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Magnetic Susceptibility of Perylene-Iodine Complex

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Synopsis. The magnetic susceptibility of a highly conductive 2:3 charge-transfer complex of perylene with iodine has been examined as a function of temperature. The paramagnetic susceptibility, which was found to be nearly independent of temperature, is considered to be due only to the perylene cation radical.

Recently, much interest has centered on the tetracyanoquinodimethane (TCNQ) anion radical salts with high electrical conductivity such as quinolinium-(TCNQ)$_2$, *N*-methylphenazinium-TCNQ and tetrathiofulvalenium-TCNQ. In these complexes, the form of the acceptor has been well established by various electronic, as well as by X-ray crystallographic, analysis. The charge-transfer complexes formed between aromatic compounds and halogens fall into another class of highly-conductive substances.[1-3] The form of halogens in these complexes, however, is not well established

Some time ago, Singer and Kommandeur showed that the spin density of the 2:3 perylene-iodine complex changes exponentially with temperature with an activation energy of 0.019 eV,† which is the same as that for electrical conduction.[4] They measured the ESR absorption intensity in order to obtain the spin density. If the iodine molecule in the complex takes the form of I_2^-, as is commonly supposed in analogy to the TCNQ anion radical salts, it contributes to the paramagnetism.

However, the paramagnetism of I_2^- in the complex can not be detected in the ESR experiments for the following two reasons: (i) the ESR absorption of I_2^- appears over a wide magnetic-field range[5,6] because of the large nuclear spin (I=5/2) and the large magnetic moment of the iodine atom, while the absorption of the complex shows a linewidth of several gauss†† at 100—300 K,[4] and (ii) the g-values of I_2^- in alkali iodides (V_k center) have been reported to be $g_{//}=1.86$—1.89 and $g_\perp=2.27$—2.30,[6] whereas the average g-value of the complex is 2.0033 and the anisotropy is very small.[4] The observed ESR absorption is therefore considered to be due only to the perylene cation radical, even though the acceptor has a paramagnetic form.

It is therefore worthwhile to examine the static magnetic susceptibility of the complex and to compare the results with those obtained by the ESR method. Therefore, the static susceptibility of the 2:3 perylene-iodine complex was measured in the temperature range of 77—296 K. In this note, the data are presented on the basis of the molecular unit of $(C_{20}H_{12})\cdot(I_2)_{1.5}$.

TABLE 1. MOLAR MAGNETIC SUSCEPTIBILITIES OF PERYLENE, IODINE AND THEIR COMPLEX AT ROOM TEMPERATURE

	$-\chi_M/10^{-6}$ emu·mol^{-1}		
	This work	Literature	Ref.
Perylene ($C_{20}H_{12}$)	160	167	7
		159	2
		166—174	8
Iodine (I_2)	80.0	91.4	9
	77.8	89—92.4	8
Complex [$(C_{20}H_{12})\cdot(I_2)_{1.5}$]	217.8	210[a]	7
		217[b]	2

a) Mole ratio=1:1.34; b) Mole ratio=1:1.63.

The magnetic susceptibilities obtained for perylene, iodine and the complex at 290 K are given in Table 1. Although the values for iodine are a little different from those found in the literature, the present value of -80×10^{-6} emu/mol††† is used in the following. From these results, the diamagnetic contribution is estimated to be -280×10^{-6} emu/mol for $(C_{20}H_{12})\cdot(I_2)_{1.5}$. The discrepancy between the observed and calculated susceptibilities for the complex can then be reasonably ascribed to the paramagnetism resulting from the complex formation; *i.e.*, $\chi_p=62\times10^{-6}$ emu/mol at 290 K.

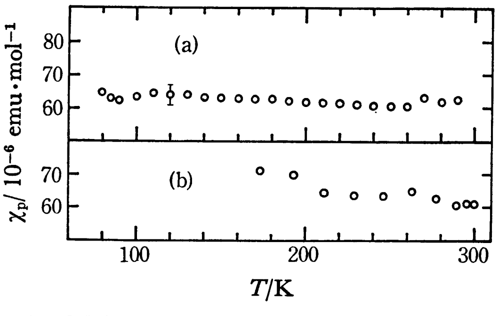

Fig. 1. Molar paramagnetic susceptibility of the perylene-iodine (2:3) complex as a function of temperature.
(a) The results by static susceptibility measurement. The error bar indicated on the point at 120 K applies to all the points.
(b) The susceptibility reproduced from the spin density data in Fig. 5 of Ref. 4.

By assuming that the diamagnetic part is independent of the temperature, the paramagnetic susceptibility at

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† 1 eV≃1.6021×10^{-19} J.

†† 1 G=10^{-4} T.

††† Molar magnetic susceptibility is expressed in m^3·mol^{-1} in the International System of Units; the values in emu·mol^{-1} should be multiplied by $4\pi\times10^{-6}$ to convert to SI units.

various temperatures is obtained as shown in Fig. 1, where the susceptibility calculated from the spin density data of Singer and Kommandeur is also shown for comparison.[4] If one considers the difficulty in the ESR intensity measurements, one may conclude that the results obtained by both methods are in complete agreement with each other.

The close agreement between the results by the resonance and static methods thus excludes the possibility that the iodine in the complex is in a paramagnetic form, such as I_2^-. The acceptor should be in diamagnetic form in the complex; it may be I_2, I_3^- or other higher polyiodides, although which cannot be said with certainty. In this connection, it may be noted that Matsunaga has suggested the existence of complex salts of phenothiazine, such as (phenothiazine)$_2^+\cdot(Br_2I)^-$,[10] and (phenothiazine)$_2^+\cdot(I_5^-)$[11] from the changes observed in the IR and electronic spectra and in the electrical resistivity when the iodine or phenothiazine was added to the phenothiazine bromide or phenothiazine-iodine complex.

The paramagnetic susceptibility of the complex was found to be independent of temperature. Similar results have been obtained for other systems such as highly conductive TCNQ complexes,[12] although no conclusive explanation has been given. One of the possible explanations is that the paramagnetism is due to the conduction electrons, as proposed by Singer and Kommandeur. In this case, there may be two possible ways to analyze the results. One is the way in which the phenomenon is regarded as Pauli paramagnetism; in which case, the susceptibility is expressed as

$$\chi_p = 2\mu_B{}^2\cdot N(\varepsilon_F)$$

where μ_B is the Bohr magneton and $N(\varepsilon_F)$ is the density of states for one spin direction. By neglecting the diamagnetic contribution of the conduction electrons, the density of states for the complex is estimated to be about 1 eV^{-1}·molecule^{-1}. This value can be compared with 7.5 eV^{-1}·molecule^{-1} for the quinolinium-(TCNQ)$_2$ complex.[12] The other is the way which has been adopted by Singer and Kommandeur.[4] They plotted $\ln(\chi_p\cdot T)$ against $1/T$ and obtained a straight line. However, in our case where the temperature range is much wider, as Fig. 1 shows, the plot does not give a straight line.

The experimental procedure was as follows. Synthesized perylene was recrystallized successively from benzene and glacial acetic acid, and finally sublimed in a vacuum. The iodine used was obtained by sublimation from a mixture of iodine, potassium iodide and calcium oxide in 10: 1: 2 weight ratios. Four samples of the complex were prepared by two different manners[2,3] and examined by the Faraday method using an apparatus described elesewhere.[13] The freshly-prepared polycrystalline complex was placed in a spherical (5 mm o.d.) thin-walled Pyrex glass container through a small capillary arm, and the container was sealed at the capillary portion with a small flame while the spherical part was immersed in a liquid nitrogen bath. After the measurement, the complex was taken out of the container and analyzed by the titration method.[2] The analysis showed that the complex examined was in a 1: 1.5 molar ratio to within the experimental error. Although only the typical results have been described here, the results obtained for other samples were essentially identical to within the range of experimental error.

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