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Electrical Conduction of Organic Semiconductors under High Pressure

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The electrical conductivity and the temperature dependency of the organic semiconductors, five simple polycyclic aromatic compounds, two charge transfer complexes and a free radical, have been observed up to 1.6×10^5 kg./cm². The conductivity thus increases to 10^5 – 10^7 times that at atmospheric pressure, while the band gaps decrease to about one fifth of the ordinary values. These abrupt changes may be caused by the overlapping of π -electron clouds of adjacent aromatic molecules.

In 1955, we studied the effect of pressure on the resistance of an organic semiconductor, iso-violanthrone, by means of a simple instrument and found that the resistance at 8×10^3 kg./cm² was decreased to five-hundredths that at atmospheric pressure.¹⁾ Recently, Drickamer and his collaborators have found that the electrical conductivity of polycyclic aromatics rises very rapidly until the pressure reaches the 10^5 kg./cm² region.²⁾ No quantitative treatment for these abrupt changes

has, however, yet been reported.

It is reasonable to assume that the increase in the electrical conductivity is caused by the overlapping of π -electron clouds of adjacent aromatic molecules. In this report, we will present some findings on the electrical conductivity and on the temperature dependency of polycyclic aromatic compounds and will discuss the contraction of the band gaps of the organic semiconductors.

Experimental Procedures

Materials.—The materials applied were purified by several methods, as will be described in the following

1) H. Inokuchi, This Bulletin, 28, 570 (1955).

2) G. A. Samara and H. G. Drickamer, *J. Chem. Phys.* 37, 474 (1962).

paragraphs.

Polycyclic Aromatic Compounds.—1) Coronene ($C_{24}H_{12}$). This compound was provided by the Badish Anilin Soda Fabrik A. G., of Germany. By repeated recrystallizations from 1, 2, 4-trichlorobenzene, plate-like crystallites of the hydrocarbon were obtained. When this material was then chromatographed under argon, it yielded pale yellow needles; these were twice sublimed at 200°C under a vacuum of 10^{-5} mmHg.³⁾

2) Quaterylene ($C_{40}H_{20}$). This stable aromatic hydrocarbon was purified by a method of vacuum sublimation, because it is virtually insoluble in all solvents at room temperature. Before applying the sublimation technique, an extraction of the impurities included in the matrix with trichlorobenzene was effective. After a vacuum sublimation was repeated at about 450°C , the compound was composed of dark green microcrystals. The details of the purification of this compound have already been reported.⁴⁾

3) Pentacene ($C_{22}H_{14}$). This dark-blue five-ringed aromatic hydrocarbon was provided by the Rütgerswerk A. G., of Germany. In order to purify the material, pentacene was sublimed in vacuo at about 250°C . Because of its instability against ultraviolet light, the hydrocarbon had to be kept in a dark room.

4) Tetrathiotetracene ($C_{18}H_8S_4$). The compound was provided by Matsunaga.⁵⁾ This sulphur compound was purified by recrystallizations from trichlorobenzene and also by fractional sublimation. The electronic properties of the material will be reported elsewhere.⁶⁾

5) α, α' -Diphenyl- β -picrylhydrazyl (DPPH). DPPH was prepared by the reaction of α, α' -diphenylhydrazine with picrylchloride in chloroform.⁷⁾ To prevent a complex formation with an applied solvent, a recrystallization of the free radical from a carbon disulphide solution was carried out.

6) Violanthrone (Violanthrone A; $C_{34}H_{16}O_2$). This dyestuff was synthesized from purified benzanthrone by a carefully-controlled alkali-fusion. An unstable by-product, denoted as violanthrone B, was removed by a vatting method.⁸⁾ The synthesized violanthrone was washed with chlorobenzene or with a sodium hydroxide solution and then recrystallized from concentrated sulphuric acid. Further, the material was repeatedly sublimed under a vacuum, it thus yielded dark-blue needle crystallites.

The Charge Transfer Complexes.—1) Violanthrone-iodine Complex ($C_{34}H_{16}I_2$). The complex was provided by Uchida. The complex formation between purified violanthrone and pure iodine was carried out by Clar's method.^{9,10)}

2) Perylene-iodine Complex ($C_{20}H_{12}I_2$). This complex was also prepared by Clar's method from

perylene, which was purified through repeated chromatographical purification, and pure iodine.

Both of the complexes had to be kept in sealed glass vessels to avoid decomposition.

Resistance Cell.—The materials described above were compressed between two steel plates under a few kbars* pressure to make a thin sheet, the thickness of which was about 0.1 mm. These samples were then fitted into a high pressure resistance cell. The cell applied in the experiment was similar to those used by Balchan and Drickamer.¹¹⁾ Figure 1 shows a schematic diagram of the cell.

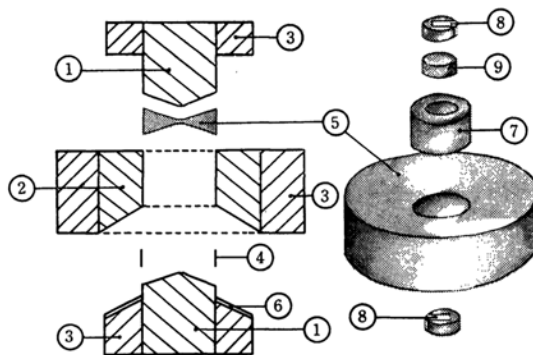


Fig. 1. Resistance cell.

1 Carboloy piston, 2 Carboloy insert, 3 steel jackets, 4 0.02 mm. mica ring, 5 pyrophyllite pellet, 6 Bakelite insulating ring, 7 pyrophyllite ring, 8 electrodes and 9 specimen

The Carboloy insert (2) was ground to a tight slip fit on the Carboloy pistons (1), and then pressed into the steel outer jacket (3). One end of each insert was ground in the truncated cone shape, with an 18° taper and 2.4 mm. diameter flat. One of the pistons was reduced in outside diameter by 0.02 mm. to permit an electrical insulation from the chamber wall with a thin strip of mica (4). A pellet of pyrophyllite (5), 0.33 mm. thick at the centre, was applied as the supporting medium for the taper. Before use, the pellet was dried in an electric oven for a few hours to remove a small amount of adsorbed water. The details of the arrangement of the electrodes in the resistance cell are illustrated in the same figure. The electrical resistances of the samples were measured by the potential drop method. To increase the electrical insulation of the cell, a boron nitride pellet (5) and ring (7) were used instead of pyrophyllite ones. As a result of this improvement, the bulk resistance of the cell reached around $10^8 \Omega$.

Pressure Calibrations**—A sharp change in the electrical resistance of bisumth at $2.54 \times 10^4 \text{ kg./cm}^2$ and $8.8 \times 10^4 \text{ kg./cm}^2$ was used in the calibration of the pressure of the resistance cell. Further, the phase transition point of lead at $1.61 \times 10^5 \text{ kg./cm}^2$ was used.

* 1 kbar = 10^3 kg./cm^2

11) A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instr.*, **32**, 308 (1961).

** Usually, there is a discrepancy between an applied pressure and a real compression on a specimen. The cause of this discrepancy is that friction and pressure in the gasket zones adsorb some of the thrust force on the piston elements.

3) H. Inokuchi, Y. Harada and T. Kondow, *J. Opt. Soc. Am.*, **54**, 842 (1962).

4) Y. Maruyama, Y. Harada and H. Inokuchi, *This Bulletin*, **36**, 1193 (1963).

5) Y. Matsunaga, *J. Chem. Phys.*, **42**, 2248 (1965).

6) M. Kochi, H. Inokuchi and Y. Harada, *Private Communication*.

7) S. Goldschmit and K. Renn, *Ber.*, **55**, 628 (1922); H. Inokuchi, Y. Harada and Y. Maruyama, *This Bulletin*, **35**, 1559 (1962).

8) J. Aoki, *ibid.*, **34**, 1817, 1820 (1961).

9) T. Uchida and H. Akamatu, *ibid.*, **35**, 981 (1962).

10) K. Brass and E. Clar, *Ber.*, **65**, 1660 (1932).

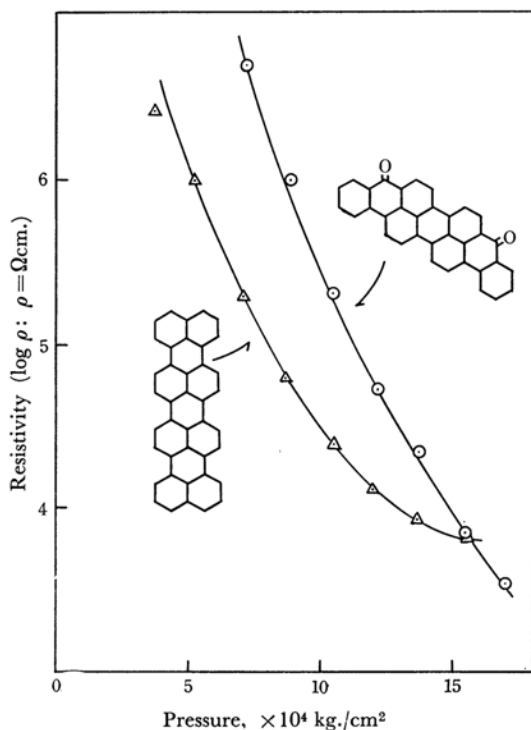


Fig. 2-(a)

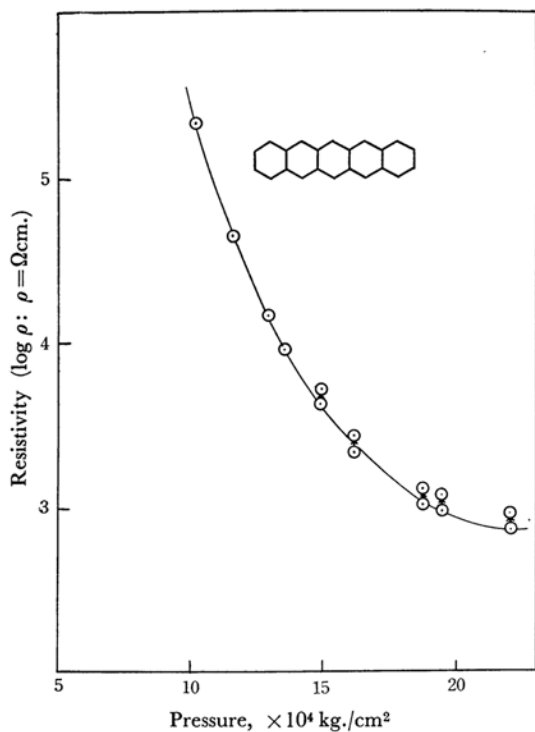


Fig. 2-(b)-1

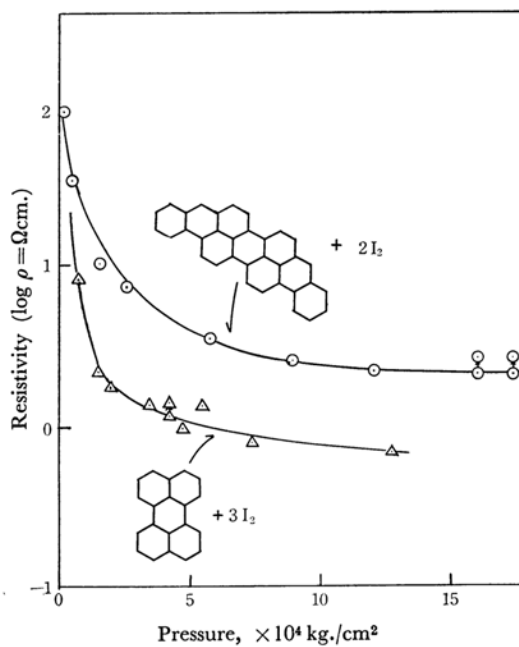


Fig. 2-(b)-2

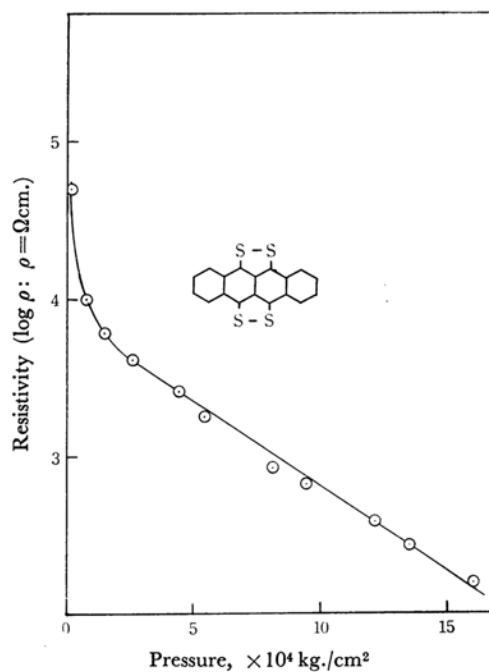


Fig. 2-(c)

Fig. 2. The electrical resistivity of organic semi-conductors as a function of hydrostatic pressure (a) quaterylene and violanthrone, (b) pentacene and two charge transfer complexes and (c) tetrathiotetracene.

Experimental Results

As has been mentioned previously,¹²⁾ the abrupt change in the electrical resistance of the purified organic semiconductors was found at a lower pressure range, 10^4 kg./cm². At a higher pressure region, three different curves between the applied pressure and the resistivity were found. Figure 2-(a) shows the pressure-resistivity curve for the first group, which displayed a leveling-off behaviour. Quaterylene and violanthrone belonged to this group.

TABLE I. THE ELECTRICAL RESISTIVITY OF ORGANIC SEMICONDUCTORS UNDER HIGH PRESSURE
($\rho = \rho_0 \exp(\Delta\epsilon/2kT)$)

Compound	At atmospheric pressure		at 1.61×10^5 kg./cm ²	
	$\rho_{15}(\Omega\text{cm.})$	$\Delta\epsilon$	$\rho_{15}(\Omega\text{cm.})$	$\Delta\epsilon$
Quaterylene	10^8	0.60	7×10^3	0.16
Violanthrone A	2.3×10^{10}	0.78	3.7×10^3	0.20
Coronene	1.7×10^{17}	1.7	$> 10^6$	—
DPPH	10^{13}	1.7	1.1×10^4 *	0.21*
Pentacene	10^{14}	1.5	2.3×10^3	0.14
Violanthrene-iodine	96**	0.15	2.3***	0.17
Peryleneiodine	10	0.06	0.6	—
Tetrathiotetracene	$4 \times 10^{4***}$	0.4 —0.5	1.6×10^2	0.34

* Under a pressure of 1.27×10^5 kg./cm²

** Under a pressure of 10^3 kg./cm²

*** At 1.20×10^5 kg./cm² compression

In the second group, the behaviour of the pressure-resistivity relation was almost identical with that of the first group. However, the resistivity was increased gradually under a constant pressure of around 10^5 kg./cm² (Fig. 2-(b)). Two charge transfer complexes, pentacene and DPPH, belonged to this group. In the second one, the resistivity of tetrathiotetracene decreased monotonously, even at a higher pressure range (Fig. 2-(c)). All of the materials examined in this experiment exhibited a sharp decrease in the band gap, as was observed from the temperature dependency of the resistivity, which is listed in Table I.

Discussion

In a previous work,¹²⁾ we assumed that the increment in electrical conductivity under the high pressure is contributed by electroncloud overlappings between molecules in the molecular lattice. The compressibility of a few of the organic molecular crystals has been observed as a function of the applied pressure.²⁾ Recently, Danno and

Kajiwarra have measured the Young modulus of a series of polycyclic aromatic compounds by means of a vibrating-reed method under atmospheric pressure; the value for triphenylene was 1.19×10^{10} dyne/cm²; for 1, 2, 3, 4-dibenzanthracene, 2.81×10^{10} dyne/cm²; for coronene, 1.10×10^{10} dyne/cm², and for the acridine-I₂ complex, 1.67×10^{11} dyne/cm².¹³⁾ From their results, we found that the average compressibility of these molecular crystals is one hundred times those of ordinary metals. The volume contraction of organic crystals by compression was expected to be anomalously large: the volumes at 1.6×10^5 kg./cm² for these molecular crystals were estimated to be 69% of those at atmospheric pressure.²⁾

The decrease in the volume upon compression is caused by the contraction of the lattice distances of adjacent molecules. The contraction, however, is not isotropic, because almost all of the crystals examined in this experiment have monoclinic or triclinic crystal structures. It is not difficult to assume that the direction perpendicular to the molecular plane, the distances of which are listed in Table II, is more compressible than the other directions. Therefore, a great increase in the electron flow in that direction of the crystal may be expected under compression.

To simplify the theoretical treatment of the charge flow in the compressed crystal, we assumed that the contraction of the crystal was isotropic. When we applied these contractions to the treatment of the tight-binding approximation, and also assumed that the carrier-scattering can be described by the constant mean free time, $\tau(k) = \tau_0$, the mobility components were given by:

$$\mu_{ij} = e\tau_0 \langle v_i v_j \rangle / kT$$

where v_i is the i th component of the carrier velocity, v , which is described by $v = (1/\hbar) \partial E(k) / \partial k$.¹⁴⁾ The $\langle v_i v_j \rangle$ quantity is a statistical average over the band. The average value of μ_{ij} in the three directions of the crystal was estimated to be 10^1 — 10^2 times larger than those at atmospheric pressure.^{14),*}

Therefore, the remarkable increase in electrical conductivity upon compression, 10^5 — 10^7 times, must result from the increase in the number of charge carriers, n in $\sigma = ne\mu$; this increment is produced from an unexpected decrease in the band gap. A similar order of decrease in the band gap was also found for some inorganic semiconductors, as is mentioned in Table III.

13) T. Danno and T. Kajiwarra, Private Communication.

14) Y. Harada, Y. Maruyama, I. Shirotani and H. Inokuchi, This Bulletin, 37, 1378 (1964).

* The anisotropic compression of some simple organic molecular crystals has been observed by Kabalkina (S. S. Kabalkina, *Fizika Tverdogo Tela.*, 4, 3124 (1962)). When we applied this finding to the tight-binding approximation roughly, the increase of mobility was estimated to be around 5×10^1 — 10^2 times value for isotropic compression, 1×10^1 — 10^2 times.

12) H. Inokuchi, I. Shirotani and S. Minomura, This Bulletin, 37, 1234 (1964).

TABLE II. THE INTERMOLECULAR DISTANCE (d) OF POLYCYCLIC AROMATIC COMPOUNDS

Compound	Crystal structure	d , Å
Benzene	Orthorhombic	3.6
Anthracene	Monoclinic	3.8
Tetracene	Triclinic	3.68
Pyrene	Monoclinic	3.53
Coronene	Monoclinic	3.4
Quaterylene	Monoclinic	3.47
Graphite	Hexagonal	3.345

TABLE III. THE DECREASE IN THE ENERGY GAP FOR ORGANIC AND INORGANIC SEMICONDUCTORS

Compound	$(dE_g/dp)_T$ (in 10^{-6} eV./bar)
Quaterylene	2.75
Violanthrone A	3.6
Pentacene	8.5
Silicon	2.0 ^{a)}
AlSb	1.6 ^{a)}

a) W. Paul and D. M. Warschauer, in "Solids under Pressure," McGraw-Hill Co., New York (1963), p. 177.

TABLE IV. THE RED-SHIFT OF THE OPTICAL ABSORPTION PEAK FOR VARIOUS POLYCYCLIC AROMATIC COMPOUNDS

Compound	Absorption peak cm^{-1}	Applied pressure $\times 10^3$ kg./cm^2	Shift per unit of pressure $\times 10^{-6}$ eV./bar
Anthracene	25300	100	4.7
Tetracene	19200*	90	6.8
	19235*	5.2	13.4
	19810	5.2	9.4
Pentacene	15000	55	9.3
Coronene	26810	4.5	13
Perylene	21368	5.2	12.5
Cu-phthalocyanine	16420	55	0.75

* 19200 cm^{-1} , observed by Drickamer, is corresponded to 19235 cm^{-1} band found by the present authors.

On the other hand, we have already determined several characteristic points in the behaviour of the optical properties of aromatic compounds under high pressure; a remarkable increase in Davydov splitting in a tetracene crystal with an increase in the pressure,¹⁵⁾ a strong red-shift of the energy transfer luminescence spectra of the

anthracene-tetracene mixed crystal, and a red-shift of the absorption spectra.¹⁶⁾ Table IV shows the red-shift of the absorption peak of aromatic compounds. Generally speaking, the value of the shift is comparable to the contractions of the band gaps; that is to say, both the anomalous changes, electrical and optical, may happen for same reasons.

In the case of a remarkable increase in Davydov splitting, the increase can be explained qualitatively by the following contribution: a decrease in lattice distances and also a rotation of molecules in the lattice points.¹⁵⁾ Under hydrostatic pressure, the crystal lattice may be diminished anisotropically; this is in contrast to the assumption adopted above. Furthermore, the contribution to the intermolecular force from dipole-quadrupole interaction and also quadrupole-quadrupole interaction between adjacent molecules must be considered.

In addition to these theoretical treatments, the accurate experimental values of compressibility in all crystal directions, and also those of electronic mobility under high pressure, which are now being examined, may be introduced as a reasonable explanation for the anomalous change in the electrical and optical properties of aromatic compounds.

The relation between pressure and resistivity above 1×10^5 — 2×10^5 kg./cm^2 for almost all samples was a leveling off; this parallels the leveling off of the compressibility of organic materials in the pressure range. The curve for tetrathio-tetracene is an exceptional one, as is illustrated in Fig. 2-(c). Above 1×10^5 kg./cm^2 , the electrical resistance still decreases monotonously.

In the second group, the resistance, after it has been leveling off, gradually increases with time. The change is assumed to be introduced by a chemical reaction between two components of the complexes or by a decomposition of the material itself. After compression, the decomposition of pentacene was confirmed by a detection of the electron spin resonance absorption signal. To the contrary of Drickamer's work, we could not find any "metallic" character of pentacene with a positive temperature coefficient.

The authors wish to thank Dr. Hiroshi Nagasaki for his kind assistance throughout this work.

15) H. Ohgishi, I. Shiotani, H. Inokuchi and S. Minomura, *J. Chem. Phys.*, **43**, 314 (1965).

16) H. Ohgishi, I. Shiotani, H. Inokuchi and S. Minomura, *J. Phys. Soc. Japan*, **19**, 1996 (1964).