Band Structure of Circumanthracene

By Yoshiya HARADA, Yusei MARUYAMA, Hiroo INOKUCHI
and Noriko MATSUBARA

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Considerable interest has developed in recent years in the theoretical interpretation of the electrical transport properties of organic molecular crystals. The characteristic nature of the crystals is their small mobilities. In fact, values of the order of 10^{-1}—10^{0} cm^2/V. sec. were observed for both electrons and holes at room temperature.[1-3] In order to account for the electron and the hole mobilities, two mechanisms have so far been considered; the usual band model (the Bloch theory), and the hopping one (the Heitler-London approach).[4] When the mobility is much larger than 1 cm^2/V. sec., the band model is applicable, while the hopping model may be better when the mobility is much smaller than 1 cm^2/V. sec.[4b] Since mobilities of the order of unity are on the borderline region between the two mechanisms, neither approach seems to be accurate enough.

The temperature dependence of the mobility also offers a condition under which one of the two models can be selected. In the usual band model the mobility should decrease with an increase in the temperature. On the other hand, the hopping model should lead to a mobility which increases exponentially with a rise in the temperature, because the thermally-activated charge carrier wanders through the crystal by jumping from one lattice site to another.* Although the mobility of anthracene decreases as the temperature increases, the situation is not favourable to the band model, because the decrement of the mobility due to the thermal expansion of the crystal has a comparable effect.[1b]

Recently, Toyozawa[5] has proposed an alternate model which is applicable to an intermediate between the above two mechanisms. He treated the carrier transport of the organic semiconductor by a localized picture and obtained, below room temperature, a mobility which is almost independent of the temperature.**

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[1] For anthracene: a) O. H. LeBlanc, *J. Chem. Phys.*, **33**, 626 (1960); b) R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960); R. G. Kepler, "Organic Semiconductors," Ed. by J. J. Brophy and J. W. Buttrey, The Macmillan Co., New York (1962), p. 1; c) I. Nakada and Y. Ishihara, *J. Phys. Soc. Japan*, **19**, 695 (1964).

[2] For pyrene: a) O. H. LeBlanc, *J. Chem. Phys.*, **37**, 916 (1962); b) K. Ohki, H. Inokuchi and Y. Maruyama, This Bulletin, **36**, 1512 (1963).

[3] For naphthalene: M. Silver, J. R. Rho, D. Olness and R. C. Jarnagin, *J. Chem. Phys.*, **38**, 3030 (1963).

[4] a) F. J. Morin, *Phys. Rev.*, **93**, 1199 (1954); b) J. Yamashita and T. Kurosawa, *J. Phys. Soc. Japan*, **15**, 802 (1960); c) T. Kurosawa, ibid., **15**, 1211 (1960).

* In the case of the hopping model, the self-trapping due to the interaction of the carrier with the lattice may be necessary. Friedman (Ref. 4) suggested the absence of the self-trapping, judging from the estimation that the bandwidths are not small compared to the binding energy of the excess carrier on the mononegative anthracene ion due to the associated lattice deformation.

[5] Y. Toyozawa, Private communication.

** His basic idea is as follows: The characteristic nature of organic semiconductors which can be clearly distinguished from inorganic ones is the existence of a large number of intramolecular vibrations. Since numerous vibronic levels resulting from these vibrational modes and their various combinations spread almost continuously over a pure electronic state (a state used for the construction of the band), and also since the distribution width of the vibronic energy states is larger than the values of the intermolecular resonance integrals, a non-localized treatment (band picture) may be a poor approach. On the other hand, since the interaction of the carrier with the lattice is relatively small (cf. preceding note), only a little activation energy may be required for the resonance transfer of the excess carrier between adjacent molecules (this is a difference from the hopping motion).

The intermolecular overlap integrals in the anthracene crystal were first calculated by Murrell.[6] Later calculations of this type were reported by Ohki et al.[2b] for pyrene. In these calculations the anisotropy of the mobility may be explained on the assumption that the overlap integrals are roughly proportional to the resonance integrals.

The tight-binding band approximation for the anthracene crystal was first calculated by LeBlanc[7] in order to describe the motion of excess charge carriers. The calculated mobility anisotropy agreed qualitatively with those experimentally observed, and the bandwidth was found to be approximately 0.56 ***kT*** at room temperature.* Subsequently, Thaxton et al.[8] extended LeBlanc's method to homologs of anthracene: naphthalene, anthracene, tetracene and pentacene. Katz et al.[9] also calculated the band structure of naphthalene, anthracene, and several polyphenyls in the tight-binding band approximation. In the calculation of intermolecular resonance integrals they used the SCF carbon atomic orbital, represented in the form of a linear combination of four Slater wave functions.[10],* The bandwidths calculated by their method were about five times larger than those found by LeBlanc. Recently, Friedman[11] calculated the electrical and thermal transport proporties of organic crystals from a Boltzmann equation treatment based on the tight-binding band structure. For anthracene the calculated mobility anisotropies in the ab plane were the same as those obtained by LeBlanc, but in the ***c'*** direction a better agreement with the experiments was found.

We have already examined in a previous paper[12] the band structure of the anthracene crystal at atmospheric pressure and also at 160 kilobars. It was found that the increase in the mobility due to the decrease in the lattice constants was found to be several tens of times at 160 kilobars. In the case of a larger hydrocarbon, the distances between molecules in the crystal, are also expected to be shorter, in addition to the change in the distribution of the carriers in the molecule.

In this report, we will attempt to calculate the band structure of circumanthracene, $C_{40}H_{16}$ (Fig. 2), by the method used by LeBlanc. Since circumanthracene is a largest hydrocarbon in the polycyclic aromatics, the electrical properties of which have been experimentally investigated,[13] it may be worth-while to compare the band structure and the mobility properties of the compound with those of anthracene.

Crystal Structure

The first step in the calculation of the band structure of the circumanthracene crystal is to estimate the coordinates of atoms in the crystal. Although the lattice constants of the crystal have been set up,[14] the orientation of the molecule in the crystal has not yet been determined. Hence, we will try to estimate the latter from the crystal structure of coronene.[15] A method of estimation is described in the Appendix. The crystal data of these two compounds, in addition to those of anthracene, are compared in Table I. The estimated orientation of the molecule in the

TABLE I. COMPARISON OF CRYSTAL DATA

	Coronene[a]	Circum-anthracene[b]	Anthracene[c]
Space group	$C^5_{2h}-P2_1/a$	$C^5_{2h}-P2_1/a$	$C^5_{2h}-P2_1/a$
a (Å)	16.10	23.77	8.561
b (Å)	4.695	4.59	6.036
c (Å)	10.15	9.98	11.163
β	110.8°	99.9°	124.7°
z	2	2	2

a) Ref. 15.
b) Ref. 14.
c) V. C. Sinclair, J. M. Robertson and A. M. Mathieson, *Acta. Cryst.*, **3**, 241 (1950).

TABLE II. ESTIMATED ORIENTATION OF THE MOLECULE IN THE CRYSTAL

$\chi_L=44.1°$	$\chi_M=107.6°$	$\chi_N=128.7°$
$\psi_L=54.8°$	$\psi_M=104.2°$	$\psi_N=38.7°$
$\omega_L=67.2°$	$\omega_M=22.9°$	$\omega_N=90.0°$

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6) J. N. Murrell, *Mol. Phys.*, **4**, 205 (1961).

7) O. H. LeBlanc, *J. Chem. Phys.*, **35**, 1275 (1961); O. H. LeBlanc, "Organic Semiconductors," Ed. by J. J. Brophy and J. W. Buttrey, The Macmillan Co., New York (1962), p. 21.

* In the calculation of the intermolecular resonance integrals, LeBlanc (and also Thaxton et al.) made some minor errors (cf. Ref. 9). The correct bandwidths obtained by his method are somewhat wide (cf. Table IV and also Figs. 5 and 6 in Text).

8) G. D. Thaxton, R. C. Jarnagin and M. Silver, *J. Phys. Chem.*, **66**, 2461 (1962).

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

10) E. Clementi and C. C. J. Roothaan, *Phys. Rev.*, **127**, 1618 (1962).

* By this choice of the atomic orbital, the behaviour of the wave function was expressed properly at large internuclear distances relevant to this problem. The calculated values of the mobility anisotropy were in better agreement with the experimental data than the mobility calculated from the single Slater-type atomic orbital.

11) L. Friedman, *Phys. Rev.*, **133**, 1668 (1964).

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

13) H. Inokuchi, N. Matsubara, Y. Maruyama and E. Clar, *Nature*, in press.

14) E. Clar, W. Kelly, J. M. Robertson and M. G. Rossman, *J. Chem. Soc.*, **1956**, 3878.

15) J. M. Robertson and J. G. White, ibid., **1945**, 607.

crystal is given in Table II,* where χ_L, ψ_L, ω_L; χ_M, φ_M, ω_M; χ_N, ψ_N, ω_N are the angles which the molecular long (L) and short (M) axes and their perpendicular (N) make with the a and b crystal axes and with their perpendicular, c′. Furthermore, all the hexagons in circumanthracene were assumed to be regular ones with a radius of 1.39 Å. Thus, the coordinates of atoms referred to orthogonal axes a, b and c′ were estimated.** Although the above estimate of the coordinates of atoms lacks confirmation, it may be adequate for the calculation of the band structure, considerering the rather rough nature of the present theoretical treatment.

Method of Calculation

The band structure and mobility tensors for circumanthracene are calculated by the method introduced by LeBlanc.⁷⁾

Disregarding the interaction between carriers (electrons or holes), the Hamiltonian operator appropriate to an electron or a hole is expressed in the form:

$$\boldsymbol{H}=(-\hbar^2/2m)\nabla^2+\sum_n V_n(\boldsymbol{r}-\boldsymbol{r}_n) \tag{1}$$

where V_n is the Hartree potential of an isolated molecule. Since the circumanthracene crystal has two molecules per unit cell, the wave function in the tight-binding band approximation is expressed by:

$$\Psi=C_1\psi_1+C_2\psi_2 \tag{2}$$

where

$$\left.\begin{aligned}\psi_1&=\textstyle\sum_A \exp[i\boldsymbol{k}\cdot\boldsymbol{r}_A]\,\phi(\boldsymbol{r}-\boldsymbol{r}_A)\\ \psi_2&=\textstyle\sum_B \exp[i\boldsymbol{k}\cdot\boldsymbol{r}_B]\,\phi(\boldsymbol{r}-\boldsymbol{r}_B)\end{aligned}\right. \tag{3}$$

in which $\phi(\boldsymbol{r})$ denotes the molecular wave function. In Eq. 3, the first sum is taken over the centre of the standard molecule and all the lattice points generated from it by primitive lattice translations; the second sum is similarly taken over the points generated from the centre of the reflected molecule at $(\boldsymbol{a}/2,\ \boldsymbol{b}/2)$. On the basis of variational principles, the band energy can be determined by the solution of a secular equation:

$$\begin{vmatrix} H_{11}-ES & H_{12} \\ H_{21} & H_{22}-ES \end{vmatrix}=0 \tag{4}$$

where

$$\left.\begin{aligned}H_{11}&=H_{22}=\int\psi_1^* H\psi_1\mathrm{d}\tau\\ H_{12}&=H_{21}^*=\int\psi_1^* H\psi_2\mathrm{d}\tau\end{aligned}\right. \tag{5}$$

Therefore, by disregarding overlap integrals, the solution of Eq. 4 becomes:

$$E=H_{11}\pm|H_{12}| \tag{6}$$

By disregarding three-centre integrals and overlap integrals, the substitution of Eq. 3 into 6 leads to:

$$\begin{aligned}E(\boldsymbol{k})=E_0+\sum_{\substack{n\\(\boldsymbol{r}_n\neq 0)}}E_n^\alpha+\sum_{\substack{l\\(\boldsymbol{r}_l\neq 0)}}E_l^\gamma\exp[-i\boldsymbol{k}\cdot\boldsymbol{r}_l]\\ \pm\Big|\sum_l E_{l+\mathrm{AB}}^\gamma\exp[-i\boldsymbol{k}(\boldsymbol{r}_l+\boldsymbol{r}_{\mathrm{AB}})]\Big|\end{aligned} \tag{7}$$

where

$$\left.\begin{aligned}E_0&=\int\phi^*(\boldsymbol{r}-\boldsymbol{r}_n)\,[(-\hbar^2/2m)\nabla^2+V_n]\\ &\qquad\times\phi(\boldsymbol{r}-\boldsymbol{r}_n)\mathrm{d}\tau\\ E_n^\alpha&=\int\phi^*(\boldsymbol{r})V_n(\boldsymbol{r}-\boldsymbol{r}_n)\phi(\boldsymbol{r})\mathrm{d}\tau\\ E_l^\gamma&=\int\phi^*(\boldsymbol{r}-\boldsymbol{r}_l)V_l(\boldsymbol{r}-\boldsymbol{r}_l)\phi(\boldsymbol{r})\mathrm{d}\tau\\ E_{l+\mathrm{AB}}^\gamma&=\int\phi^*(\boldsymbol{r}-\boldsymbol{r}_l-\boldsymbol{r}_{\mathrm{AB}})\\ &\qquad\times V_{l+\mathrm{AB}}(\boldsymbol{r}-\boldsymbol{r}_l-\boldsymbol{r}_{\mathrm{AB}})\phi(\boldsymbol{r})\mathrm{d}\tau\end{aligned}\right\} \tag{8}$$

in which E^α and E^γ denote the coulomb and the intermolecular resonance integrals respectively. In Eq. 7, while the sum, $\sum_n$ is taken over all molecules except the one with a centre located at the origin, the sum, $\sum_l$, is carried out over the primitive lattice translations.

In the actual calculation of the circumanthracene crystal, E^γ's with values of less than 10^{-16} erg were disregarded (cf. Table III). Therefore, Eq. 7 becomes

$$\begin{aligned}E(\boldsymbol{k})=\text{const.}&+2E_b\cos\boldsymbol{k}\boldsymbol{b}+2E_c\cos\boldsymbol{k}\boldsymbol{c}\\ &+2E_{b\bar{c}}\cos\boldsymbol{k}(\boldsymbol{b}-\boldsymbol{c})\\ &\pm|2E_{a/2\ b/2}[\cos\boldsymbol{k}(\boldsymbol{a}/2+\boldsymbol{b}/2)\\ &+\cos\boldsymbol{k}(\boldsymbol{a}/2-\boldsymbol{b}/2)]|\end{aligned} \tag{9}$$

which shows the interaction of the centre molecule with ten neighbouring ones (Fig.

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[*] The inclination of molecules to the ac face and also the perpendicular distances between the planes of molecules overlying each other in the b axial direction are collected in the following table. Since ovalene, $C_{32}H_{14}$, has a molecular structure intermediate between those of coronene and circumanthracene, and also since its crystal structure is similar to that of coronene, the estimated data for circumanthracene may be regarded as appropriate.

	Coronene[a]	Ovalene[b]	Circumanthracene[c]
Inclination of molecule	43.7°	42.7°	38.7°
Distance between the molecular planes	3.40 Å	3.45 Å	3.58 Å

a) Ref. 15.
b) D. M. Donaldson and J. M. Robertson, *Proc. Roy. Soc.*, **A220**, 157 (1953).
c) Calculated from Table II.

[**] While, in the case of coronene, the shortest distance between carbon atoms of the standard molecule and those of the reflected molecule at $(a/2,\ b/2)$ is 3.77 Å, the corresponding distance of circumanthracene is found to be 3.90 Å, showing the estimated coordinates of atoms to be appropriate.

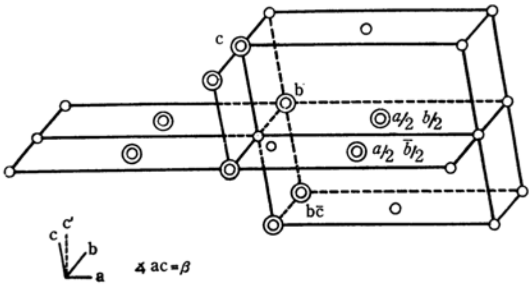

Fig. 1. The unit cell of the circumanthracene crystal. The interaction of the centre molecule (O) with molecules marked with double circles was considered.

1). The constant in Eq. 7 is immaterial to the determination of bandwidths and mobilities.

The molecular wave functions, ϕ, are linear combinations of Slater-type $2p_z$ atomic orbitals:

$$\phi=\sum_i a_i\chi_i \tag{10}$$

with

$$\chi_i=(\alpha^5/\pi)^{1/2}r_i\cos\xi_i\exp(-\alpha r_i) \tag{11}$$

and

$$\alpha=1.64\text{ a. u.}=3.08\times10^8\text{ cm}^{-1}$$

The coefficients, a_i, are determined using the approximation of Hückel. Although the orbital energies and the bond orders of the circumanthracene molecule had already been investigated by Baudet and Pullman,16) we recalculated the orbital coefficients (cf. Fig. 2), because the latter were not shown in their paper. In cases of multiple signs the upper signs are associated with the lowest antibonding orbital (for the electron) and the lower signs with the highest bonding orbital (for the hole).

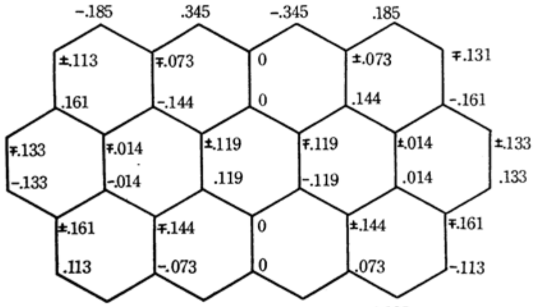

Fig. 2. Values of the coefficients for the Hückel wave functions. The magnitudes of these coefficients are the same for holes and electrons; when they differ in phase, the upper sign is for the electron and the lower for the hole.

The intermolecular resonance integrals, E_b, E_c, etc., were calculated by the method used by LeBlanc except that all of the two-centre interatomic integrals were considered for the evaluation of each intermolecular resonance integrals.

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:

$$\mu_{ij}=e\tau_0\langle v_i v_j\rangle/kT \tag{12}$$

where v_i is the ith component of the carrier velocity, and is given by:

$$v=(1/h)\partial E(\boldsymbol{k})/\partial\boldsymbol{k} \tag{13}$$

The quantity $\langle v_i v_j\rangle$ is a statistical average over the band.

Results of Calculation

The intermolecular resonance integrals of the circumanthracene crystal are given in Table III in comparison with those of anthracene.*

TABLE III. INTERMOLECULAR RESONANCE INTEGRALS (10^{-16} erg)

	Circumanthracene*		Anthracene	
	Electron	Hole	Electron	Hole
E_b	−86.0	−89.7	25.2	−33.5
E_c	−34.0	34.8	0.802	0.167
$E_{b\bar{c}}$	1.91	−2.10	−0.000100	0.000291
$E_{a/2\ b/2}$	−1.23	−1.20	−39.7	−29.0
$E_{a/2\ b/2\ c}$	0.207	−0.282	1.02	6.64

* The values of some of other resonance integrals are in unit of erg; $E_a=0.494\times10^{-32}$, $E_{bc}=0.748\times10^{-16}$, $E_{a/2\ b/2\ \bar{c}}=-0.750\times10^{-23}$ for the electron; $E_a=-1.30\times10^{-31}$, $E_{bc}=-0.916\times10^{-16}$, $E_{a/2\ b/2\ \bar{c}}=0.571\times10^{-23}$ for the hole.

In the reduced zone scheme given by $-\pi<\boldsymbol{k}\boldsymbol{a}, \boldsymbol{k}\boldsymbol{b}, \boldsymbol{k}\boldsymbol{c}<\pi$, the electron and hole band structures of circumanthracene in the reciprocal crystal axis direction are shown in Figs. 3 and 4. The origins of the energy scales are arbitrarily taken in both figures. The band structures of the anthracene crystal are also given in Figs. 5 and 6.

In Table IV we present the values of the bandwidths in the $\boldsymbol{a}^{-1}$, $\boldsymbol{b}^{-1}$, and $\boldsymbol{c}^{-1}$ directions,

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16) J. Baudet and B. Pullman, *Compt. rend.*, **244**, 777 (1957).

* The band structure of the anthracene crystal was calculated by the same method. For the evaluation of the band energy, the interaction of the centre molecule with twelve neighbouring ones was considered (cf. Ref. 12):

$$E(\boldsymbol{k})=\text{const.}+2E_b\cos\boldsymbol{k}\boldsymbol{b}+2E_c\cos\boldsymbol{k}\boldsymbol{c}$$
$$\pm\{2E_{a/2\ b/2}[\cos\boldsymbol{k}(\boldsymbol{a}/2+\boldsymbol{b}/2)+\cos\boldsymbol{k}(\boldsymbol{a}/2-\boldsymbol{b}/2)]$$
$$+2E_{a/2\ b/2\ c}[\cos\boldsymbol{k}(\boldsymbol{a}/2+\boldsymbol{b}/2)+\boldsymbol{c})+\cos(\boldsymbol{a}/2-\boldsymbol{b}/2+\boldsymbol{c})]\}:$$

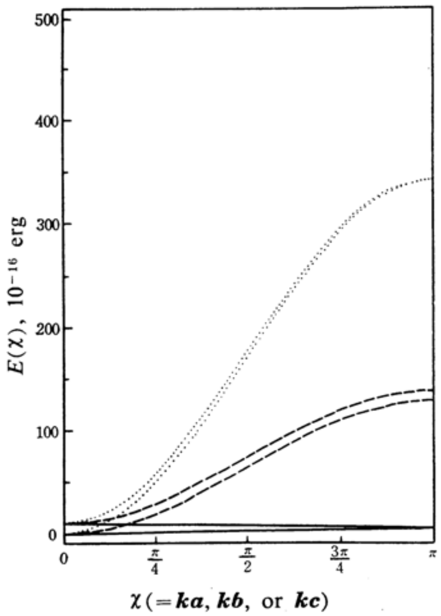

Fig. 3. Electron band structure of circumanthracene in the $\boldsymbol{a}^{-1}$ (solid line), $\boldsymbol{b}^{-1}$ (dotted line) and $\boldsymbol{c}^{-1}$ (dashed line) directions.

TABLE IV. BANDWIDTHS AND SPLITTINGS IN THE $\boldsymbol{c}^{-1}$ DIRECTION OF CIRCUMANTHRACENE AND ANTHRACENE (10^{-4} eV.)

	Circumanthracene		Anthracene	
	Electron	Hole	Electron	Hole
$\boldsymbol{a}_{-}^{-1}$	3.1	3.0	96.7	55.7
$\boldsymbol{a}_{+}^{-1}$	3.1	3.0	96.7	55.7
$\boldsymbol{b}_{-}^{-1}$	212.9	232.3	37.1	139.3
$\boldsymbol{b}_{+}^{-1}$	206.8	226.3	159.6	37.1
$\boldsymbol{c}_{-}^{-1}$	80.3	81.8	7.1	33.5
$\boldsymbol{c}_{+}^{-1}$	80.3	81.8	3.1	32.7
$\boldsymbol{c}_{\text{splitting}}^{-1}$	6.1	6.0	193.4	111.5

and also the splittings in the $\boldsymbol{c}^{-1}$ direction. Since there are two branches in each band, the lower and the upper branches are shown by $-$ and $+$ suffices respectively.

The velocity components and the mean square velocities of circumanthracene are given in Table V, in addition to those of the anthracene crystal.

Discussion

Band Structure.—As is shown in Figs. 3—6, and also in Table IV, while the bandwidths of both the electrons and holes of circumanthracene are largest in the $\boldsymbol{b}^{-1}$ direction (ca. 2×10^{-2} eV.), the widths in the $\boldsymbol{a}^{-1}$ direction are only 3×10^{-4} eV. In the case of anthracene, the direction of the smallest bandwidth is that of $\boldsymbol{c}^{-1}$. Moreover, the splittings between the upper lying bands and the lower ones of circumanthracene are smaller by a factor of 30 than those of the anthracene crystal. These relations may be due to the differences in molecular and crystal structure between these two hydrocarbons. In spite of a larger size of the molecular long axis, however, the c axis of the circumanthracene crystal is shorter than that of anthracene. This leads to far larger E_c values of circumanthracene (Table III) and, accordingly, larger bandwidths in the $\boldsymbol{c}^{-1}$ direction. On the

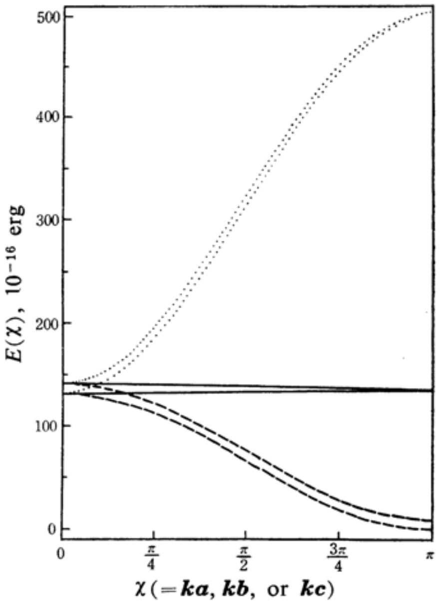

Fig. 4. Hole band structure of circumanthracene in the $\boldsymbol{a}^{-1}$ (solid line), $\boldsymbol{b}^{-1}$ (dotted line) and $\boldsymbol{c}^{-1}$ (dashed line) directions.

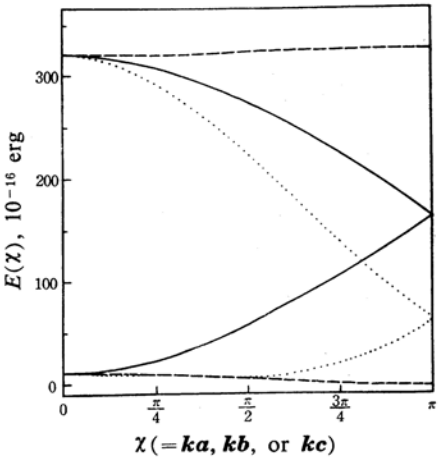

Fig. 5. Electron band structure of anthracene in the $\boldsymbol{a}^{-1}$ (solid line), $\boldsymbol{b}^{-1}$ (dotted line), and $\boldsymbol{c}^{-1}$ (dashed line) directions.

TABLE V. THE VELOCITY COMPONENTS AND THE MEAN SQUARE VELOCITIES (10^{10} cm²/sec²)

	Electron			Hole		
	Circumanthracene	Anthracene	Ratio	Circumanthracene	Anthracene	Ratio
$\langle v^2_a \rangle$	0.69	10.4	0.06	0.72	5.60	0.13
$\langle v^2_b \rangle$	28.0	9.34	3.00	30.5	10.2	3.00
$\langle v^2_{c'} \rangle$	20.2	0.041	490	21.2	1.34	16
$\langle v^2 \rangle$	49.0	19.8	2.5	52.4	17.1	3.1

TABLE VI. OBSERVED ELECTRICAL CONDUCTIVITY AT 15°C OF CIRCUMANTHRACENE AND ANTHRACENE

Circumanthracene[a] (Single crystal, ∥ b axis)		Anthracene[b] (powder)			
σ_{15}, $\Omega^{-1}\cdot$cm^{-1}	$\Delta\varepsilon$, eV.	σ_{15}, $\Omega^{-1}\cdot$cm^{-1}	$\Delta\varepsilon$, eV.	$n_{\text{circum}}/n_{\text{anth}}$	$\mu_{\text{circum}}/\mu_{\text{anth}}$
1.7×10^{-13}	1.8	10^{-21}	2.7	7.4×10^{7}	2

a) Ref. 13.
b) H. Inokuchi, unpublished.

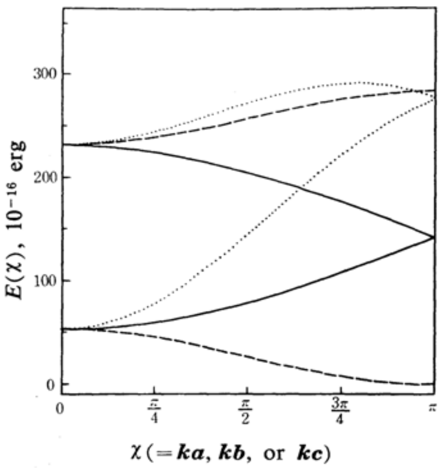

Fig. 6. Hole band structure of anthracene in the $\boldsymbol{a}^{-1}$ (solid line), $\boldsymbol{b}^{-1}$ (dotted line), and $\boldsymbol{c}^{-1}$ (dashed line) directions.

other hand, the much longer a axis of circumanthracene brings about smaller $E_{a/2\,b/2}$ values, with the consequence that the bandwidths in the $\boldsymbol{a}^{-1}$ direction and also the splittings between the upper and lower branches become very small (cf. Eq. 9). The large bandwidths in the $\boldsymbol{b}^{-1}$ direction of circumanthracene may be due to the remarkably short b axis.

As is shown in Figs. 3—6, the total bandwidths are slightly larger for circumanthracene. The total widths of the electron and the hole band of circumanthracene are 0.021 eV. (0.82 $\boldsymbol{k}T$) and 0.031 eV. (1.22 $\boldsymbol{k}T$); the corresponding widths of anthracene are 0.020 eV. (0.79 $\boldsymbol{k}T$) and 0.018 eV. (0.70 $\boldsymbol{k}T$) respectively.

Mobility Tensors.—It can be noted from Table V that the anisotropy properties of the band structure also appear in the mobility anisotropy. In the case of circumanthracene, the largest mobilities of both electrons and holes are found in the $\boldsymbol{b}$ direction, corresponding to the widest bands in the $\boldsymbol{b}^{-1}$ direction. Moreover, the mobilities in the $\boldsymbol{a}$ direction are found to be much smaller than those in the other directions, a corollary of the small bandwidths in the $\boldsymbol{a}^{-1}$ direction. On the other hand, the mobilities of anthracene are fairly isotropic on the ab plane and smaller perpendicular to it, reproducing the anisotropy properties of the bandwidths in the reciprocal lattice directions. We may, therefore, conclude that the significant differences between the mobility anisotropies of the two compounds may also be due to the differences in their crystal geometry and molecular structure.

If we assume that the values of τ_0 are comparable for these hydrocarbons, it can be seen, by comparing the values of their mean square velocities, that the mobility of circumanthracene is, on the whole, 2 or 3 times larger than that of anthracene. In general, as the resonance structure of aromatic compounds becomes larger, the electron and the hole densities at a carbon atom are smaller one side, while the distances between molecules in the crystal become shorter on the other side. The former effect may decrease the mobilities of the carriers, since it may reduce the electron and the hole densities at positions favourable to making the resonance integrals large. On the other hand, the latter effect may clearly lead to a larger mobility. Since the change in the molecular distances has a greater influence on the mobilities,* the latter effect may decide the variation in the mobility, as is found in the cases of circumanthracene and anthracene.

A Comparison with Experimental Results.—The experimental results for the electrical conductivity of circumanthracene and anthracene are summarized in Table VI. The

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* In the case of anthracene, the one percent change of the lattice distances (corresponding to the application of a pressure of 3000 atm.) leads to an increase in the mobility by a factor of 1.1—1.4 (cf. Refs. 1b, 9 and 12).

conductivity of the former was measured in the direction parallel to the b axis of a single crystal. However, in the case of anthracene, the values of a powder specimen were used.* In Table VI the ratios of the number of carrier concentrations, $n_{\rm circum}/n_{\rm anth}$, and of the mobilities, $\mu_{\rm circum}/\mu_{\rm anth}$, are estimated from two relations, $n \propto \exp(-\Delta\varepsilon/2kT)$ and $\sigma \propto n\mu$. In Table V it is found that, assuming that the values of τ_0 are comparable for both compounds, the mobilities of both the electrons and the holes of circumanthracene are three times larger than those of anthracene in the ***b*** direction, and also two or three times larger in the mean (corresponding to the mean square velocity). Thus, the calculated mobility ratio is roughly in agreement with the experimentally estimated one (Table VI), the values of the mobility of circumanthracene perhaps being several cm^2/V. sec. It is also pointed out from Table VI that, in the case of circumanthracene, while the increment of the conductivity due to the increase in the mobility is relatively small, the great increase in charge carriers due to the lowering of the energy gap value causes a sharp drop in the resistivity. When the organic crystal is compressed under high pressure, it behaves similarly.[12] The increase in the conductivity, which amounts to a factor of 10^4—10^6 at high pressure, is also due mostly to the increase in the concentrations of carriers, 10^3—10^4 times.

As for the mobility anisotrotropy of circumanthracene, although interesting properties are expected theoretically, no experimental confirmation has been obtained.**

Finally, it can be noted that, judging from the estimated magnitude of the mobility, the band model may be not satisfactory enough for us to understand the conduction in the circumanthracene crystal, as has been discussed in the introduction to the present paper. Although the substance is among the largest polycyclic aromatics, its conduction mechanism may still be distinguished from that of graphite, the electrical-transport properties of which can be satisfactorily explained by the band model.[17]

Summary

The band structure and mobility tensors of circumanthracene have been calculated by the tight-binding band approximation.

The total bandwidths of the compound have been found to be slightly larger than those of anthracene; the total widths of the electron and the hole band being $0.82\,kT$ and $1.22\,kT$ room temperature.

The values of the calculated mobilities for the electron and the hole are comparable in the ***b*** and the ***c'*** directions, but the corresponding values in the ***a*** direction are smaller by a factor of about 30∼40, reproducing the anisotropy properties of the bandwidths in the reciprocal lattice directions. Thus, the anisotropy of the band structure of the compound is considerably different from that of anthracene. This behaviour may be associated with the differences in their crystal geometry and molecular structure.

The magnitude of the mobility is three times larger than that of anthracene in the ***b*** direction, and two or three times larger in the mean, the calculated ratio being roughly in agreement with the experimentally-estimated one. Hence, it has been concluded the sharp drop in the resistivity in going from anthracene to circumanthracene is due mostly to the great increase in the concentrations of charge carriers, 10^7 times, as a result of the lowering of the energy gap value.

Finally, it has been pointed out that, although circumanthracene is among the largest polycyclic aromatics, judging from the estimated magnitude of the mobility (several cm^2/V. sec), the band model may be not satisfactory enough for us to understand the conduction in the crystal.

We would like to thank Professor Yoshihiko Saito and Professor Yutaka Toyozawa for their helpful discussions.

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

Appendix

Both coronene and circumanthracene have a monoclinic unit cell containing two molecules, one at the corner and the other in the centre of the ab face. The very short b axis is a striking feature of the circumanthracene crystal structure. This periodicity and that of the c axis are almost identical with the corresponding axial lengths in coronene. On the other hand, the length of the a

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* We adopted the values of anthracene given in Table VI for the following two reasons. Firstly, although various data for single crystals and powder specimens are found in the literature, few of them are reliable. Secondly, since the value of the conductivity of a powder specimen may be close to that on the ab plane of a single crystal, and also since the conductivity is almost isotropic on the plane, the values in Table VI may be taken as those in the **b** direction. In fact, Nakada's values, recently obtained on the ab plane of a single crystal, are near above-mentioned values.

** Since the single crystal used by Matsubara et al. was a fine needle developed in the b axial direction (0.2 ×0.2×5 mm.), the conductivity in other directions could not be observed.

[17] C. A. Coulson, *Nature*, **159**, 265 (1947); P. R. Wallace, *Phys. Rev.*, **71**, 622 (1947); R. R. Hearing and S. Mrozowski, *Progress in Semiconductors*, **5**, 273 (1960).

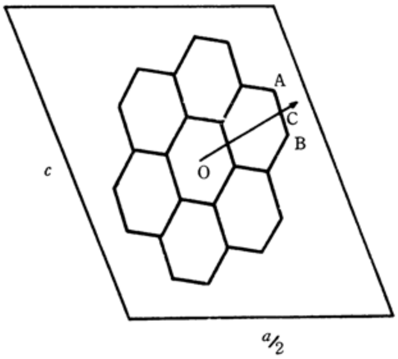

Fig. A1. Projection of the coronene structure on (010). C is the middle point of AB.

axis of circumanthracene is considerably longer that of coronene. These relations suggest that the orientations of molecules are similar in the two cases, and also that the long axis of the molecule is in the direction of the monoclinic a axis. The projection of the coronene structure on the ac face is shown in Fig. A1. In the estimation of the molecular orientation of circumanthracene, the molecule was first arranged in the same orientation as the coronene molecule, the molecular long axis being directed toward the OC axis of coronene, as is shown in Fig. A1. Then, since the circumanthracene crystal has a slightly shorter b axis, the molecule was rotated by 5° about the intersection of the molecular plane and the ac face, so as to reduce the inclination of the molecular planes to (010).