Organic Semiconductors with High Conductivity. III.
Perylene-Iodine Complex

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Polycyclic aromatic hydrocarbons with halogens form molecular complexes in solid state and those complexes of the charge transfer type possess relatively high electrical conductivity. The preliminary survey for the semiconductive properties of these complexes has been given in the first paper¹⁾ of this series of investigations. Concerning the mechanism of electronic conduction in organic solids, the charge transfer complexes are so suggestive that their structures with their physical properties are specially interesting. In the preceding paper²⁾, the violanthrene-iodine system was investigated in connection with its structure. In this paper, the investigation of the perylene-iodine system, another typical example for this series of complexes, is presented.

Preparation and Composition of Perylene-Iodine Complex.—The formation of a solid molecular compound between perylene and iodine has been known for many years since the investigations of Clar and Brass³⁾, and also, by Zinke et al.⁴⁾ However, concerning the composition of this complex, these investigators did not come to agreement with each other.

When perylene is added to the benzene solution of iodine, the molecular complex is obtained as a black precipitate which consists of needle-shaped minute crystals. This complex is somewhat unstable in the atmosphere and has tendency to liberate iodine. The following procedure was employed for the determination of the composition. Perylene (100∼130 mg.) and iodine (appropriate amount) were dissolved in 50 ml. of benzene. By heating this solution under reflux condenser, both components were homogeneously dissolved. Then the container was transferred into a thermostat of 20°C, and the complex was precipitated from the solution. For the purpose of keeping the equilibrium between the precipitated complex and the solution, the container was held at this temperature for more than 15 hr. being continuously vibrated. Then by a suction through a glass filter, the precipitate was separated from the solution as quickly as possible, and was kept in a desiccator. The iodine content in the solution was determined by the titration with sodium thiosulfate solution. The iodine content of the precipitate was also determined by the same method after dissolving it into benzene.

In Fig. 1, the iodine content of the benzene solution which is in equilibrium with the precipitate is plotted against the composition of the precipitate. The composition is expressed with the number of iodine molecules added to one molecule of perylene (mole ratio).

On this curve, the isotherm for the heterogeneous equilibrium of the perylene-iodine system, the horizontal part AB indicates that the precipitate should consist of two sorts of solid phase, one is perylene and the other is the complex which has the composition of

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1) H. Akamatu, H. Inokuchi and Y. Matsunaga, This Bulletin, **29**, 213 (1956).

2) H. Akamatu, Y. Matsunaga and H. Kuroda, ibid., **30**, 618 (1957).

3) E. Clar and K. Brass, *Ber.*, **65**, 1660 (1932); **72**, 604 (1939).

4) A. Zinke and A. Pongratz, ibid., **70**, 214 (1937); A. Zinke and H. Troger, ibid., **74**, 107 (1941); M. Pestemer and E. Treiber, ibid., **74**, 964 (1941).

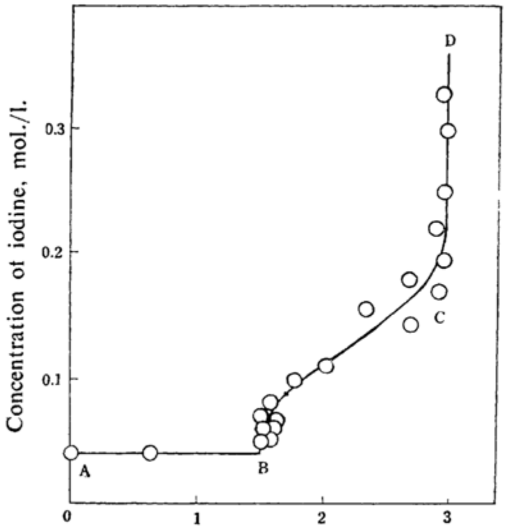

Fig. 1. The isotherm of perylene-iodine system. The concentration of iodine in benzene solution is plotted against the composition of precipitate.

Perylene·1.5 I_2. It can be seen directly or under a microscope that the precipitate is a mixture of yellow crystals (perylene) and black needles (complex). As will be shown in the latter section, the magnetic susceptibility measurement also verifies the existence of Perylene·1.5 I_2. At the vertical part CD, the precipitate is made of one phase which has the composition of Perylene·3I_2. Thus, there are two kinds of complexes which have different compositions. The precipitate at the intermediate part BC should be made of a solid solution of these two kinds of complexes. The shape of the curve BC is similar to that of the violanthrene-iodine system, which was discussed in the previous paper[2].

The spectrophotometric measurement was made for the mixed solution of perylene and iodine in benzene and also in chloroform, but the absorption band due to the complex formation could not be found over 3000~7000 Å range. This result implies that the molecular complex has poor solubility or it might be stable only in the solid state. Thus the equilibrium between perylene and iodine, for instance when the concentration of iodine is high enough, can be expressed as

$$\text{Perylene(soln.)} + 3I_2\text{(soln.)} \rightleftarrows [\text{Perylene}\cdot 3I_2]$$

The equilibrium constant in benzene solution has been found to be $K_c = 2.1 \times 10^5$ (in mol./l. unit, 20°C). This leads to the free energy of the complex formation, $-\boldsymbol{RT} \ln K_c = -7.1$ kcal./mol.

Electrical Properties.—The electrical resistivity of perylene-bromine complex is not stable because of the substitution reaction of bromine as reported in the previous paper[1]. This is not the case, however, for the perylene-iodine complex; the substitution reaction does not take place between iodine and hydrogen, and the complex can be kept stable if it is sealed in the dry atmosphere.

The precipitate from the benzene solution was applied to the resistivity measurement. The specimen powder was compressed between the metal electrodes in an ebonite tube having inside diameter of 8.0 mm. The electrode surfaces were coated with platinum plates. The electrical field applied to the specimen was about 20 V./cm. and the resistance was read with an ohmmeter.

The observed resistivity was dependent on the applied pressure and it decreased with the reciprocal of pressure in a linear way when the applied pressure was above 50 kg./cm². This might be due to the presence of contact resistance between particles. Thus, the limiting value was read by the extrapolation to the infinite pressure. This value, $\rho(p=\infty)$, is assumed as the intrinsic resistivity of the sample and is shown in Table I, where the observed

TABLE I. SEMICONDUCTIVE DATA OF PERYLENE-IODINE COMPLEX

Composition in mole ratio, I_2/perylene	Electrical resistivity at 15°C, ohm.cm. $p=116$	$p=\infty$	ε eV.	Temperature range
Perylene	4.0×10^{18}		2.0_1	108~−170°C
0.23	6.8×10^3	500	0.09	Room temp.~− 80°C
0.86	74	30	0.06	Room temp.~−170°C
1.08	27	15	0.06	〃
1.56	16	9	0.06	〃
1.80	19	9	0.06	〃
2.42	19	10	0.05	〃
2.96	20	10	0.06	〃
5.8	22	15	0.07	Room temp.~−150°C
Iodine*	$5.8_6\times10^6$		4.5_1	25~113°C

* M. Rabinowitsch, *Z. Physik. Chem.*, **119**, 82 (1926).

resistivity at the pressure of 116 kg./cm^2 is also shown for comparison.

The voltage dependence for the current was examined with the complex having the composition of Perylene·2.53 I_2. The linear relationship was observed between the current and the applied voltage when the voltage was not higher than 25 V./cm. In this region where the Ohm's law holds, the current was stable and quite reversible. This indicates that the conduction is the electronic one. However, when a higher voltage than this value was applied, the larger current deviating from the linear relationship was observed instantaneously and then it decreased gradually. After the external field was removed, the cell was still polarized slightly for a while.

The temperature dependence for the resistivity was observed in the range from room temperature down to −170°C. No higher temperature can be applied to the sample for it decomposes and liberates iodine.

It was observed that the resistivity increases with decreasing temperature, and a good linear relationship was found between the logarithm of resistivity and the reciprocal of temperature. This linear relation was found even in a case of which the sample consisted of two solid phases (perylene and complex) or of the solid solution, similarly as in the case of a pure simple compound (for instance perylene).

Assuming the formula $\rho=\rho_0\exp(\varepsilon/2\boldsymbol{kT})$, where ρ is the resistivity and ρ_0 is a constant, the value of ε, the "energy gap" for the generation of charge carriers was estimated. This value is shown in Table I.

In Table I, it is seen that the ε-value is nearly constant (about 0.06 eV.) over a very wide range of the mole ratio. This might be due to the fact that the observed value was the one having the narrowest energy gap which participated predominantly in the generation of charge carriers at the low temperature range where the experiment was carried out.

There are two kinds of intermolecular compounds, as mentioned in the preceeding section, Perylene·1.5 I_2 and Perylene·3I_2. It is noticeable, however, that no important distinction can be found for the values of the energy gap between those complexes, similarly for the values of resistivity. Therefore, it can be concluded that both complexes, Perylene·1.5 I_2 and Perylene·3 I_2, possess resistivity of 9∼10 ohm.cm. and an energy gap of 0.06 eV. In consequence the solid solution of these complexes possesses the same values regardless of its composition.

For the purpose of knowing the principal charge carriers, whether electrons or positive holes, the preliminary examination of the thermoelectric power of the cell was made. Both leads of the cell were connected to a galvanometer. When the one side of the cell was heated to a higher temperature than the other side, the flow of a minute current was observed. The direction of the current indicated that the warm side electrode was negative against the cold side electrode of the cell. The amount of the thermoelectric power was roughly estimated as a few micro volts per degree. This indicates that positive holes contribute to the current more predominantly than electrons.

Magnetic Susceptibility.—Both perylene and iodine are diamagnetic substances. In the case of the formation of the charge transfer complex, however, the magnetic susceptibility of the system shows a large deviation from the additive property of diamagnetism⁵⁾. This offers a method to examine the composition of the intermolecular compound formed in the system. The Gouy method was employed for the susceptibility measurement at the room temperature. The observed values are summarized in Table II and illustrated in Fig. 2 as the function of iodine content.

The remarkable depression of diamagnetism from the value given by the additivity rule

TABLE II. THE DIAMAGNETIC SUSCEPTIBILITY OF PERYLENE-IODINE SYSTEM

Wt. percentage of I_2	Mole ratio I_2/perylene	Specific susceptibility $\chi\times10^6$
0	0	-0.632 ± 0.007
22.6	0.29	-0.517 ± 0.004
44.0	0.78	-0.418 ± 0.007
62.2	1.63	-0.343 ± 0.009
65.7	1.90	-0.324 ± 0.006
68.8	2.20	-0.338 ± 0.007
75.1	3.00	-0.337 ± 0.009
100		-0.36*

* International Critical Table VI, p. 355.

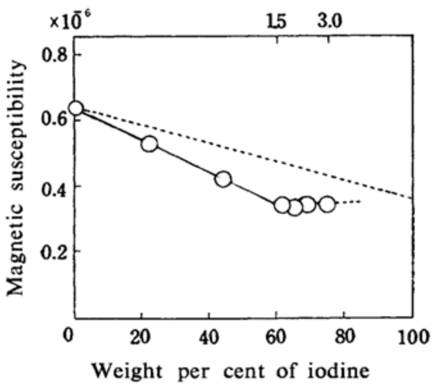

Fig. 2. The plot of the diamagnetic susceptibility of perylene-iodine system as the function of iodine content.

(the dotted line) is seen in Fig. 2. The depression proceeds in a linear way as the iodine content increases up to 60 per cent. Then, from 60 per cent up the susceptibility appears almost constant; but probably it proceeds toward the value of iodine. Thus a sharp break is found at the iodine content of 60 per cent (the mole ratio is 1.5). The linear part of susceptibility below this iodine content follows the additivity rule in regard to the mixture of pure perylene and the complex of this composition. This proves the complex formation of Perylene·1.5 I_2. Its molar susceptibility is -217×10^{-6}, which implies that the depression from the diamagnetic additivity is 80×10^{-6} per mole of perylene. However, the recognition of the formation of Perylene·3 I_2 is difficult from the magnetic susceptibility measurement, as its value is almost the same as the value of Perylene·1.5 I_2 and also is not far from the value of iodine. This suggests that in the formation of Perylene·3 I_2 from Perylene·1.5 I_2 by further addition of iodine, the electronic state of the system is not greatly influenced. The molar susceptibility of Perylene·3 I_2 is -342×10^{-6} and the diamagnetic depression is 92×10^{-6}. This is comparable to that of Perylene·1.5 I_2.

ESR Absorption.—The diamagnetic depression from the additivity rule should be attributed to the paramagnetic contribution of the unpaired electrons which are generated in association with the formation of charge transfer complex, as Matsunaga[5,6] has pointed out previously. The electron spin resonance absorption was examined for the perylene-iodine system as the function of iodine content. An x-band microwave spectrometer, Hitachi MPS-1 was employed. The measurement was carried out at room temperature. The spin concentration and the *g*-value were determined referring to the values of DPPH. The results are summarized in Table III.

The *g*-value was observed to be constant, 2.0043, regardless of the composition of the complex. The spin concentration varies with the iodine content, but the number of spins assigned to one molecule of perylene becomes nearly constant in any system whose mole ratio is more than 1.5. In the last column of the table, the number of unpaired electrons calculated from the diamagnetic depression in molar susceptibility is shown. These values are in good agreement with those observed by ESR absorption. The most interesting point in this result is that the number of unpaired electrons assigned to one perylene molecule is essentially constant for both Perylene·1.5 I_2 and Perylene·3 I_2. This suggests again, with the electrical property, that the electronic states are not greatly different from each other in those two complexes.

TABLE III. THE ELECTRON SPIN RESONANCE ABSORPTION OF PERYLENE-IODINE SYSTEM (AT ROOM TEMPERATURE)

Mole ratio I_2/perylene	Line width at half maximum gauss	Number of spins per g.	Number of spins per one molecule of perylene	
			ESR	Static*
0.29	8	1.8×10^{19}	0.01	0.01
0.78	8	2.3× 〃	0.02	0.03
1.52	8	5.5× 〃	0.06	0.06
1.84	11	5.2× 〃	0.06	0.06
2.22	11	5.2× 〃	0.06	0.06
2.53	13	3.3× 〃	0.05	0.06
3.00	13	3.0× 〃	0.05	0.07

* These values were calculated with the deviation from the additivity rule for molar susceptibility, dividing by 1270×10^{-6}.

On the Structure of Perylene-Iodine Complex.—The X-ray diffraction patterns have been examined with the association of the "Geigerflex" diffractometer for the complexes which have the compositions of Perylene·1.5 I_2 and Perylene·3 I_2 respectively. Both complexes give sharp crystalline patterns which are quite different from that of perylene. This is in marked contrast to the violanthrene-iodine complex, which gives an amorphous pattern[2]. The main diffraction lines of Perylene·1.5 I_2 and Perylene·3 I_2 are in common with each other regarding the position as well as the intensity ratio. This indicates that these two complexes have structures very similar to each other.

Concerning the crystal system, no information could be obtained from the observed values of spacing alone, because it possesses low symmetry. However, three series of diffraction lines could be found in the observed principal lines. The first series consists of lines whose spacing is 13.5Å and possesses the largest intensity compared to the other series. The second and the third series consist of lines which have the spacing of 11.5 and 10.7Å respectively. In all of these series, the first order diffraction lines are weak in intensity, but the second order diffraction lines possess enough intensity and are well resolved.

Hassel and Strømme[7] have made investigation on the crystal structure of the benzene-bromine complex. It was concluded that in this solid complex the molecules of bromine and benzene are arranged alternately with each other, directing the molecular axis of bromine

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[5] Y. Matsunaga, This Bulletin, **28**, 475 (1955).

[6] Y. Matsunaga, *J. Chem. Phys.*, **30**, 855 (1959).

[7] O. Hassel and K. O. Stromme, *Acta Chem. Scand.*, **12**, 1146 (1958).

nearly perpendicular to the molecular plane of benzene. A similar structure could be assumed for the perylene-iodine complex. If an iodine molecule is sandwiched between two perylene molecules, directing its molecular axis perpendicularly to the plane of the perylene molecule, the distance between the two perylene molecules would be 10.7 Å (the thickness of aromatic molecular plane = 3.7 Å and the length of iodine molecule = 7.0 Å). This value is in coincidence with the observed spacing of 10.7 Å The molecular plane of perylene possesses enough area to accommodate three iodine molecules. Thus, it is likely that the complex is made of a structural unit such as is shown in Fig. 3. The reflection planes which have the spacing of 13.5 Å and give the strongest diffraction lines should be the planes which contain iodine molecules in the highest density, and could be constructed by stacking such structural units. However, no further information can be derived from the powder diffraction diagram alone.

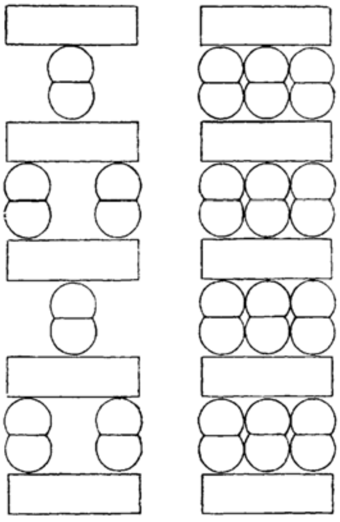
(a) Perylene$\cdot$1.5 I_2 (b) Perylene$\cdot$3 I_2

Fig. 3. The proposed structure of perylene-iodine complex. (a) Perylene$\cdot$1.5 I_2 (b) Perylene$\cdot$3 I_2

The density of the perylene-iodine system has been examined. The pycnometer was employed in association with an aqueous medium containing a small amount of surfactant. In Fig. 4, the specific volume is plotted against the iodine content. The specific volume of perylene is 0.741 cc./g. and that of iodine is 0.202 cc./g. The broken line indicates the specific volume of the binary system assuming the additivity of volume. The observed values are situated above this line. This indicates that complex has the structure with interstices where water molecules can not penetrate. However, when the iodine content increases up to the composition of Perylene$\cdot$3 I_2, the observed specific volume is 0.340 cc./g.; this value is in good agreement with the calculated value assuming the additivity law. This indicates that this complex has the most closed packing structure.

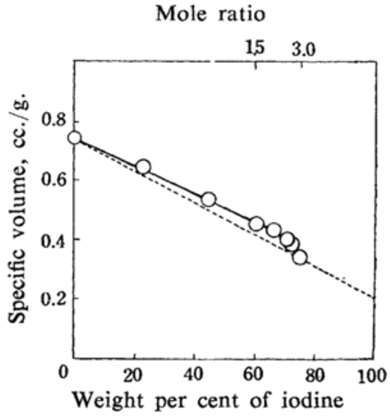

Fig. 4. The specific volume of perylene-iodine system.

Discussion

Most organic compounds are electrical insulators, because the intermolecular coupling is so poor that electrons can hardly transfer from molecule to molecule, even in the electronic excited state. In organic semiconductors, the activation energy for generating charge carriers possesses relatively low values (1 eV. or less), whereas the resistivity possesses high values ($10^7 \sim 10^{14}$ ohm. cm.). However, if, in the formation of crystal, the condensation of molecules is caused by an interaction such as that which is associated with the exchange of electrons between molecules, it could be expected that those electrons can move throughout the crystal lattice. This could result in the drift mobility under the applied electrical field. This is the case of charge transfer complex in the solid state.

In the solid complex, in order to expect the conductance, the donor molecules (D) and the acceptor molecules (A) should be arranged alternately with each other in such a way as D$\cdot$A$\cdot$D$\cdot$A$\cdots$, thus the charge transfer interaction could be conjugated between neighboring molecules throughout the crystal lattice. The proposed model for the perylene-iodine complex illustrated in Fig. 3 is likely to be reasonable.

In the case of simple semiconductive compounds (polycyclic aromatic hydrocarbons), the resistivity and also the activation energy for generating charge carriers are depending markedly on the size of the aromatic molecule.

However, in the case of the charge transfer complex, their semiconductive property is quite independent of the size of the hydrocarbon molecule, as is seen in Table IV. This implies that the charge transfer interaction itself, between donors and acceptors, is the principal cause for generating mobile electrons which can contribute to the electrical conduction. The ESR absorption is observed commonly in charge transfer complexes and a close connection between the unpaired electrons and the charge carriers be presumed[8].

TABLE IV. THE SEMICONDUCTIVE DATA OF AROMATIC HYDROCARBONS AND IODINE COMPLEXES

Complex	Mole ratio	$\rho_{15^\circ C}$ ohm.cm.	ε eV.
Perylene-iodine	1 : 1.5	9	0.06
Perylene-iodine	1 : 3	10	0.06
Pyranthrene-iodine	1 : 2	20	0.09
Violanthrene-iodine	1 : 2	13	0.15
Pure hydrocarbon			
Perylene		4.0×10^{18}	2.0
Pyranthrene		4.5×10^{16}	1.07
Violanthrene		2.0×10^{14}	0.94

The isotherm for the phase equilibrium of perylene-iodine system indicates the formation of two sorts of intermolecular compounds which have the composition of Perylene·1.5 I_2 and Perylene·3I_2 respectively. The investigation of the magnetic susceptibility also suggests the existence of the compound of Perylene·1.5I_2. However, concerning the electrical property almost no difference could be found between those two sorts of compounds. These two compounds possess not only the same semiconductive property but also the similar structure and almost the same number of unpaired electrons. These facts lead to the assumption that when three iodine molecules combine with two perylene molecules, not only the framework of the crystal structure but also the electronic state (for the charge transfer type of combination) are completed, and almost no further improvement takes place by adding the three more iodine molecules. Those added iodine molecules can occupy the interstices in the framework to complete the closed packed structure (mainly with non-bonding type of combination), but result in no further important change in the electronic state for the complex formation.

Summary

Concerning the solid complex of perylene-iodine system, it has been clarified that two sorts of molecular addition compounds are formed. One has the composition of Perylene·1.5 I_2 (or 2 Perylene·3 I_2) and the other is Perylene·3I_2. Both complexes are semiconductive with low resistivity; the resistivity at the room temperature is 9∼10 ohm.cm. and the energy gap is 0.06 eV. Concerning those values, both complexes possess almost the same values. Not only the elecrical properties and the magnetic properties, but also, both complexes possess similar crystal structures. To explain those facts, the structural units for those complexes have been proposed. These consist of the conjugation between perylene molecules and iodine molecules with the charge tranfer type of interaction.

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[8] J. Kommandeur and L. S. Singer, Conference on Electronic Conductivity in Organic Solids, Duke University, April, 1960; D. R. Kearns, G. Tollin and M. Calvin, *J. Chem. Phys.*, **32**, 1020 (1960).