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ELECTRIC AND MAGNETIC PROPERTIES OF TETRABENZO[de,hi,op,st]PENTACENE -ALKALI METAL COMPLEXES

Kenichi IMAEDA,* Toshiaki ENOKI, Hiroo INOKUCHI,
Junji AOKI,† Minoru TAKEKAWA,† and Satoshi IWASHIMA††
Institute for Molecular Science, Okazaki 444
†Department of Chemistry, Faculty of Science, Toho University,
Funabashi, Chiba 274
††Department of Chemistry, Faculty of Science and Technology,
Meisei University, Hino, Tokyo 191

The electric and magnetic properties of the charge transfer complexes of tetrabenzo[de,hi,op,st]pentacene (TBPA) with various Cs compositions have been investigated. The nonplanarity of a TBPA nanocyclic aromatic molecule causes the restriction against complex formation in contrast with other nanocyclic ones. TBPA-Cs complexes were good conductors, which was consistent with their characteristics of a partial charge transfer.

Condensed polycyclic aromatic hydrocarbons form charge transfer complexes with alkali metals in various compositions. It has been reported that the composition of isoviolanthrene A (isoVEA) complexes with potassium, isoVEA-K_x, ranges from x=0 to 4.55 and their electrical conductivities are greatly enhanced through the complex formation.1-3) Tetrabenzo[de,hi,op,st]pentacene (TBPA) shown in Fig.1 is one of the nanocyclic aromatic molecules as well as isoVEA.4,5) While a conjugated system of isoVEA spreads over all the molecule because of its planar structure, TBPA has two divided conjugated sub-systems because of a distortion due to two bay structures with a configuration which two adjacent hydrogen atoms repulse each other as shown in Fig.1. Therefore, it is interesting to know how TBPA forms charge transfer complexes with alkali metal. In the present work, we investigated ESR spectra and electrical conductivity

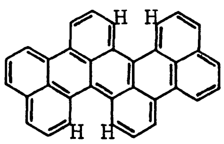

Fig. 1. TBPA.

of TBPA-Cs complexes in order to make clear the relation between the structures and the solid state properties.

TBPA was prepared by means of the synthesis shown in the previous paper.5) TBPA-Cs complexes were prepared using a double furnace method.6) In a glass tube evacuated to a pressure of about 7×10^{-4} Pa, TBPA was placed at one end and Cs metal distilled three times in vacuum was introduced to the other end. TBPA was maintained at a temperature T_2 and Cs at T_1 for two days. T_1 was held constant at 150 °C and the temperature difference $\Delta T(=T_2-T_1)$ was chosen as 0, 25, 50, 75, and 100 °C. The reason why Cs was selected as donor metal is as follows: TBPA has a lower melting point 335 °C in comparison with other nanocyclic aromatic hydrocarbons, and Cs has higher vapor pressure than the other alkali metals at a temperature. Taking into account these facts, for Cs, T_2 can be chosen in the widest range because T_1 can be set at a lower temperature than for the other alkali metals. Moreover, judging from the case of graphite alkali metal intercalation compounds,7) the composition of alkali metal in the complexes is supposed not to depend on the sort of metals among K, Rb, and Cs. The compositions of five complexes were examined by means of volumetric and gravimetric analyses. ESR spectra were measured using a conventional X-band spectrometer with a continuous flow helium cryostat between liquid helium and room temperatures. The calibration of the magnetic field was carried out with a DPPH standard sample. The powder samples were transferred in vacuum from the glass tube to a quartz ESR tube. The electrical resistivity was measured using a two probe method between liquid nitrogen and room temperatures. The samples were prepared as evaporated films (about 3×10^3 Å in thickness) on quartz plates with evaporated gold electrodes.

The correlation between the composition of TBPA-Cs$_x$ and the temperature difference ΔT is shown in Fig.2. The Cs concentration x of the complex was maximum at ΔT=0 °C and then decreased as ΔT increased, as well as the case of graphite intercalation compounds.6) The concentration x approached a steady state around ΔT=100 °C. For all the samples, the line shapes of ESR spectra

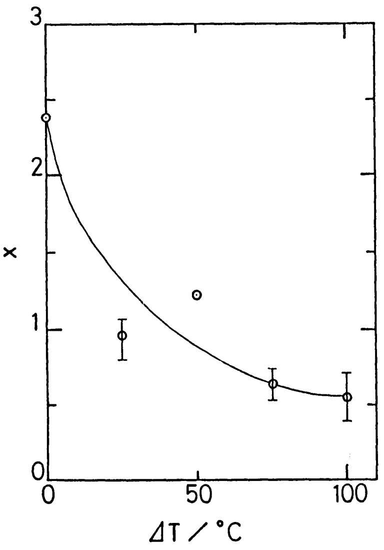

Fig. 2. The x-ΔT relationship of TBPA-Cs complexes. The solid line denotes a guide for eyes.

were Lorentzian and g values were nearly constant at about 2.003. The temperature dependence of the ESR intensity obeyed the Curie-Weiss law with the Weiss temperature of about -6 K to -22 K. Figure 3 shows the temperature dependence of the linewidth ΔH of TBPA-Cs complexes. For the samples with $\Delta T=0$, 25, and 50 °C, ΔH decreased monotonously as temperature decreased, while for the samples with $\Delta T=75$ and 100 °C, ΔH showed a weakly raise with lowering temperature. Figure 4 shows the Cs concentration dependence of the spin concentration estimated with DPPH as a reference. The spin concentration had a linear dependence of x in low Cs concentrations ($0 \leq x \lesssim 1.0$), where ΔH had a weak temperature dependence shown in Fig.3, and then it became constant in high Cs concentrations ($1.0 \lesssim x \leq 2.4$), where ΔH had a strong temperature dependence. These facts are considered that weak interactions between spins cause narrow linewidths with weak temperature dependence at lower spin concentrations, while samples with higher spin concentrations have stronger spin-spin interactions. Table 1 summarizes the results of the electrical resistivity of the two samples, $\mathrm{TBPA\cdot Cs_{0.6}}$ and $\mathrm{TBPA\cdot Cs_{2.4}}$. They were good conductors, similar to $\mathrm{isoVEA\cdot K_{4.05}}$, where $\rho_{RT}=100$ Ωcm and Ea=0.08 eV.$^{1)}$

As shown in Fig.2, TBPA complex has a narrow range of composition ($0 \leq x \leq 2.4$)

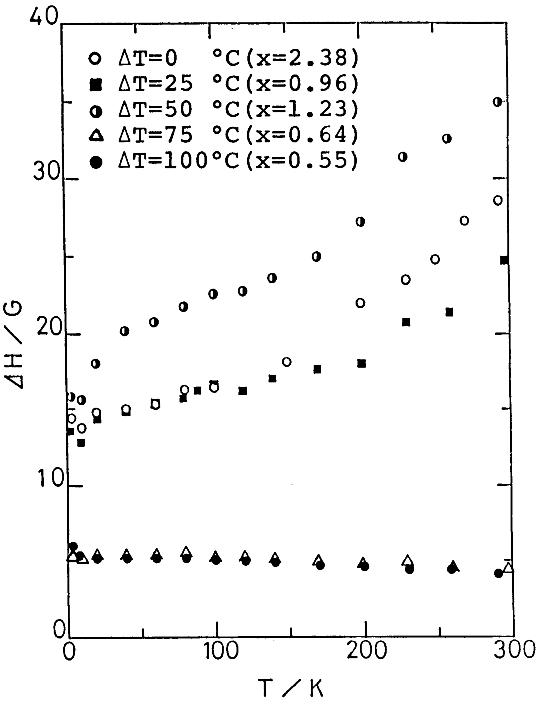

Fig. 3. The temperature dependence of the linewidth ΔH of TBPA-Cs complexes.

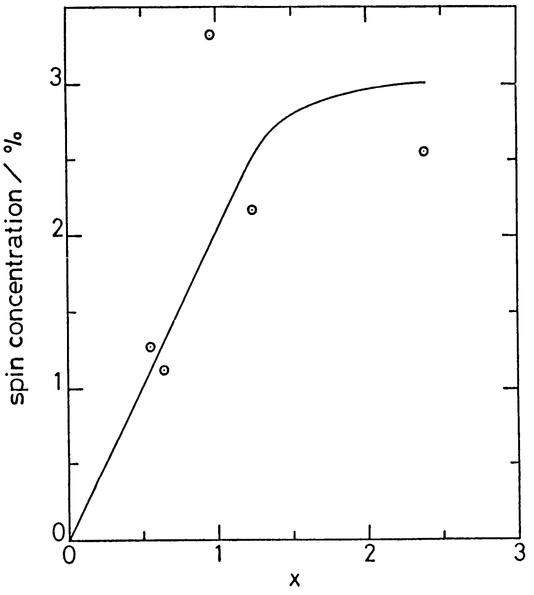

Fig. 4. The correlation of the spin concentration with the Cs concentration of TBPA-$\mathrm{Cs_x}$ complexes. The solid line denotes a guide for eyes.

in contrast with a wide range in isoVEA one. In an isoVEA molecule, a conjugated system consists of nine benzene rings, while a molecule of TBPA has two divided conjugated systems, one of which has the four rings. The present result reveals that the small conjugated system of TBPA is unable to accept more donor atoms than the large one of isoVEA. Therefore, it is considered that the nonplanarity of TBPA molecule causes the restriction against the complex formation. The saturation behavior of spin concentration as a function of x at higher Cs concentrations may be considered to result from the restriction. The finding of the small spin concentration value 1-3% of TBPA-Cs complexes in Fig.4 shows a partial charge transfer from Cs to TBPA. The good conductivity of TBPA-Cs complexes is considered to be caused by the partial charge transfer[8)] and not to be affected by the nonplanarity of the TBPA molecule.

Table 1. The resistivity of TBPA-Cs complexes

Sample	Resistivity at room temperature ρ_{RT} / Ωcm	Activation energy Ea / eV
$TBPA\cdot Cs_{2.4}$	4.1	0.01
$TBPA\cdot Cs_{0.6}$	0.8	0.06
TBPA	$1.4x10^5$	0.26

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