Electrical Conductivity of Organic Semiconductors at High Pressure

By Yoshiya HARADA, Yusei MARUYAMA, Ichimin SHIROTANI
and Hiroo INOKUCHI

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Recently, the effect of high pressure on the electrical conductivity of polycyclic aromatic hydrocarbons and quinones has been studied.[1] In each case, the observed conductivity increases by several orders of magnitude at high pressure. This behaviour seems to be closely associated with the increase in the amount of overlap between adjacent molecules.

In this report, we will attempt to calculate the band structure of the anthracene crystal at atmospheric pressure and also at 160 kilobars in order to see what differences may be expected in the electrical conductivity.

Following LeBlanc,[2] the treatment of the tight-binding approximation was used. In the calculation of the band energy for both electrons and holes, the interaction of the anthracene molecule, sited in the crystal with a monoclinic structure C_{2h}^{5},[3] with twelve neighbour molecules was considered:

$$\begin{aligned} E(\boldsymbol{k}) = {} & \text{const} + 2E_b \cos \boldsymbol{kb} + 2E_c \cos \boldsymbol{kc} \\ & \pm \mid 2E_{a/2\,b/2} [\cos \boldsymbol{k}(\boldsymbol{a}/2 + \boldsymbol{b}/2) \\ & + \cos \boldsymbol{k}(\boldsymbol{a}/2 - \boldsymbol{b}/2)] + 2E_{a/2\,b/2\,c} [\cos \boldsymbol{k}(\boldsymbol{a}/2 \\ & + \boldsymbol{b}/2 + \boldsymbol{c}) + \cos \boldsymbol{k}(\boldsymbol{a}/2 - \boldsymbol{b}/2 + \boldsymbol{c})] \mid \qquad (1) \end{aligned}$$

where $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ denote the unit-cell vectors,

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[1] a) G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, 37, 474 (1962); b) H. Inokuchi, I. Shirotani and S. Minomura, This Bulletin, 37, 1234 (1964).

[2] O. H. LeBlanc, Jr., *J. Chem. Phys.*, 35, 1275 (1961); G. D. Thaxton, R. C. Jarnagin and M. Silver, ibid., 66, 2461 (1962).

[3] V. C. Sinclair, J. M. Robertson and A. M. Mathieson, *Acta Cryst.*, 3, 251 (1950).

and E_b, E_c, $E_{a/2\,b/2}$ and $E_{a/2\,b/2\,c}$ represent intermolecular resonance integrals. These integrals were calculated[*1] by the method used by LeBlanc, except that all of the two-centre interatomic integrals were considered for the evaluation of each intermolecular integral (Eqs. A10 and A11 given by LeBlanc have been corrected by Katz et al.[4]). Since the crystal structure of anthracene under pressure has not yet been determined, the resonance integrals at high pressure were calculated by assuming that the crystal is compressed isotropically without changes in the orientations of lattice vectors and molecules. From the relation between pressure and volume given by Samara and Drickamer,[1a] the lattice distances at 160 kilobars were estimated to be 88% of those at atmospheric pressure. Figure 1 shows the contour of $E(\boldsymbol{k})$ for each band at 160 kilobars in the $\boldsymbol{b}^{-1}$ direction in the Brillouin zone. The total band widths of the electrons and holes at 160 kilobars are 1.65×10^{-13} erg and 1.39×10^{-13} erg, these values being 5.2 and 5.8 times as large as those calculated at atmospheric pressure. If we assume that the carrier-scattering can be described by the constant mean free time, $\tau(\boldsymbol{k})=\tau_0$, the mobility components are given by:

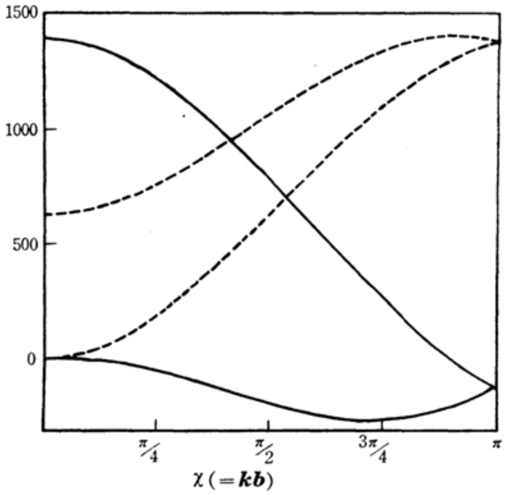

Fig. 1. Energy contours for both electrons (solid line) and holes (dashed line) in the $\boldsymbol{b}^{-1}$ direction at 160 kilobars. The origins of the energy scales have been arbitrarily chosen to make $E(0)$ the same for both bands.

$$\mu_{ij}={}_e\tau_0\langle v_i v_j\rangle/\boldsymbol{k}T \tag{2}$$

where v_i is the ith component of the carrier velocity, $\mathbf{v}$, which is given by:

$$\mathbf{v}=(1/\hbar)\partial E(\boldsymbol{k})/\partial\boldsymbol{k} \tag{3}$$

The quantity $\langle v_i v_j\rangle$ is a statistical average over the band. The velocity components and the mean square velocities of both carriers in the a, b and c′ directions are given in Table I.[*2]

Table I shows that the mobilities, on the whole, increase the magnitude by several tens times at 160 kilobars.[*3] (The values of the c' components are incredible. In order to obtain reasonable results for this component, a refined treatment such as Katz et al.'s[4] is necessary.) The observed pressure effect on the conductivity of quaterrylene, $C_{40}H_{20}$, and violanthrone, $C_{34}H_{16}O_2$, is given in Table II,[1b] where the ratios of the number of carriers, $n_{160\,\mathrm{kb}}/n_{\mathrm{atm}}$, and of the mobilities, $\mu_{160\,\mathrm{kb}}/\mu_{\mathrm{atm}}$, are estimated from the $n\propto\exp(-\Delta\varepsilon/2\boldsymbol{k}T)$ and $\sigma\propto n\mu$ relations. On the basis of this estimation, the sharp drop in the resistivity at a high pressure is attributed to the great increase in the concentrations of charge carriers, $10^3\sim10^4$ times, and to the increment of the mobilities, $10^1\sim10^2$ times, as is to be expected from the band theory treatment. When the electrical conductitvity of the anthracene crystal is compared with that of a larger aromatic hydrocarbon crystal, a similar behaviour is found. In the case of the circumanthracene ($C_{40}H_{16}$) crystal, it is found theoretically that the mobilities of the carriers are $2\sim3$ times as large as those of the anthracene crystal.[5] On the other hand, the increase in the concentrations of charge carriers is estimated to be 10^7

[*1] To faciliate the calculation, a digital computer, Facom 202, was programmed. About 20 sec. are required to compute a intermolecular resonance integral of the anthracene crystal.

[4] J. I. Katz, S. A. Rice, S. Choi and J. Jortner, *J. Chem. Phys.*, **39**, 1683 (1963).

[*2] Recently, Katz et al. (Ref. 4) refined the band calculation using the SCF carbon atomic orbital represented in the form of a linear combination of four Slater wave functions. The band widths calculated by their method are about five times larger than those found by LeBlanc. Although the present treatment is inadequate for the evaluation of the magnitude of the band widths and the velocity components, it might be useful for the estimation of the ratios of these values at a high pressure to those at atmospheric pressure. This is illustrated by the following table, which shows the mobility change due to the application of a pressure of 3000 atm.

Crystal direction	$\mu_{3000\,\mathrm{atm}}/\mu_{\mathrm{atm}}$					
	Electron			Hole		
	Exp.[a]	Calcd.[b]	Calcd.[c]	Exp.[a]	Calcd.[b]	Calcd.[c]
a	1.4	1.1	1.2	1.4	1.0	1.2
b	1.3	1.2	1.3	1.4	1.1	1.3
c′	1.0	0.9	1.3	1.4	1.3	1.6

a) R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).
b) Katz et al.
c) Present work.

[*3] For the pressure dependence of the mobility, the change in the mean free time may have a much less important role than the change in the unit-cell dimensions (Ref. 4).

[5] Y. Harada, Y. Maruyama, H. Inokuchi and N. Matsubara, to be published.

TABLE I. VELOCITY COMPONENTS AND MEAN SQUARE VELOCITY

	Electron			Hole		
	Atm. pressure (10^{10} cm^2/sec^2)	160 kb. (10^{10} cm^2/sec^2)	Ratio	Atm. pressure (10^{10} cm^2/sec^2)	160 kb. (10^{10} cm^2/sec^2)	Ratio
$\langle v^2_a \rangle$	10.4	111	11	5.6	34	6
$\langle v^2_b \rangle$	9.3	262	28	10.2	404	40
$\langle v^2_{c'} \rangle$	0.04	46	1100	1.3	386	290
$\langle v^2 \rangle$	19.8	419	21	17.1	824	48

TABLE II. THE OBSERVED PRESSURE DEPENDENCE OF THE CONDUCTIVITY

	Atm. pressure		160 kb.			
	σ, $\Omega^{-1}\cdot$cm^{-1}	$\Delta\varepsilon$, eV.	σ, $\Omega^{-1}\cdot$cm^{-1}	$\Delta\varepsilon$, eV.	$n_{160\text{ kb}}/n_{\text{atm}}$ [a]	$\mu_{160\text{ kb}}/\mu_{\text{atm}}$
Quaterrylene	8.3×10^{-9}	0.61	1.4×10^{-4}	0.16	6×10^3	3
Violanthrone	4.3×10^{-11}	0.78	1.4×10^{-3}	0.20	8×10^4	400

a) $n_{160\text{kb}}$ and n_{atm} mean the concentrations of charge carriers at 160 kilobars and at atmospheric pressure, respectively.

times (anthracene, $\Delta\varepsilon=2.7$ eV.[6]; circumanthracene, $\Delta\varepsilon=1.8$ eV.[7]). Hence, in this case also, the increment of the conductivity may be due mostly to the great increase in charge carriers resulting from the lowering of the energy gap value.

Summary

In order to study the effect of high pressure on the electrical conductivity of organic semiconductors, the band structure of the anthracene crystal has been calculated at atmospheric pressure and also at 160 kilobars, using the treatment of the tight-binding approximation. The total band widths of both electrons and holes at 160 kilobars are 5~6 times as large as those at atmospheric pressure. Although the mobilities of both carriers, on the whole, increase in magnitude by several tens times at 160 kilobars, the sharp drop in the resistivity at high pressure may be due mostly to the great increase in the concentrations of the charge carriers (10^3~10^4 times).

The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo

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[6] H. Inokuchi, This Bulletin, 29, 131 (1956).

[7] N. Matsubara, H. Inokuchi and Y. Maruyama, to be published.