Organic Semiconductors with High Conductivity. I. Complexes between Polycyclic Aromatic Hydrocarbons and Halogens

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Introduction

Some of the polycyclic aromatic compounds have a pretty good electrical conductivity in the solid state, and from this and other properties they are considered to be organic semiconductors[1]. However, their electrical resistivity at room temperature is of the order of 10^7–10^{12} ohm-cm., even for the most favourable compounds. Hence, it is hoped to learn whether there are any simple organic substances having higher electrical conductivity.

As reported in a preceding paper[2], we have found that some complexes formed between polycyclic aromatic hydrocarbons and halogens have a very good electrical conductivity in the solid state. It is rather surprising to know that such simple organic substances have electrical resistivity as low as 1–10^3 ohm-cm.. Therefore, studies on the electrical properties as well as the structures of these complexes should give us information about the necessary conditions for electrical conduction in organic materials.

Complexes between Polycyclic Aromatic Compounds and Halogens

Brass and Clar[3] have reported that from a benzene solution of perylene, by the addition of bromine, a black coloured precipitate is obtained. Zinke and Pongratz[4] have also found that perylene absorbs bromine vapour directly and changes to a black substance. These authors were in agreement in considering this black substance as a complex or an additive compound formed between perylene and bromine, but there was a little controversy between them over the composition of this substance.

We have found that not only perylene but also most polycyclic aromatic hydrocarbons may form molecular complexes with bromine or iodine, by a method similar to that of Brass and Clar or Zinke.

When we applied Brass and Clar's method, a known quantity of sample was dissolved or suspended in benzene, and an excess amount of bromine or iodine was added to it while boiling the solution. After cooling the solution by itself, the precipitate so obtained was filtered through a glass filter and washed with benzene.

Zinke's method was applied solely to the formation of bromine complex. In this case, a known quantity of sample was taken on a glass filter and put in contact with bromine vapour in a closed glass vessel. The absorption of bromine is completed generally within about ten minutes. After the excess bromine adsorbed is removed by aspiration and dried under reduced pressure, the increased weight of the sample is measured, from which the bromine content of the complex is known.

In the case of bromine complex formation by either method, there occurs a substitution reaction of bromine in the aromatic rings, with simultaneous liberation of hydrogen bromide. This substitution reaction proceeds with a moderate velocity while the complex is forming and continues after the complex is fully formed. This is the reason for confusion about the composition of the complex. Consequently, the apparent bromine content is not fixed but fluctuates in a small range according to the conditions of preparation, even in the case when excess bromine is added to the solution in Brass and Clar's method or when the absorption is completed in Zinke's method. This will be discussed in a later section.

In the preliminary experiments, the following substances were found to form complexes with bromine by Zinke's method. The complex formation is made obvious by the strong colour change and the increment in mass. Benzanthrone (reddish brown), perylene (black), dibromoperylene (black), dibenzoylperylene (brown), distearylperylene (brown), 1,2-benzperylenequinone (dark brown), anthanthrene (black), mesonaphtho-dianthrone (black), pyranthrene (black), violanthrene

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[1] H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950); **20**, 1481 (1952), H. Inokuchi, This Bulletin, **24**, 222 (1951); **25**, 28 (1952); **27**, 22 (1954), D.D. Eley, G. Parfitt, M. Perry and D. Taysum, *Trans. Faraday Soc.*, **49**, 79 (1953).

[2] H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature*, **173**, 168 (1954).

[3] K. Brass and E. Clar, *Ber.*, **65**, 1660 (1932); **69**, 1977 (1936).

[4] A. Zinke and A. Pongratz, *Ber.*, **69**, 1591 (1936); **70**, 214 (1937).

(black), violanthrone (dark violet), dibenzpyrene (black), dibenzcoronene (black), and ovalene (black).

The following compounds were found to make complexes with iodine by Brass and Clar's method: perylene (black), violanthrene (black), and dinaphthylene oxide (black).

It was concluded that most of the hydrocarbons can readily form complexes with bromine or iodine and darken their colours nearly to black. Whilst, in the case of quinones, iso-dibenzpyrenequinone could not form a complex with bromine nor iodine, violanthrone formed a complex with bromine but not with iodine. It seems less easy to make them complexes with halogens and even though they form complexes the colour does not change as much as in the case of the hydrocarbons.

The Electrical Conductivity Measurement

The conductance measurement was made by the potential drop method in the following conditions. The sample powder was packed in an ebonite cylinder and attaching to each end a silver coated metallic cap, compressed under about 200 kg. per cm^2 pressure.

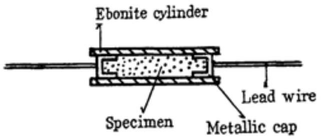


Fig. 1. Specimen cell for the conductance measurement.

It was found that most of the black complexes cited above show good conductance. The values of resistivity lie between about 5 ohm-cm of dibromoperylene-bromine complex and about 900 ohm-cm of dinaphthylene oxide-iodine complex. However, the resistivity is not stable and increases rapidly at first and then gradually over a period of days. The values cited above are that of the freshly prepared specimens, as the resistivity increases to kilo ohm-cm after several weeks even in the case of dibromoperylene-bromine complex. The features are shown in Fig. 2. The reason for this instability of resistivity will be considered in detail in the following section.

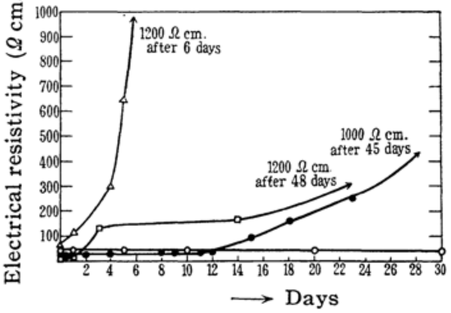


Fig. 2. Change of resistivity with time.
● Perylene-bromine
○ Violanthrene-iodine.
□ Dibromoperylene-bromine
△ Violanthrene-bromine.

There is one further problem to be considered concerning the observed conductance, that is the question whether it is an intrinsically electronic conductance or not.

It was found, during the measurement of resistivity, that after application of the potential through the specimen cell, the cell itself developes a small electromotive force of a few millivolts in a direction opposite to the applied potential. Therefore, a part of the conductance at least must be attributed to ionic conductance. The resistivity due to the ionic conductance (R_i) and that due to the electronic conductance (R_e) can be separately estimated by the following way. Assuming the total resistivity (R) which is measured in the usual way, to be made up of R_e and R_i in parallel, then $1/R=1/R_e+1/R_i$, where R_i can be estimated from the current which results from the electromotive force of the specimen cell itself, without any applied potential from outside, measured by reference to a standard resistor. In most cases, the conductance due to ionic ($1/R_i$) is 10–20 per cent of the total conductance for fresh specimens and thereafter decreases to 5 per cent or less. The remainder is assumed to be electronic conductance ($1/R_e$). If we take the value of R_e, they were found to be more stable than R itself. In Fig. 2, the R_e is plotted as a function of time (days).

Furthermore, it was soon found that if moisture is carefully excluded and the specimen is made from a thoroughly dried sample, the ionic conductance part decreases to an almost undetectable value. Therefore the larger part of the observed conduction may be considered as due to the electronic conductance. All values cited in the present paper, however, are those R_e calibrated in the above way.

Further evidence against ionic conduction can be obtained by the following consideration. A specimen of violanthrene-iodine complex, as an example, contained 150 mg. of iodine as its component. If the observed current is wholly due to electrolytic conduction, it must drop within sixteen minutes after the current of 120 mA has passed through the cell. It did not do so, however, and the stable current was observed as long as five hours or more, excepting a small drop in resistance which is due to the thermal effect of the current. This latter drop in resistance recovered to the initial value after the current was ceased.

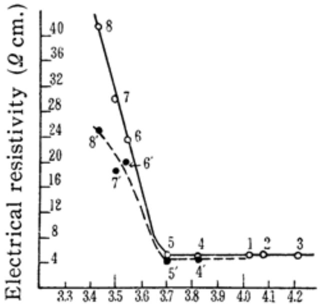
The Conductivity of Perylene-Bromine Complex

The resistivity of perylene-bromine complex is several ohm-cm at the freshly prepared state, but it changes over a period of days and increases to 10^3 ohm-cm. or more after several weeks. Therefore, it must be ascertained whether the nature of conduction itself is so unstable or the complex itself is unstable and changes its structure. Concerning the latter possibility, in the case of the bromine complex the liberation of hydrogen bromide is observed as mentioned above. This is due to the substitution reaction of bromine. Therefore, the specimen is in a dynamic state in which a part of bromine combined as the molecular compound at the beginning takes place substitution reaction to make bromoperylene and at the same time the equivalent bromine is liberated as hydrogen bromide. Moreover, decomposition is caused in the specimen cell at the place of contact of the metallic electrodes.

Hence, the electrical resistivity as a function of the composition was investigated in the following way. A set of samples of perylene-bromine complex was made by Zinke's method. Their composition was one perylene molecule to nearly four bromine atoms in the fresh state. Specimen cells for the conductivity measurement were made using parts of these samples, and the resistivity was measured in as fresh a state as possible. The resistivity and the bromine content of these specimens are shown by the points of 1, 2, and 3 in Fig. 3. The remaining parts of the samples were preserved in a desiccator over potassium hydroxide. At an appropriate period of days, the decrease in mass of the preserved samples was measured. From this the bromine content was determined, and at the same time the resistivity was measured, using a part of the sample. The resistivities thus obtained as the function of the bromine content are shown in Fig. 3 by the points of 4, 5, etc.

When the sample in which the bromine content had decreased was put into bromine vapour, it absorbed bromine again and its conductivity recovered to a certain degree. This is shown in Fig. 3 by the points of 4′, 5′, etc., (concerning these points, the bromine content on the abscissa has no meaning).

From this investigation, it is understood that the instability of the conductivity of the complex is due to the change of the bromine content of the complex itself.



Bromine content n ($n\mathrm{Br}/\mathrm{C}_{20}\mathrm{H}_{12}$)

Fig. 3. Electrical resistivity of perylene-bromine complex as the function of total bromine content.

Perylene-bromine complex decomposes spontaneously as mentioned above. The change of the total apparent bromine content through a period of days, for an example, is shown in Fig. 4. If it is assumed that the decomposition is solely due to the substitution reaction to make dibromoperylene, the reaction is

$$(\mathrm{C}_{20}\mathrm{H}_{12}\text{–}4\mathrm{Br}) \longrightarrow \mathrm{C}_{20}\mathrm{H}_{10}\mathrm{Br}_2 + 2\mathrm{HBr}.$$

Hence, the complex of which the apparent composition is one perylene molecule to n bromine atoms is in fact made of dibromoperylene-bromine complex and perylene-bromine complex. This is expressed by

$$(\mathrm{C}_{20}\mathrm{H}_{12}\text{-}n\mathrm{Br}) \simeq \alpha\mathrm{C}_{20}\mathrm{H}_{10}\mathrm{Br}_2 + (1-\alpha)\mathrm{C}_{20}\mathrm{H}_{12} + (n-2\alpha)\mathrm{Br}.$$

The amount of the additively combined bromine can be estimated, and distinguished from substituted bromine, by titration with sodium thiosulphate solution. In the case shown in Fig. 4, n was 4.03 in the fresh complex and it changed to 3.30 at a final

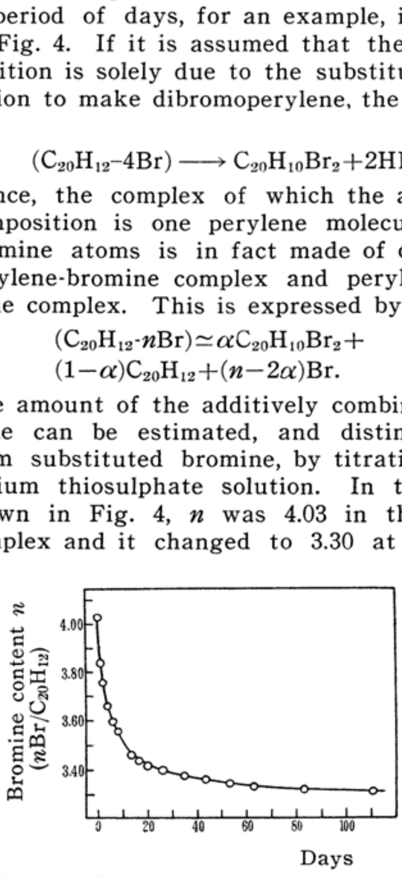


Fig. 4. Change of total bromine content following the decomposition of perylene-bromine complex.

state after the decomposition had proceeded. In this final complex, the content of the free bromine was found to be 0.97 atoms per one perylene molecule, consequently 2.33 atoms were substituted bromine. During this decomposition process, 0.73 bromine atoms per one perylene molecule were lost and the equivalent amount had been substituted, therefore, the content of bromine as dibromoperylene contained in the initial fresh complex was 1.60 $(=2.33-0.73)$ atoms per one perylene molecule. This means $\alpha=0.8$ in the above scheme.

The complex of which the apparent composition is one perylene molecule to 4 bromine atoms was in fact a mixture of 80 per cent of dibromoperylene dibromide and 20 per cent of perylene tetrabromide, even in the initial fresh state. From this it is understood that the substitution reaction of bromine is relatively rapid at least at the beginning, and a large part of the perylene changes to dibromoperylene during complex formation. The resistivity of the " perylene-bromine (1:4) complex " agrees well with that of dibromoperylene-bromine (1:2) complex, both in the fresh state, and is about 5 ohm-cm.

Dibromoperylene dibromide, further changes to tetrabromoperylene with simultaneous liberation of hydrogen bromide,

$$2(C_{20}H_{10}Br_2-2Br)\rightarrow C_{20}H_8Br_4 + C_{20}H_{10}Br_2+2HBr.$$

With the progress of this reaction, the content of the additively combined bromine is progressively lost. Hence, passing the point 5 in Fig. 3, all perylene molecules have changed to dibromoperylene and thereafter only the above reaction takes place, at the same time the conductivity of the complex begins to decrease rapidly. In this stage, the reabsorption of bromine leads to a recovery of the conductivity in a certain limited degree, but not completely. This is due to the formation of the additive compound between dibromoperylene and bromine, but it is supposed that tetrabromoperylene can scarcely form a complex.

It is concluded that the instability or decrease in the conductivity of the complex is due to the loss of bromine which combines to form the additive compound. In other words, the origin of the conductivity is attributed to the interaction between a molecule of perylene or its bromine derivative and additively combined bromine molecules.

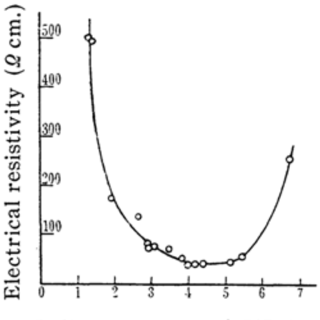
Violanthrene-Iodine Complex

If there is any system in which the substitution reaction of halogen does not take place, such a complex will be stable of itself as well as of electrical property. It was found that the violanthrene-iodine complex is such a case.

This complex was made by Brass and Clar's method. About 600 mg. of violanthrene were suspended in 50 cc. of benzene, and boiled with 5 g. of iodine. The suspension was precipitated, forming the complex. Since the solubility of violanthrene in benzene is negligibly small, the increased weight of the precipitate was assumed to be due to the iodine content of the complex formed, from which the composition was determined as one violanthrene molecule to 4 iodine atoms. However, the composition can be varied by controlling the ratio of violanthrene to iodine, adding more or less.

The mass of this complex did not change when it was kept in a desiccator, therefore it was concluded that no decomposition takes place. Furthermore, it is quite stable up to 60°C. When it is heated beyond this temperature in a sealed glass tube, it is observed that iodine vapour is liberated. However, the recombination of iodine takes place spontaneously when it is cooled down.

The conductivity of violanthrene-iodine complex is quite stable and does not show any change over a period of weeks. The resistivity as the function of the composition is shown in Fig. 5. In this figure, it is seen that the maximum conductivity is attained at the composition of $n=4$, beyond this composition the conductivity again begins to decrease. It is assumed that in the range of the composition up to $n=4$, iodine content is insufficient to make up the additive compound with all molecules of violanthrene, whilst beyond $n=4$ excess iodine molecules are present, in some other state than the above additive compound, they fail to contribute to the conduction, giving rise to an insulating effect. Hence, 4 iodine atoms per



Iodine content n (nI/$C_{34}H_{18}$)

Fig. 5. Electrical resistivity of violanthrene-iodine complex as the function of the composition.

one violanthrene molecule is the saturation value of the composition of this additive compound and its resistivity is about 40 ohm-cm. at room temperature.

The Temperature Coefficient of the Resistivity

The temperature dependence of the resistivity was measured, for some complexes, in the range from room temperature down to the temperature of liquid air. The resistivity increases with decreasing temperature and a good linear relationship was observed between the logarithm of the resistivity and the reciprocal of temperature, as expressed in $\rho=\rho_0 \exp(\Delta\varepsilon/2kT)$ where ρ is the resistivity and $\Delta\varepsilon$ is the energy gap for conductivity. An example of the results is shown in Fig. 6, for violanthrene-iodine complex. The behaviour is as found with typical semiconductors. In Table I the values of $\Delta\varepsilon$ of the complexes are shown referring to $\Delta\varepsilon^*$ of the corresponding hydrocarbons. The decrement in the energy gap for conductivity is remarkable when the molecular complex is formed.

Discussion

Among simple organic substances, excepting graphite or carbons, no substance has ever been known with so high an electrical conductivity as in the present case. Violanthrene itself is assumed to be an intrinsic semiconductor, but its resistivity is still 2×10^{14} ohm-cm., and the resistivity of perylene is presumably more than 10^{22} ohm-cm. It is concluded that the high conductivity of the complexes between polycyclic aromatic hydrocarbons and halogens is due to an appropriate electronic state following the formation of the additive compound. Hence, in such a state, it must be assumed that there are strongly labile electrons and they can transfer from molecule to molecule under the influence of an electric field.

TABLE I
SEMICONDUCTIVITY DATA OF COMPLEXES

Complex	Resistivity at room temp. (ohm-cm.)	Temp. range (°C.)	$\Delta\varepsilon$ (eV.)	$\Delta\varepsilon^*$ (eV.)
Perylene-bromine (1:4.4)*	7.8	−20∼−170	0.13	—
Pyranthrene-bromine (1:3.3)	220	〃	0.20	1.07
Violanthrene-bromine (1:4.5)	66	〃	0.20	0.85
Violanthrene-iodine (1:4.0)	45	〃	0.15	〃
Violanthrene-iodine (1:4.0)	45	10∼60	0.14	〃

* The composition is an apparent one, expressed in one hydrocarbon molecule to halogen atoms.

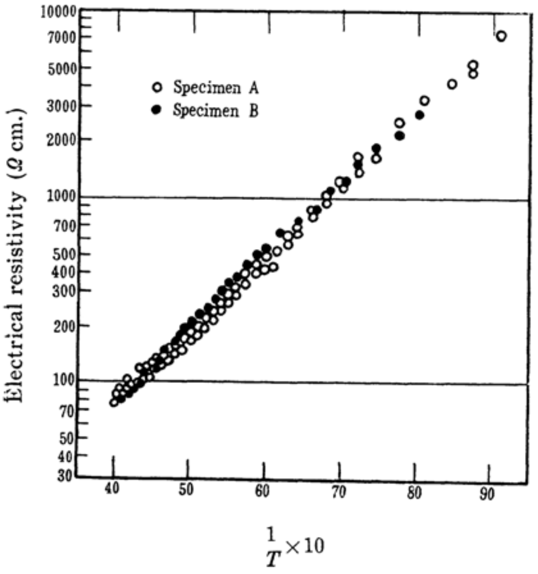


Fig. 6. Temperature dependency of resistivity of violanthrene-iodine complex.

It is known that in benzene solution of iodine, a complex formation takes place between a benzene molecule and an iodine molecule. Mulliken[5] pointed out the possibility of the intermolecular charge transfer force between them, from the presence of the corresponding spectrum, that is to say, an electron transfer takes place from a benzene molecule toward an iodine molecule accompanied by an overlapping of the molecular orbitals. The formation of the present complexes can be assumed to be due to the similar force as in the case of benzene-iodine complex. However, there is a noteworthy difference between these two cases.

In a benzene solution of iodine, a stoichiometric one to one molecular complex is formed in a state isolated from each other. On the other hand, in the present case the complexes are formed in the crystalline state, in which the molecular orbital for any one

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[5] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

molecule might overlap, if possible, with those of more than one of its neighbours. Moreover, the stoichiometric relationship is not necessarily fulfilled. In the case of violanthrene-iodine complex, the relative composition is 1:4 in the saturated state. Nevertheless, in fact, in the range where the iodine content is far less than this ratio, the complex still has a pretty good conductance. Hence, in this range of composition, it would not be a mechanical mixture of violanthrene tetraiodide and violanthrene, but it would be a non-stoichiometric molecular compound as a whole, in which iodine molecules are distributed among violanthrene molecules or vice versa. In such a state, there is not a one to one correspondence between violanthrene molecules and iodine molecules.

In the present complexes, the bond character between a hydrocarbon molecule and a halogen molecule is presumably far from an ionic one, and even from a dative covalent bond, and it might be shifted to the more metallic-like bond with delocalized electrons. Such a bond character might be attributed to an appropriate balance between the low ionization potential of a hydrocarbon molecule, which decreases with an increasing number of aromatic rings, and the high electron affinity of the halogen molecule.

Results from magnetic susceptibility measurements show that the presumable diamagnetism decreases and the paramagnetism increases, from which the presence of non-paired electrons is predicted. The details of the magnetic measurements has been presented by one of us[6].

When examined by X-rays, violanthrene-iodine complex gives merely a very diffused amorphous pattern. This agrees with the discussion mentioned above. On the other hand, in the case of perylene-bromine complex, the X-ray diffraction pattern is made of sharp lines, of which the features are varied according to the relative composition of the complex. Hence, the non-stoichiometric or amorphous state is not necessary for conductance.

Recently, Holmes-Walker and Ubbelohde[7] have reported that complexes formed between anthracene and alkali metals show semiconductor behaviour with electrical conductivity ranging 10^{-8}–10^{-12} (ohm-cm.)$^{-1}$. It was suggested that the complexes are formed by a non-stoichiometric electron transfer between alkali metal atoms and hydrocarbon molecules.

Besides these molecular complexes, even the polycyclic aromatic compounds themselves show semiconductor behaviour, and their resistivity decreases with an increase in the number of aromatic rings. In this case, it can be assumed, analogous to the complexes, that each molecule behaves as an electron-donor or electron-acceptor, one by one, and a sort of inner complex is formed between the same kind of molecules in the crystalline state.

All of these cases suggest strongly that there takes place an intermolecular overlapping of the molecular orbitals stretching throughout the crystal, whilst the molecular crystals are commonly considered as being held together merely by the force of van der Waals type between the molecules.

Summary

It was found that most polycyclic aromatic hydrocarbons form molecular complexes with bromine or iodine. Those complexes which are black behave as typical semiconductors with energy gaps for conductivity of 0.1–0.2 eV., as well as with low electrical resistivity ranging from 10^0 to 10^3 ohm-cm. The complexes are unstable and a substitution reaction of halogen takes place; when this is not the case, e. g. the violanthrene-iodine complex, and the complex itself is quite stable, so also is the electrical property. It is concluded that the origin of the high conductivity is due to the interaction between hydrocarbon molecules and halogen molecules, and this is presumably due to the overlapping of molecular orbitals stretching throughout the crystal.

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6) Y. Matsunaga, This Bulletin, 28, 475 (1955).

7) W. A. Holmes-Walker and A. R. Ubbelohde, *J. Chem. Soc.*, **1954**, 720.