCl_5$, (d) of TTA·$SbCl_5$, measured, at 35.0 MHz, 4.2 K. The vertical lines show the free-proton position.

Table 3. Isotropic hyperfine constants obtained by the NMR spectra in the crystalline state and the ESR spectra in solution

Compound	a_{N} (Gauss)	a_{O} (Gauss)	a_{m} (Gauss)	$a_{\mathrm{CH_3}}$ (Gauss)
TCA·ClO_4[a)]	—	−2.16	+1.27	—
TCA·$SbCl_5$	—	−2.35±0.15	+1.23±0.10	—
TCA (solution)[b)]	9.56	1.12	0.56	—
TTA·ClO_4	—	−2.01±0.15	+1.04±0.10	+4.28±0.30
TTA·$SbCl_5$	——	−2.23±0.15	+0.96±0.10	+4.16±0.30
TTA (solution)[b)]	9.45	2.06	1.03	3.89

a) Ref. 8, b) Ref. 7.

tinuously down to 1.5 K, following the Curie-Weiss law. By plotting the reciprocal of the paramagnetic shift *vs.* the temperature, the Weiss constants of TCA·ClO_4 and TTA·ClO_4 were determined to be −2.0 and −0.5 K respectively. The 4.2 K spectra measured at 20 MHz are shown in Figs. 3(a) and (c). The broadening of the shifted lines is due to the existence of an anisotropic hyperfine coupling coming from the third term of Eq. (1), which could lead to an asymmetric line shape for our polycrystalline samples. In the spectrum of TTA·ClO_4, only the absorption line of the *meta* protons shifted to the lower field can be detected; the lines of the *ortho* and methyl protons broaden out to the upper field and the lower field respectively. In addition to the shifted lines, an unshifted line was observed. In the measurements of TCA·ClO_4 after a month, we observed an increase in the intensity of the unshifted line, compared with that of the shifted lines. As the radical is not so stable and gradually decomposed, the diamagnetic impurities due to the radical decomposition are probably responsible for the unshifted line. The weak signal of the protons arising from the background is also attributable to the unshifted line.

A broad maximum in the paramagnetic shift of TCA·$SbCl_5$, which indicates an antiferromagnetic interaction, has been observed at about 40 K. The 4.2 K spectrum measured at 35.0 MHz shows an asymmetrical line at the free-proton position, as is shown in Fig. 3(b). However, a quantitative treatment is difficult since the magnitude of the shift is not very large.

The temperature dependence of the relative electron susceptibility of TTA·$SbCl_5$ obtained from the paramagnetic shift is illustrated in Fig. 4. In the spectra, the paramagnetic shift was defined as the distance between the free-proton position and some shifted lines which was proportional to the resonance frequency. When the temperature was lowered from 15 K, the paramagnetic shift deviated from the Curie-Weiss law and reached a broad maximum at 6.0 K. The 4.2 K spectrum measured at 35.0 MHz is shown in Fig. 3(d). The absorption line of *meta* protons was observed as the shoulder of the unshifted line arising from the radical decomposition. The absorption due to the methyl protons involves two lines at least, for the methyl protons are no longer equivalent at 4.2 K. This means that the methyl group is either completely locked or rotates rather slowly.[16] When the temperature is lowered from 4.2 K, the shifted line becomes so broad that the paramagnetic shift can not be estimated below 3.0 K.

The data of the paramagnetic shift can be interpreted by means of the one-dimensional Heisenberg model based on Bonner and Fisher's calculation,[17] rather than by means of the well-known pair model. The kT_m/J ratio is 1.282 for the one-dimensional Heisenberg model, where T_m is the temperature at which the susceptibility reaches its maximum value and where J is the exchange coupling constant. The J value for TTA·$SbCl_5$ is estimated to be −4.7 K from the T_m value obtained experimentally. In Fig. 4, the relative electron susceptibility obtained from the paramagnetic shift is compared with the theoretical curve for the one-dimensional Heisenberg model of $J=-4.7$ K, which is fitted at the temperature of T_m. The broadening of the shifted lines below 4.2 K can no longer be explained by the third term of Eq. (1). Their behavior is perhaps attributable to an increase in the correlation time of the exchange motion because of the short-range magnetic ordering below the temperature of the susceptibility maximum.[18] Taking the results for the neutral organic radicals into account,[2,3] the mechanism of such a week interaction may be considered to be due to the overlap of π-orbitals occupied by the unpaired electron rather than to the charge-transfer stabilization. Although the interpretation, in which it is assumed that the cation radicals form chain-like arrays of molecules, is tentative, for lack of data on the crystal structure, the data of the paramagnetic shift are consistent with the linear Heisenberg antiferromagnetic exchange model.

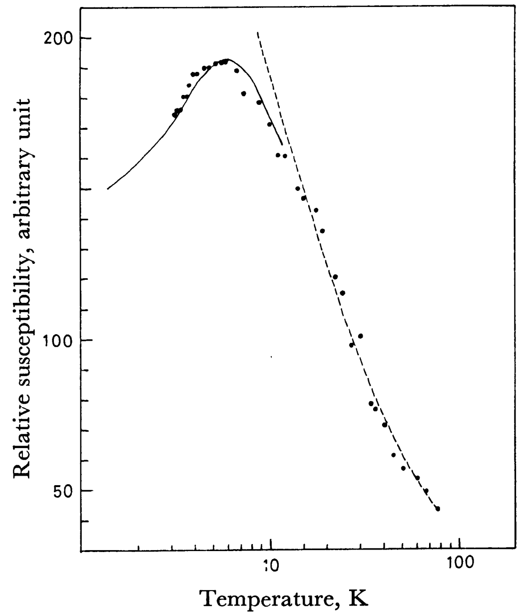

Fig. 4. The relative susceptibility of TTA·$SbCl_5$ obtained from the paramagnetic shift as a function of temperature. The solid line is the theoretical curve for one-dimentional Heisenberg model of $J=-4.7$ K, which is fitted at the temperature T_m. The dashed line represents the curve for the Curie-Weiss law, with the Weiss constant $\theta=-10$ K.

On the other hand, the perchlorates exhibit a very small exchange interaction. The crystal structure of triphenylmethyl perchorate has been determined, and it has been reported that the carbonium ion is propeller-shaped, with a three-coplanar central bond, and that triphenylmethyl tetrafluoroborate is isomorphous with the perchlorate.[19] Provided that the aminium perchlorates have a crystal structure similar to that of triphenylmethyl perchlorate, they may be expected to form a three-dimensionally interacting spin-system rather than a one- or two-dimensionally interacting spin-system. Therefore, it is possible that the aminium perchlorates go into a three-dimensionally ordered antiferromagnetic state if the temperature is lowered below 1.5 K.

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