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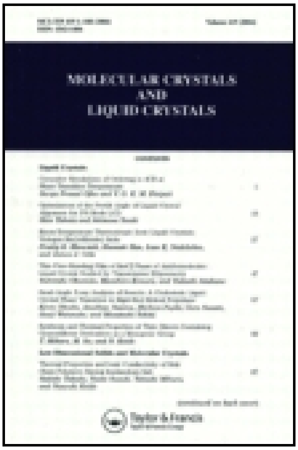

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Charge Transport in Aromatic Hydrocarbon Crystals

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Charge Transport in Aromatic Hydrocarbon Crystals

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The calculation of two-center transfer integrals (TIs) has been critically examined and closed form analytical expressions have been obtained for them. It has been found that the TI between similar molecules (0,0,0) and (l,m,n) [molecular center located at $l\mathbf{a}+m\mathbf{b}+n\mathbf{c}$] is not the same as that between (0,0,0) and ($l,\bar{m},n$). This necessitates a reformulation of the band theory of charge transport in organic semiconductors. The revised theory has been applied to a number of aromatic hydrocarbon crystals belonging to the space group $P2_1/a$ ($Z=2$). In view of the Munn-Siebrand theory of charge transport in anthracene, an attempt has been made to predict the likely mechanism of charge transport (coherent or hopping) in various directions in these crystals. Effect of the molecular size on semiconduction has also been discussed.

INTRODUCTION

There have been several attempts at understanding charge transport in aromatic hydrocarbons in general and anthracene in particular. One approach has been to calculate increasingly more reliable carrier band structure.[1-7] In these studies the electron-phonon interactions are introduced phenomenologically through an adjustable mean free time or mean free path. The second approach[8,9] considers the electron-phonon interactions explicitly. Depending on the relative magnitudes of the electron-exchange, electron-phonon and the phonon-dispersion energies, three limiting cases arise in this approach:

a) Slow-phonon coherent (band) transport, where electron-exchange energies dominate over both the electron-phonon and the phonon dispersion energies. Mobility decreases exponentially with temperature.

b) Slow-phonon hopping, where electron-exchange energies are small compared with the electron-phonon energies but larger than the phonon dispersion energies. Mobility shows a slight increase with temperature.

c) Slow-electron hopping, where the electron-exchange energies are small compared with both the electron-phonon and the phonon-dispersion energies. The temperature dependence of mobility is essentially the same as for slow-phonon hopping.

Clearly the calculation of conventional carrier band structure is valid only under the applicability of case (a). Though the Munn-Siebrand theory is not completely worked out for the intermediate regions, by qualitatively interpolating between the above limits, these authors were able to show[8] that the transport of electrons in the $C'(\perp ab)$ direction of anthracene could be ascribed to the slow-electron hopping or its extension into the intermediate region with slow-phonon hopping whereas all the other diagonal mobility components for carriers of both signs could be described by coherent transport or a mode intermediate between coherent and hopping transports in the slow-phonon limit. This explains why the band structure approach[1-5] could not predict the correct temperature dependence of the drift mobilities in anthracene, although it did explain fairly well the mobility anistropies. Changes in crystal parameters with a change in temperature might also be important[7,10]) for the temperature variation of mobility.

At the heart of the calculations in either of the two approaches (Munn-Siebrand or the conventional band approach) lies an evaluation of the intermolecular transfer intergrals (TIs) which describe the electron-exchange interactions. We have therefore critically examined the calculation of the two-center TIs and obtained closed form analytical expressions for them. We have also reformulated the band structure calculations for the space group $P2_1/a(Z=2)$ and applied them to the case of naphthalene, anthracene, β-perylene, biphenyl, p-terphenyl and p-quaterphenyl. In the absence of accurate information about the electron-phonon interactions in these hydrocarbons, we have taken them to be of the same magnitude as that estimate by Munn and Siebrand,[8] for anthracene. Under this perhaps not too unreasonable assumption, we have compared the electron-exchange interactions in these hydrocarbons with those in anthracene and thus attempted to predict the mode of charge transport in different directions in these crystals.

TRANSFER INTEGRALS

TIs are integrals of the form

$$E_n = \langle \phi_c (r-r_n) \mid V^{\mathrm{nevt}} (r-r_n) \mid \phi_c (r) \rangle \tag{1}$$

where V^{neut} is the potential of an isolated neutral molecule, ϕ_c the one-electron molecular orbital (MO) appropriate to the excess carrier (hole or electron) and r_n the vector to the center of the molecule n. Obviously the accuracy of the TIs depends on the accuracy of the MOs, ϕ_c and the molecular potential V^{neut} used in the calculation. Therefore, before coming to the actual calculation of the TIs themselves, an examination of the MOs and the molecular potential is in order.

Molecular orbitals

The MOs, ϕ_c used in Eq. (1) are represented by a linear combination of neutral carbon $2p_\pi$ atomic orbitals (AOs), u_i as

$$\phi_c = \sum_i C_{ci}\, u_i \tag{2}$$

where C_{ci} is the coefficient of the i^{th} AO in the MO describing the c^{th} energy level of the molecule. Two types of AOs have been used for TI calculations in the past – Slater-type orbitals (STOs) and self-consistent-field (SCF) AOs. Use of SCF AOs has to be preferred because of the poor description provided by a STI at large distance. Recently Morris and Yates[11] have used in their calculations for coronene and ovalene, STOs with a reduced screening parameter and claimed their results to be comparable with those to be obtained with SCF AOs. However, in the present study we have chosen to work with SCF AOs, which in turn are expressed as a linear combination of three STOs

$$u_i (r) = (\mathrm{n}_i . r) \sum_{j=1}^{3} a_j \,(\alpha_j^5 / \pi)^{1/2} \exp(-\alpha_j r) \tag{3}$$

where n_i is the unit vector in the direction of $2\mathrm{p}_\pi$ orbital and a_j and α_j are respectively the coefficients and the exponents given by Mulliken *et al.*[12] The three-STO combination for SCF AOs has been preferred over an available four-STO combination,[13] because our preliminary calculations showed no significant differences in the values of TIs for the two cases while the former has the advantage of being economical in computer time.

Once it is decided to use SCF AOs, the question of making a proper choice of the MO coefficients C arises. That is, the choice of SCF AOs as basis should also be reflected in some way in the construction of MOs. Since SCF AOs have a much larger overlap than STOs, particularly so at the large distances, it is no longer proper to neglect overlap integrals in the calculation of MOs. This point has been very well demonstrated by Devaux[14] who found that Hückel MOs taken along with STOs, implied an electronic charge of 1.09 over MO describing the hole band and of 0.67 over the electron band, both of which are different from unity. Ruedenberg's analysis[15] further stresses the importance of overlap integrals: he found that for AOs with neighbor overlap greater 0.3, not only neigbor but non-neighbor effects as well have to be considered. Since neighbor overlap for AOs defined by Eq. (3) is 0.34, the need to retain all the overlap integrals in MO calculations is obvious. Further in the calculation of intermolecular TIs, interatomic TIs between all the atoms which are closer than 10Å are to be included, so that it is hard to justify the neglect of non neighbor resonance integrals in the MO calculation. These points have already been discussed by us earlier.[16, 17]

MOLECULAR POTENTIAL

The potential of an isolated neutral molecule is written as[4]

$$V^{\text{neut}}\,(r-r_n) = \sum_{i=\text{atoms}} V_i + 2\sum_{i=\text{occ}} J^i_n - \sum_{i=\text{orc}} K^i_n \tag{4}$$

summation extends over all the carbon nuclei in the molecule (the effect of the hydrogen atoms has been shown to be negligible)[6] and the other two summations over all the occupied MOs, ϕ_{ni} of the molecule n. J^i_n are the Coulomb and the exchange operators respectively. V_i is the common GMS neutral atom potential[18] used by Katz *et al.*[2] Using Eq. (3) for u_i

$$\begin{aligned} V_i = {} & -(e^2/r_i)\,\Big(\sum_{k,n} a_n\,\alpha_n^{5/2}\,a_k\,\alpha_k^{5/2}\,/\,\beta_{kn}^5\Big)^{-1}\sum_{k,n}\exp(-2\beta_{kn}\,ri) \\ & \times(a_k\,\alpha_k^{5/2}/\beta_{kn}^5)\left[\frac{4}{3}\,(\beta_{kn}\,ri)^3 + 4\,(\beta_{kn}\,ri)^2 + 6\,(\beta_{kn}\,ri) + 4\right] \end{aligned} \tag{5}$$

where

$$\beta_{kn} = (\alpha_k + \alpha_n)\,/\,2.$$

Substituting from Eqs. (2) and (4) into Eq. (1) and neglecting the three-center integrals, the final expression for TI becomes[19]

$$\begin{aligned} E_n = \sum_{i,j} C_{ci}\,C_{cj}\Big\{ & <i\left|V_i\right|j> + (q_i-1)<ii\left|\frac{1}{r_{12}}\right|ij> \\ & -\frac{q_i}{2}<ii\left|\frac{1}{r_{12}}\right|ij>\Big\} \end{aligned} \tag{6}$$

where $|i\rangle$ is centered on the atom i of the molecule 0 and $|j\rangle$ on the atom j of the molecule n. q_i are the charge densities. The three terms in Eq. (6) are respectively the GMS contribution, contribution due to a non-uniform charge distribution over the molecule and the exchange contribution. Of these, the contribution due to the non-uniform charge distribution vanishes with HMOs (q_i=1), but with the present choice of MOs it has some finite value as all q_i are different from unity.

EVALUATION OF $<i|V_i|j>$

Integrals $<i|V_i|j>$ can be expanded in the form[1,20]

$$<i\left|V_i\right|j> = -\left[(\mathrm{n}_i.\mathrm{R}_{ij})\ (\mathrm{n}_j.\mathrm{R}_{ij})\middle|\mathrm{R}^2{}_{ij}\right](S_{ij}\,|\,\pi) + \left\{(\mathrm{n}_i.\mathrm{n}_j) - \left[(\mathrm{n}_i.\mathrm{R}_{ij})\ (\mathrm{n}_j.\mathrm{R}_{ij})\middle|R^2_{ij}\right]\right\}(C_{ij}\,|\,2\pi) \tag{7}$$

where R_{ij} is the vector from atom i to atom j and

$$S_{ij} = \int r_i r_j \cos\gamma_i \cos\gamma_j\ V_i \left[\sum_l a_l\,\alpha_l{}^{5/2}\exp(-\alpha_l r_i)\right] \left[\sum_m a_m\alpha_m{}^{5/2}\exp(-\alpha_m\nu_j)\right] d\tau \tag{8}$$

$$C_{ij} = \int r_i\ r_j\ \sin\gamma_i \sin\gamma_j\ V_i \left[\sum_l a_l\alpha_l{}^{5/2}\exp(-\alpha_l\gamma_i)\right] \left[\sum_m a_m\alpha_m{}^{5/2}\exp(-\alpha_m\nu_j)\right] d\tau \tag{9}$$

γ_i and γ_j are the angles that r_i and r_j make with R_{ij}.

At this point, attention may drawn to an error present in all the existing band structure calculations. It is easy to see that for any atom (x,y,z) on the molecule 0 and an atom $(x'+\frac{2l+1}{2}, y+\frac{2m+1}{2}, z'+n)$ on the molecule $(\frac{2l+1}{2}, \frac{2m+1}{2}, n)$ one can always find, because of the reflectional relationship, another pair of atoms $(\bar{x},\bar{y},\bar{z})$ on the molecule 0 and $(x+\frac{2l+1}{2}, y+\overline{\frac{2m+1}{2}}, z+n)$ on the molecule $(\frac{2l+1}{2}, \overline{\frac{2m+1}{2}}, n)$ which gives the same value for (N_i, R_{ij})

(N_j, R_{ij}) in Eq. (7). This makes the center molecules $(\frac{2l+1}{2}, \frac{2m+1}{2}, n)$ and $(\frac{2l+1}{2}, \overline{\frac{2m+1}{2}}, n)$ equivalent. However, there do not exist such equivalent pairs of atoms for the corner molecules (l,m,n) and $(l,\bar{m},n)$ so that these molecules are not equivalent as assumed by the earlier workers.

Katz *et al.*[2] reduced the three dimensional integrals in Eqs. (8) and (9) to one dimensional integrals by utilizing the cylindrical symmetry of S_{ij} and C_{ij} and a certain choice of coordinates. Then the resulting one dimensional integrals were solved numerically. However we have obtained closed form analytical expressions for S_{ij} and C_{ij} in a manner similar to that of LeBlanc[1] for STOs.

The computation is best effected by transforming polar coordinates of the two atoms to spheroidal coordinates ξ, η, ϕ given by

$$\xi = (r_i + r_j)\,\Big|\,R_{ij}\,, \quad \eta = (r_i - r_j)\,\Big|\,R_{ij}\,, \quad \phi = \phi_a = \phi_b \tag{10}$$

The coordinate ξ ranges from 1 to ∞ and η from -1 to $+1$. Substituting from Eqs. (5) and (10) into Eq. (8),

$$\begin{aligned} S_{ij}\,\Big|\,\pi = {} & (R_{ij}\,\Big|\,2)^4\; 2e^2 \Big(\sum_{k,n} a_n\, \alpha_n{}^{5/2}\, \alpha_k{}^{5/2}\,\Big|\,\beta^5_{kn}\Big)^{-1} \\ & \times \sum_{k,n,l,m} \Big(a_k\, \alpha_k{}^{5/2}\, a_n\, \alpha_n{}^{5/2}\,\Big|\,\beta^5_{kn}\Big)\, a_l\, \alpha_l{}^{5/2}\, \alpha_m^{5/2} \\ & \times \Big\{ \frac{t^3}{6}\,[\,(B_2A_6 - B_6A_2) + 2\,(B_3A_5 - B_5A_3) + (B_4A_0 - B_0A_4) \\ & \qquad\qquad + 2\,(B_3A_1 - B_1A_3)\,] \\ & + t^2\,[\,(B_2A_5 - B_5A_2) + (B_3A_4 - B_4A_3) + (B_3A_0 - B_0A_3) \\ & \qquad\qquad + (B_2A_1 - B_1A_2)\,] \\ & + 3t\,[\,(B_2A_4 - B_4A_2) + (B_2A_0 - B_0A_2)\,] \\ & + 4\,[\,(B_2A_3 - B_3A_2) + (B_1A_0 - B_0A_1)\,] \Big\} \end{aligned} \tag{11}$$

where

$$A_k(ut) = \int_1^\infty \xi^k e^{-ut\xi} d\xi = e^{-ut} \sum_{\mu=1}^{k+1} k!\,/\,[(ut)^\mu (k-\mu+1)!\,] \tag{12}$$

$$B_k(vt) = \int_{-1}^{+1} \eta^k\, e^{-vt\eta}\, d\eta = -e^{-vt} \sum_{\mu=1}^{k+1} k!\,/\,[(vt)^\mu\, (k-\mu+1)!\,] \tag{13}$$

$$-e^{\nu t}\sum_{\mu=1}^{k+1}(-1)^{k-\mu}k!\;/\;[(\nu t)^{\mu}\,(k-\mu+1)!\,]$$

$$t=\beta_{kn}\,R_{ij}\,,\quad u=1+(\alpha_l+\alpha_m)\,/\,2\beta_{kn}\,,\quad \nu=1+(\alpha_l-\alpha_m)\,/\,2\beta_{kn} \tag{14}$$

Similarly, the expression for $C_{ij}/2\,\pi$ becomes

$$\begin{aligned}
C_{ij}\Big|\,2\pi &= (R_{ij}\Big|\,2)^4\;e^2\Big(\sum_{k,n}a_n\alpha_n{}^{5/2}a_k\alpha_k{}^{5/2}\,\beta^5_{kn}\Big)^{-1}\\
&\times\sum_{k,n,l,m}\Big(a_k\alpha_k{}^{5/2}\,a_n\alpha_n{}^{5/2}\,\Big|\,\beta^5_{kn}\Big)\,a_l\alpha_l{}^{5/2}a_m\alpha_m{}^{5/2}\\
&\times\Big\{\frac{t^3}{6}\,[(B_2A_6-B_6A_2)+2\,(B_3A_5-B_5A_3)+(B_6A_0-B_0A_6)+2\,(B_5A_1-B_1A_5)\\
&+(B_4A_2-B_2A_4)+(B_0A_4-B_4A_0)+2\,(B_1A_3-B_3A_1)]\\
&+t^2\,[(B_2A_5-B_5A_2)+B_3A_4-B_4A_3)+B_5A_0-B_0A_5)+(B_4A_1-B_1A_4)\\
&+(B_0A_3-B_3A_0)+(B_1A_2-B_2A_1)]\\
&+3t\,[B_2A_4-B_4A_2)+(B_4A_0-B_0A_4)+(B_0A_2-B_2A_0)]\\
&+4\,[(B_2A_3-B_3A_2)+(B_3A_0-B_0A_3)+(B_1A_2-B_2A_1)+(B_0A_1-B_1A_0)]\Big\}
\end{aligned} \tag{15}$$

Finally, defining

$$A=\frac{1}{u}+\frac{1}{\nu},\qquad B=\frac{1}{u}-\frac{1}{\nu},\qquad C=\frac{1}{u}\cdot\frac{1}{\nu} \tag{16}$$

and substituting from Eqs. (12) and (13) into Eqs. (11) and (15)

$$\begin{aligned}
S_{ij}\Big|\,\pi &= R^4_{ij}\,e^2\,\Big(\sum_{k,n}a_n\alpha_n{}^{5/2}a_k\alpha_k{}^{5/2}\,\Big|\,\beta^5_{kn}\Big)^{-1}\sum_{k,n,l,m}\Big(a_k\alpha_k{}^{5/2}a_n\alpha_n{}^{5/2}\,\Big|\,\beta^5_{kn}\Big)\\
&\times a_l\alpha_l{}^{5/2}a_m\alpha_m{}^{5/2}\,(C/t^7)\,\Big\{e^{(B/C)t}[t^4BK_1+t^3K_2+3t(tB-2C)\,K_3]\\
&-Be^{-(A/C)t}\,[\tfrac{2}{3}t^6A+2t^5K_5+t^4K_6+t^3K_7\\
&+3\,(t^2A^2+2tAC+2C^2)\,K_4]\Big\}
\end{aligned} \tag{17}$$

and

$$C_{ij} \Big| 2\pi = -R_{ij}^4 e^2 \Big(\sum_{k,n} a_n \alpha_n^{5/2} a_k \alpha_k^{5/2} \Big| \beta_{kn}^5\Big)^{-1} \sum_{k,n,l,m} \Big(a_k \alpha_k^{5/2} a_n \alpha_n^{5/2} a_n \alpha_n^{5/2} \Big| \beta_{kn}^5$$

$$\times a_l \alpha_l^{5/2} a_m \alpha_m^{5/2} (C/t^7) \Big\{ e^{(B/C)t} [t^3 K_1 + t^2 BK_8 + 3(tK_3 - BCK_4)]$$

$$+ Be^{-(A/C)t} [\tfrac{2}{3} t^5 + 2t^4 K_9 + t^3 K_{10} + t^2 K_{11} + 3(tA + C) K_4] \Big\} \qquad (18)$$

where

$$K_1 = 2 - 2C + 3A - 3AC + 3A^2 + 2A^3$$

$$K_2 = 22C^2 - 14C + 45AC^2 - 33AC + 4A^2 - 51A^2C + 9A^3 - 50A^3C + 12A^4 + 10A^5$$

$$K_3 = 8C^2 - 4C + 20AC^2 - 12AC + A^2 - 22A^2C + 3A^3 - 25A^3C + 5A^4 + 5A^5$$

$$K_4 = 1 - 2C + 3A - 5AC + 5A^2 + 5A^3$$

$$K_5 = -C + A + 2A^2$$

$$K_6 = -4C + 3A - 13AC + 9A^2 + 12A^3$$

$$K_7 = 5C^2 - 3C + 2A - 15AC + 9A^2 - 30A^2C + 18A^3 + 20A^4$$

$$K_8 = 4 - 6C + 9A - 12AC + 12A^2 + 10A^3$$

$$K_9 = 1 + 2A$$

$$K_{10} = 3 - 5C + 9A + 12A^2$$

$$K_{11} = 2 - 6C + 9A - 18AC + 18A^2 + 20A^3$$

For the particular case of a single STO, $A = 3/2, B = -1/2$ and $C = 1/2$ in which case expressions (17) and (18) reduce to those given by LeBlanc[1] provided the $e^{-(A/C)t}$ terms are neglected.

Although Eqs. (17) and (18) are most general, the present choice of SCF AOs as a combination of three STOs presents one special problem. The exponents of the three STOs have values[12] $\alpha_1 = 0.898$, $\alpha_2 = 1.416$ and $\alpha_3 = 2.694$, so that for the particular case of $k = n = 1 = 1$ and $m = 3$, the value of ϑ in Eq. (14) becomes zero making the values of A, B and C infinite in Eq. (16). Hence it is no longer possible to calculate S_{ij}/π and $C_{ij}/2\pi$ from Eqs. (17) and (18) unless this particular combination of k, n, l and m is dealt with in some other manner. This can be accomplished by taking the following limiting values of $B_k(\nu t)$ as νt approaches zero,

$$B_k(\mathrm{o}) = 2/(k+l) \text{ for } k \text{ even}, \qquad = 0 \text{ for } k \text{ odd} \ldots \tag{19}$$

Then the summations in Eqs. (17) and (18) should be understood to exclude the combination $k = n = 1 = 1$ and $m = 3$ and the following expressions be added in its place,

$$\text{to } S_{ij} \Big| \pi, \ R_{ij}^4 e^2 (\sum_{k,n} a_n \alpha_n{}^{5/2} a_k \alpha_k{}^{5/2} \Big| \beta_{kn}^5)^{-1} a_1{}^3 \alpha_1{}^{5/2} a_3 \alpha_3{}^{5/2}$$

$$\times \frac{2e^{-3p}}{27p^4} \left(\frac{74}{81} + \frac{74}{27}p + \frac{61}{45}p^2 - \frac{187}{45}p^3 - \frac{257}{105}p^4 - \frac{26}{35}p^5 - \frac{4}{35}p^6\right) \tag{20}$$

$$\text{to } C_{ij} \Big| 2\pi, \ - R_{ij}^4 e^2 (\Sigma a_n \alpha_n{}^{5/2} a_n \alpha_n{}^{5/2} \Big| \beta_{kn}^5)^{-1} a_1{}^3 \alpha_1{}^{5/2} a_3 \alpha_3{}^{5/2}$$

$$\times \frac{2e^{-3p}}{81p^4} \left(\frac{74}{27} + \frac{74}{9}p + \frac{431}{45}p^2 + \frac{61}{15}p^3 + \frac{34}{35}p^4 + \frac{4}{35}p^5\right) \tag{21}$$

where

$$p = \alpha_1 R_{ij}.$$

EVALUATION OF $<ii|\frac{1}{r_{12}}|ij>$

An exact evaluation of the integral $<ii|\frac{1}{r_{12}}|ij>$ in Eq. (6) is quite involved, therefore we use here an approximation given by Chen[21] which, according to him, is valid for interatomic distances in excess of 3Å. Since the shortest interatomic contact between two molecules found in the crystals studied here exceeds this limit, we can justifiably use Chen's approximation. Then the integral $<ii \ \frac{1}{r_{12}} \ ij>$

$$<ii \left|\frac{1}{r_{12}}\right| ij> \approx <i \left|\frac{1}{r_i}\right| j> \tag{22}$$

The latter integral can be evaluated in a closed form using just the same methods as those used for evaluating $<l|V_i|j>$. The final expressions are

$$<i \ \frac{1}{r_i} \ j> = - [(\mathrm{n}_i.\mathrm{R}_{ij})(\mathrm{n}_j.\mathrm{R}_{ij}) \ \ R_{ij}^2](S'_{ij} \Big| \pi)$$

$$+ \Big\{(\mathrm{n}_i, \mathrm{n}_j) - [(\mathrm{n}_i, \mathrm{R}_{ij})(\mathrm{n}_j, \mathrm{R}_{ij}) \ \ R_{ij}^2]\Big\}(C'_{ij} \Big| 2\pi) \tag{23}$$

with

$$S'_{ij}\bigg|\pi = (R_{ij}^4\bigg|4)\, e^2 \Bigg\{ \sum_{\substack{k,n\\k\neq n}} a_k {\alpha_k}^{5/2}\; a_n {\alpha_n}^{5/2}\; C'\,[e^{B'}(-2B' - 4B'^2$$

$$- 3B'^3 + 6B'^2C' - 2C' - 6B'C'^2) + B'e^{-A'}(6A'C' + 6C'^2 + 2A'$$

$$+ 3A'^2)] + \Sigma\, a_k^2 \alpha_k^5\; 2\,\frac{e^{-A'}}{A'}\;\frac{1}{3} - \frac{1}{A'^2} - \frac{1}{A'^3}\Bigg\} \tag{24}$$

and

$$C'_{ij}\bigg|2\pi = (R_{ij}^4\bigg|4)\, e^2 \Bigg\{ \sum_{\substack{k,n\\k\neq n}} a_k {\alpha_k}^{5/2}\; a_n {\alpha_n}^{5/2}\; C'\,[e^{B'}(2 + 4B' + 3B'^2$$

$$- 3B'C') + B'e^{-A'}(2 + 3A' + 3C')] + \Sigma\, a_k^2\, \alpha_k^2\; 2\,\frac{e^{-A'}}{A'^2}$$

$$\times\left(\frac{1}{3} + \frac{1}{A'} + \frac{1}{A'^2}\right)\Bigg\} \tag{25}$$

where $t = \beta_{kn}\, R_{ij}$, $A' = \alpha_k R_{ij}$, $B' = \alpha_n R_{ij}$, $C' = 2/t(A' + B')$.

BAND STRUCTURE AND MOBILITY

Crystals studied in the present paper belong to the space group $P2_1/a$ with two molecules per unit cell. One can look upon the crystal as comprising of two interpenetrating monoclinic sub-lattices. Following Mathur and Kumar[7] the Bloch sums for the two sub-lattices can be written as

$$\psi_1(\mathrm{k}) = (N)^{-1/2} \sum_{l=1}^{N} \exp(i\mathrm{k}\,,\, r_l)\, \phi_1\,(r - r_l) \tag{26}$$

and

$$\psi_2(\mathrm{k}) = (N)^{-1/2} \sum_{l=1}^{N} \exp(i\mathrm{k}\,.\{\, r_l + r_{12}\,\})\, \phi_2\,(r - r_l - r_{12}) \tag{27}$$

where the two summations extend over all the N unit cells, and ϕ_2 are the MOs for the two molecules in the l^{th} unit cell and r_{12} the radius vector between them. ϕ_1 and ϕ_2 are same except for their spatial orientation. We write

$$H_{ij}\,(\mathrm{k}) = <\psi_i\,(\mathrm{k})\; \mathrm{I}\, H\, \mathrm{I}\; \psi_j\,(\mathrm{k})> \qquad ,\, i\,,\, j = 1{,}2 \tag{28}$$

then the energy eigenvalues are the solutions of

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12}^{*} & H_{22} - E \end{vmatrix} = 0$$

or

$$E=\frac{1}{2}(H_{11}+H_{22})\pm\left\{\frac{1}{2}(H_{11}-H_{22})\right\}^{2}+|H_{12}|^{2}\ ^{1/2} \tag{29}$$

where + and – signs give two bands corresponding to the two molecules per unit cell. We shall denote these bands by superscripts (1) and (2) respectively. Clearly expression (29) can reduce to the usual expression for the symmetric and antisymmatric bands only if $H_{11}=H_{22}$. In the earlier band structure calculations, this condition was erroneously fulfilled by not differentiating between TIs for the molecules (l,m,n) and (l,m,n). However, as pointed out in Section 2C, they were really non-equivalent and hence the new expression. This point may be further elaborated by writing out the explicit expressions for H_{11} and H_{12} as follows,

$$\begin{aligned}
H_{11} &= 2\,E_1 \cos k\,,\,(a+2c)\\
&+ 2\,E_3 \cos k\,,\,(-a-b+c)\\
&+ 2\,E_4 \cos k\,,\,(-a+b)\\
&+ 2\,E_5 \cos k\,,\,(-a+b+c)\\
&+ 2\,E_8 \cos k\,,\,(-2b+c)\\
&+ 2\,E_9 \cos k\,,\,(-b+c)\\
&+ 2\,E_{10} \cos k\,,\,c\\
&+ 2\,E_{11} \cos k\,,\,(b+c)\\
&+ 2\,E_{12} \cos k\,,\,(2b+c)\\
&+ 2\,E_{15} \cos k\,,\,(a-b+c)\\
&+ 2\,E_{16} \cos k\,,\,(a+c)\\
&+ 2\,E_{17} \cos k\,,\,(a+b+c)\\
&+ 2\,E_{19} \cos k\,,\,(-a+b)\\
&+ 2\,E_{20} \cos k\,,\,b\\
&+ 2\,E_{21} \cos k\,,\,2b\\
&+ 2\,E_{24} \cos k\,,\,a\\
&+ 2\,E_{25} \cos k\,,\,(a+b)
\end{aligned} \tag{30}$$

$$\begin{aligned}H_{12} &= 2\ E_2\ [\cos \mathrm{k}\ .\ (-\tfrac{3}{2}\ \mathrm{a} + \tfrac{1}{2}\ \mathrm{b} + \mathrm{c}) + \cos \mathrm{k}\ .\ (-\tfrac{3}{2}\ \mathrm{a} - \tfrac{1}{2}\ \mathrm{b} + \mathrm{c})]\\ &+ 2\ E_6\ [\cos \mathrm{k}\ .\ (-\tfrac{1}{2}\ \mathrm{a} + \tfrac{1}{2}\ \mathrm{b} + \mathrm{c}) + \cos \mathrm{k}\ .\ (-\tfrac{1}{2}\ \mathrm{a} - \tfrac{1}{2}\ \mathrm{b} + \mathrm{c})]\\ &+ 2\ E_1\ [\cos \mathrm{k}\ .\ (-\tfrac{1}{2}\ \mathrm{a} + \tfrac{3}{2}\ \mathrm{b} + \mathrm{c}) + \cos \mathrm{k}\ .\ (-\tfrac{1}{2}\ \mathrm{a} - \tfrac{3}{2}\ \mathrm{b} + \mathrm{c})]\\ &+ 2\ E_{13}\ [\cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} + \tfrac{1}{2}\ \mathrm{b} + \mathrm{c}) + \cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} - \tfrac{1}{2}\ \mathrm{b} + \mathrm{c})]\\ &+ 2\ E_{14}\ [\cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} + \tfrac{3}{2}\ \mathrm{b} + \mathrm{c}) + \cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} - \tfrac{3}{2}\ \mathrm{b} + \mathrm{c})]\\ &+ 2\ E_{18}\ [\cos \mathrm{k}\ .\ (\tfrac{3}{2}\ \mathrm{a} + \tfrac{1}{2}\ \mathrm{b} + \mathrm{c}) + \cos \mathrm{k}\ .\ (\tfrac{3}{2}\ \mathrm{a} - \tfrac{1}{2}\ \mathrm{b} + \mathrm{c})]\\ &+ 2\ E_{22}\ [\cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} + \tfrac{1}{2}\ \mathrm{b}) + \cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} - \tfrac{1}{2}\ \mathrm{b})]\\ &+ 2\ E_{23}\ [\cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} + \tfrac{3}{2}\ \mathrm{b}) + \cos \mathrm{k}\ .\ (\tfrac{1}{2}\ \mathrm{a} - \tfrac{3}{2}\ \mathrm{b})] \qquad (31)\end{aligned}$$

where the numbering of the molecules has been shown in Figgure 1. All those molecules which have any interatomic contacts closer than 10Å with the reference molecules, have been included. Molecules have been numbered arbitrarily in the order of decreasing *z*-, increasing *x*-, and increasing *y*-coordinate, with *z*-coordinate varying least rapidly and *y*- the most rapidly. Since a two-fold rotation about the *b*-axis plus a translation that transforms the crystal into itself, transforms type 1 molecules into type 2 molecules, the TI (*l*,*m*,*n*) for type 2

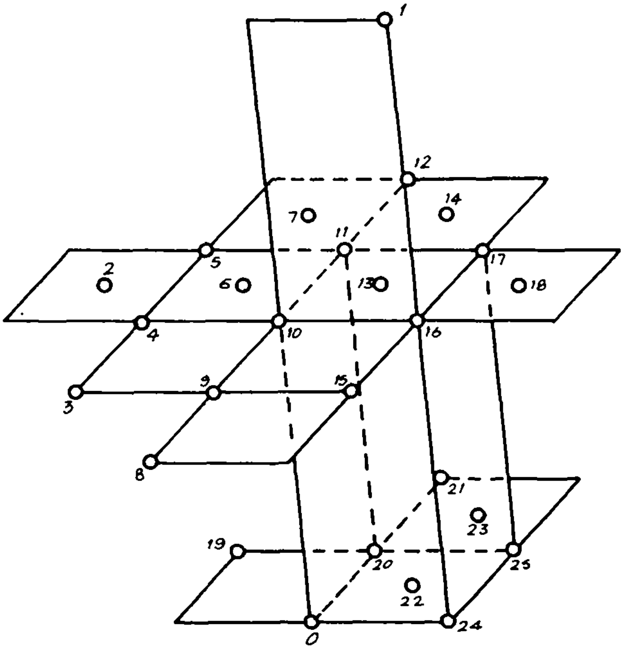


FIGURE 1 Schematic representation of the unit cell of space group $P2_1/a(Z=2)$ showing the numbering of the molecules.

molecules equals (l,m,n) for type 1 molecules and vice versa. Therefore the expression for H_{22} may be derived from that of H_{11} by just substituting $-b$ for b everywhere. Obviously H_{11} can be equal to H_{22} only if one does not distinguish between the molecule pairs such as (3,5), (8,12) etc.

Expressions for the band structure in special cases when k is parallel to one of the reciprocal lattice vectors, can be written as

$$E\,(\mathrm{k} \parallel \mathrm{a}^{-1}) = [H_{11} \pm |H_{12}|]_{\mathrm{k}\,.\,\mathrm{b}\,=\,\mathrm{k}\,.\,\mathrm{c}\,=\,0} \tag{32}$$

$$E\,(\mathrm{k} \parallel \mathrm{b}^{-1}) = [H_{11} \pm |H_{12}|]_{\mathrm{k}\,.\,\mathrm{c}\,=\,\mathrm{k}\,.\,\mathrm{a}\,=\,0} \tag{33}$$

$$E\,(\mathrm{k} \parallel \mathrm{c}^{-1}) = [H_{11} \pm |H_{12}|]_{\mathrm{k}\,.\,\mathrm{a}\,=\,\mathrm{k}\,.\,\mathrm{b}\,=\,0} \tag{34}$$

Components of the mobility tensor in the constant mean free time (const τ) and the constant mean free path (const λ) approximations are respectively

$$\mu_{ij} = (e\tau_0/kT) < v_i v_j > \tag{35}$$

and

$$\mu_{ij} = (e\lambda_0/kT) < v_i v_j / |v(\mathrm{k})| > \tag{36}$$

where the angular brackets indicate averaging over Boltzmann Distribution of electrons in the energy bands and v_i is the i^{th} component of the velority vector $v(k)$.

RESULTS AND DISCUSSION

All the numerical calculations were carried out on IBM 360/44 and ICL 1909 electronic computers.

Charge densities and MO coefficients for the aromatic hydrocarbons studied are collected in Table 1. The numbering of the atomic sites within the molecules is shown in Figure 2. Crystal structure data for the hydrocarbons are collected in Table 2 and the TIs obtained between molecule 0 and the other molecules are presented in Table 3. Atom pairs separated by more than 10Å were neglected. Though, to save on space, contributions due to the GMS potential, non-uniform charge distribution and the exchange potential are not listed separately, it may be mentioned that the exchange contribution was more significant than the GMS contribution. Table 3 shows the TIs for the non-equivalent molecules 3 and 5; 8 and 12; 9 and 11; 15 and 17; 19 and 25 to differ not only in magnitude but very often in the sign as well, a fact which necessitates a reformulation of the band structure calculations. Molecules 6, 10, 13, 20, 22 have large TIs and are,

Table I

Charge Densities, Highest Occupied (HOMO) and Lowest Empty (LEMO) Molecular Orbitals for Various Aromatic Hydrocarbons
(Irreducible representation of point group D_{2h}, to which a particular MO belongs, has been indicated within parantheses alongside the first coefficient of each MO).

Hydrocarbon	Atomic site, i	q^i	$C_{\text{HOMO},i}$	$C_{\text{LEMO},i}$
Naphthalene [a]	1	1.01968	0.41419(a_u)	0.51035(b_{2g})
	2	1.01966	0.27206	−0.32284
	9	0.92133		
Anthracene [b]	1	1.02133	0.30647(b_{3g})	0.37972(b_{1u})
	2	1.02506	0.24269	−0.27583
	9	1.05509	−0.45531	−0.47818
	11	0.92607	−0.10231	0.10052
Perylene [c]	1	1.05807	0.32462(a_u)	0.32000(b_{3g})
	2	1.01499	−0.10068	0.14182
	33	1.05766	−0.34690	−0.36647
	18	0.96952		
	19	0.92086		
	20	0.92410	0.20720	−0.28683
Biphenyl [c]	1	0.90812	0.32730(b_{2g})	0.45459(b_{1u})
	2	1.03191	0.31381	−0.33947
	3	0.99804	−0.11667	−0.18523
	4	1.03199	−0.40384	0.49154
p-Terphenyl [c]	1	0.90698	0.19507(b_{2g})	0.31530(b_{1u})
	2	1.03700	0.26397	−0.27980
	3	0.99802	−0.06315	−0.12452
	4	1.03802	−0.31214	0.37649
	7	0.93292	−0.36746	0.42552
	12	1.02602	−0.23127	−0.24274

p-Quaterphenyl [c]	1	0.93055	0.28390(b_{2g})	0.34442(b_{1u})
	2	1.03051	0.23843	−0.23577
	3	1.02555	−0.16987	−0.18570
	4	0.93816	−0.33364	0.37423
	13	0.90696	0.12868	0.24058
	14	1.03828	0.21797	−0.23452
	15	0.99803	−0.03950	−0.09391
	16	1.03959	−0.25017	0.30572

[a] Ref. (17).
[b] Ref. (16).
[c] Unpublished calculations.

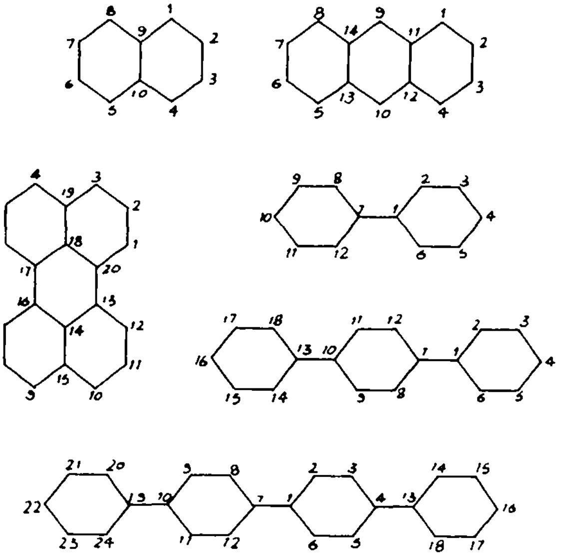


FIGURE 2 Numbering of atomic sites in various aromatic hydrocarbons.

therefore, expected to dominate the charge transport. Another point to be noted is that the molecule 22 gives consistently a larger TI for electrons than for the holes, and hence it should contribute more to the electron-transport than to the hole transport.

To compare the electron-exchange interactions in other aromatic hydro-

TABLE 2

Unit Cell Parameters of Various Aromatic Hydrocarbon Crystals

Crystal	a(A)	b(A)	c(A)	β
Naphthalene [d]	8.235	6.003	8.658	122°55′
Anthracene [e]	8.562	6.038	11.184	124°42′
β-Perylene [f]	11.27	5.88	9.65	92.1°
Biphenyl [g]	8.12	5.63	9.51	95.1°
p-Terphenyl [h]	8.106	5.613	13.613	92° 1′
p-Quaterphenyl [i]	8.05	5.55	17.81	95.8°

[d] Cruickshank, D.W.J., *Acta Cryst.* 10, 504 (1957).
[e] Mason, R., *Acta Cryst.* 17, 547 (1964).
[f] Tanaka, J., *Bull. Chem. Soc. Japan* 36, 1237 (1963).
[g] Hargreaves, A. and Rizvi, S.H., *Acta Cryst.* 15, 365 (1962).
[h] Rietveld, H.M., Maslen, E.N. and Clews, C.J., *Acta Cryst.* B26, 693 (1970).
[i] Pickett, L.W., *J. Am. Chem. Soc.* 58, 2299 (1936).

TABLE 3

Intermolecular Transfer Integrals in Units of 10^{-4} eV for Various Aromatic Hydrocarbon Crystals

Molecule	Naphthalene		Anthracene		β-Perylene		Bipheneyl		*p*-Terphenyl		*p*-Quaterphenyl	
number	Hole	Electron	Hole	Electron	Hole	Electron	Hole	Electron	Hole	Electron	Hole	Electron
0	Reference				Molecule							
1	0.00	-0.01										
2									-0.01	-0.02	-0.00	-0.01
3									0.08	0.05	0.04	0.03
4									-7.16	3.42	-4.41	2.57
5									-0.53	0.18	-0.33	0.13
6	-0.33	-0.49	0.12	0.31	-0.02	0.99	0.22	-1.06	69.23	50.40	41.34	-33.46
7					-0.01	-0.01			0.07	0.06	0.03	0.05
8					0.00	-0.01						
9	-2.17	1.39	1.65	-0.71	-1.43	-2.49	-7.57	-1.16	-2.80	-1.02	-1.53	-0.86
10	1.36	-21.34	-4.63	-5.78	164.91	-283.46	-290.14	-34.71	-165.82	16.02	-110.19	29.64
11	4.11	0.95	-1.85	-0.39	1.93	-2.46	0.60	0.08	0.03	0.48	-0.07	0.49
12											-0.00	0.00
13	-160.80	-21.38	151.31	13.57	-73.39	40.74	126.78	-79.23	0.27	-0.78	0.22	-0.61
14	0.29	-0.05	-0.13	0.03	0.33	0.06	0.19	0.09			-0.00	-0.00
15	-1.03	-0.42	0.21	0.05			0.26	0.09				
16	54.38	17.50	-23.63	-7.30	0.48	-0.10	-14.83	5.69				
17	0.41	-0.32	-0.23	0.26	0.01	0.00	-0.97	0.18				
18	0.03	0.12	0.11	-0.02			-0.02	-0.03				
19	-0.32	-0.21	-0.08	-0.46			-0.11	0.86	-0.10	0.31	0.41	0.24
20	-386.18	101.98	-462.66	314.94	-1201.8	117.57	292.19	444.20	291.37	489.67	344.97	617.72
21	0.03	0.06	-0.02	0.03	-0.14	-0.40	0.00	0.39	-0.00	0.42	-0.01	0.54
22	171.30	-242.63	-286.30	-555.67	-10.00	234.06	86.26	-341.07	-14.13	-331.00	-35.01	-399.24
23	0.42	0.16	0.19	0.05	0.06	0.97	-0.05	0.08	-0.01	0.06	0.03	0.35
24	1.94	-0.72	2.26	2.49	0.01	0.14	-4.92	0.37	-4.64	1.21	-4.57	0.46
25	3.00	-0.72	0.53	0.37	0.08	-0.42	-0.36	0.41	-0.06	1.14	-0.05	1.85

carbon crystals with those in anthracene, we may use the following expression for mobility derived by Munn and Siebrand[9] from linear response theory,

$$\mu = (e/kT) \Sigma (E_n r_n)^2 \gamma_n \tag{37}$$

where summation extends over all the molecules and γ_n is a complicated function of the model parameters. From this expression it is obvious that the relative contribution of any TI, E_n to the mobility varies as $|E_n r_n|$. The mechanism of charge transport in a particular direction will then be determined by the TI which gives the largest contribution in that direction. Table 4 lists the dominant contributions $|E_n r_n|$ along *a, b* and *c* (⊥*ab*) directions in all the crystals. Combining the results for anthracene with Munn and Siebrand's assignment of transport mechanisms in various directions, we may limit the three regions as

$|E_n r_n| < 125 \times 10^{-4}$ eV–Å slow-electron hopping

125×10^{-4} eV–Å $< |E_n r_n| < 1225 \times 10^{-4}$ eV–Å slow-phonon hopping

$|E_n r_n| > 1225 \times 10^{-4}$ eV–Å slow-phonon coherent transport.

On the basis of this criterion, the likely mode of transport in various directions in other crystals is also indicated in Table 4. It is found that band theory is the dominant mechanism of transport, with slow-electron hopping predicted for no case other than the electrons in *c*' direction of anthracene. However, in some directions the transport is likely to occur by slowphonon hopping. It can also be seen that the transport in the *b*-direction is always in bands except for the case of electrons in naphthalene where it is by slow-phonon hopping. This is not quite unexpected as *b* being the shortest axis (Table 2), electron-exchange interactions are expected to be strong in this direction. The slow-phonon hopping cases are most likely to occur for holes in the *a* direction and for electrons in the *c*' direction. Another feature to be noted from Table 4 is that, in general, the transport mechanism in the a-direction is governed by the molecule 22, that in the *b*-direction by 20 and in the *c*' direction by 13 or 10.

Having established the general applicability of band theory of charge transport to the crystals studied here, we feel justified to proceed with the band structure calculations. However, the results in those directions where a different transport mechanism is indicated in Table 4, should bh accepted with caution. The calculated band structures are plotted in Figure 3 and the bandwidths and the splittings along the c—^{1} direction collected in Table 5. An important point to be noted about the band structure is that the hole bands along c^{-1} in biphenyl, *p*-terphenyl and *p*-quaterphenyl which were crossing (splitting zero) in Katz *et al.* 's treatment,[2] no longer cross because of the reformulation of band theory. Since the new theory involves a sort of configuration interaction treat-

TABLE 4

Values of the Dominant Contributions $|E_n r_n|$ to the Mobilities and The Assigment of Transport Mechanism in Various Aromatic Hydrocarbon Crystals

Crystal	$|E_n r_n|$, (10^{-4} eV−Å)					
	Hole			Electron		
	a	*b*	*c*′(⊥*ab*	*a*	*b*	*c*′(⊥*ab*)
Naphthalene	705(22) *PH*	2210(20) *B*	1169(13) *PH*	999(22) *PH*	728(22) *PH*	155(13) *PH*
Anthracene	1226(22) *B*	2794(20) *B*	1391(13) *B*	2379(22) *B*	1902(20) *B*	125(13) *EH*
β-Perylene	388(13) *PH*	7067(20) *B*	1590(10) *B*	1320(22) *B*	1376(22) *B*	2733(10) *B*
Biphenyl	407(13) *PH*	2645(20) *B*	2748(10) *B*	1385(22) *B*	2501(20) *B*	750(13) *PH*
p-Terphenyl	314(6) *PH*	1635(20) *B*	2256(10) *B*	1342(22) *B*	2749(20) *B*	686(6) *PH*
p-Quaterphenyl	241(6) *PH*	1915(20) *B*	1953(10) *B*	1609(22) *B*	3428(20) *B*	593(6) *PH*

(Numbers within the parantheses refer to the molecule to which the particular contribution is due.
B = slow-phonon coherent transport; *PH* = slow-phonon hopping transport; *EH* = slow-electron hopping transport).

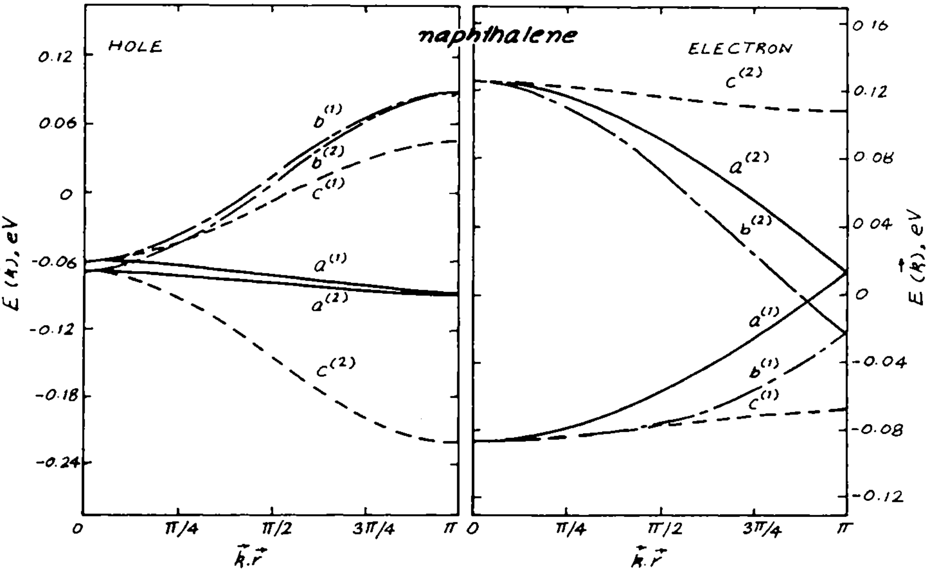
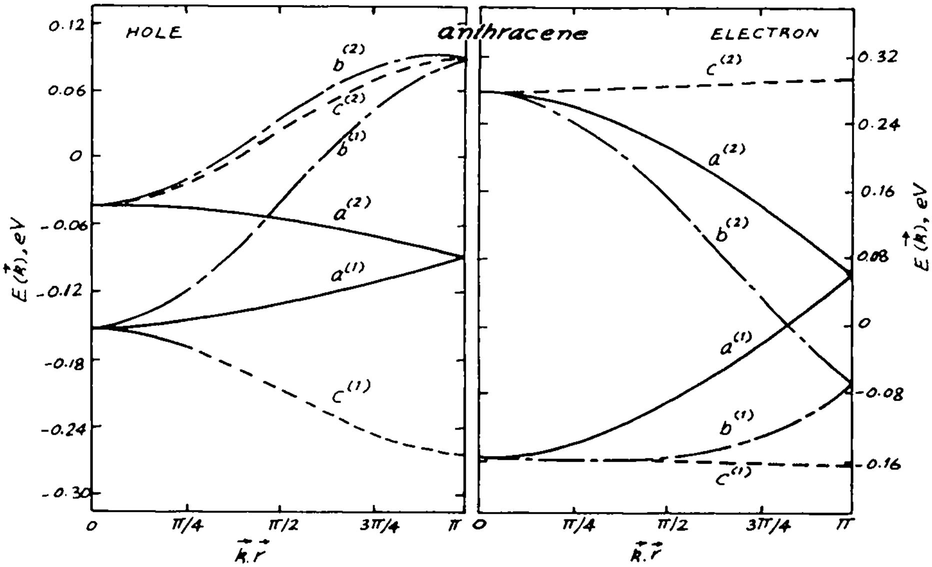
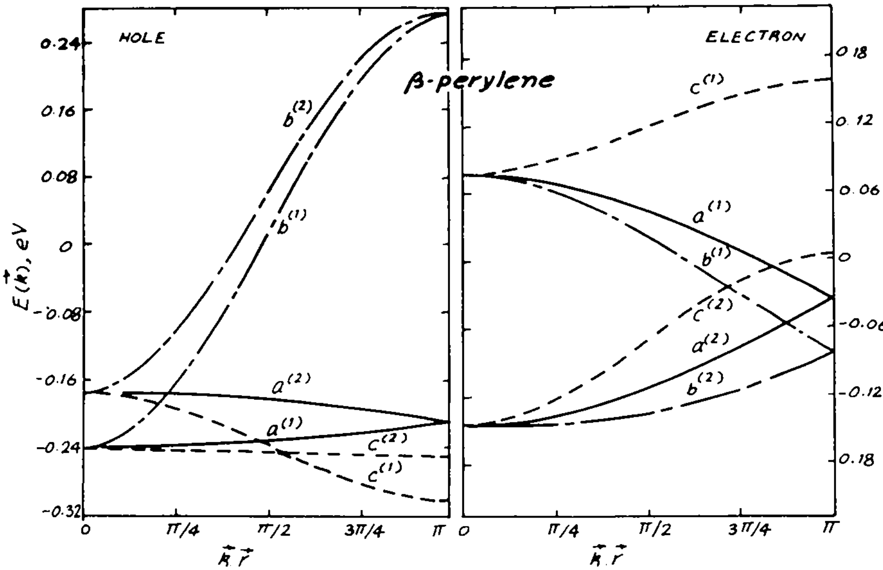
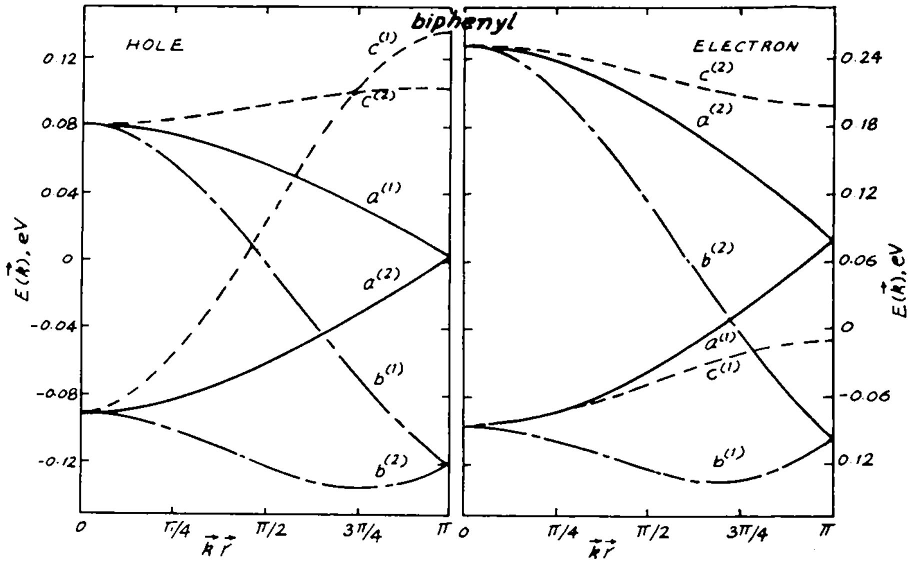
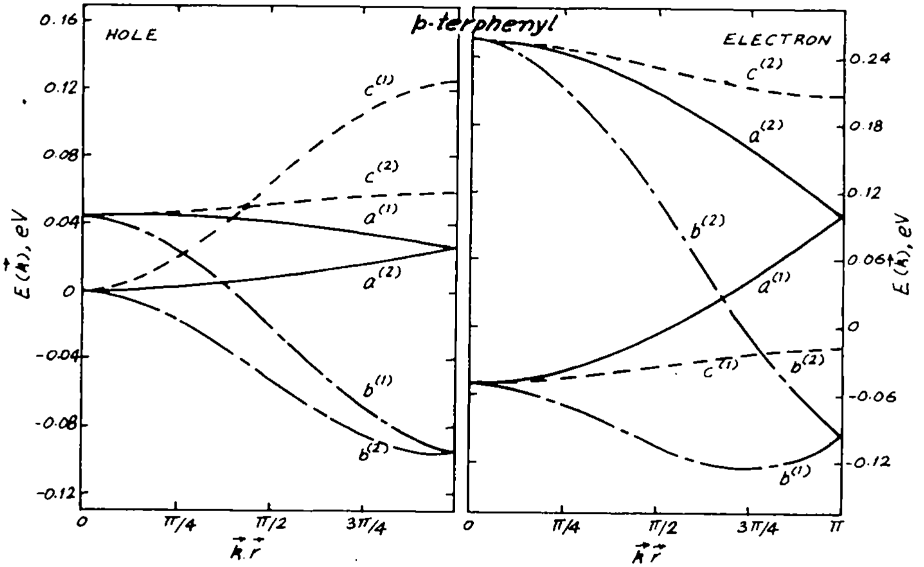


FIGURE 3 Band structure of naphthalene, anthracene, *c*-perylene, biphenyl, *p*-terphenyl and *p*-quaterphenyl.




β-perylene
HOLE
ELECTRON
0.24
0.16
0.08
0
-0.08
-0.16
-0.24
-0.32
0.18
0.12
0.06
0
-0.06
-0.12
-0.18
E(k), eV
0
π/4
π/2
3π/4
π
k·r
b(2)
b(1)
a(2)
a(1)
c(2)
c(1)
c(1)
a(1)
b(1)
c(2)
a(2)
b(2)


biphenyl
HOLE
ELECTRON
0.12
0.08
0.04
0
-0.04
-0.08
-0.12
0.24
0.18
0.12
0.06
0
-0.06
-0.12
E(k), eV
0
π/4
π/2
3π/4
π
k·r
c(1)
c(2)
a(1)
a(2)
b(1)
b(2)
c(2)
a(2)
b(2)
a(1)
c(1)
b(1)



ment,[11] the (1) and (2) bands interchange their respective roles at the point of intersection and the new bands just touch at that point, splitting still being zero. No such cases occur for electrons, all of which show a splitting along c^{-1}. Even in the cases where both the hole and the electron bands do show a splitting, the splitting for electrons is larger than for the holes. In conformity with the predic-

TABLE 5

Bandwidths and Splittings in c^{-1} direction (in eV) for Various Aromatic Hydrocarbon Crystals

Crystal	$a^{(1)}$	$a^{(2)}$	$b^{(1)}$	$b^{(2)}$	$c^{(1)}$	$c^{(2)}$	splitting
	Hole						
Naphthalene	0.03	0.02	0.15	0.16	0.11	0.15	0.01
Anthracene	0.06	0.05	0.24	0.13	0.11	0.13	0.11
β-Perylene	0.03	0.03	0.51	0.45	0.06	0.07	–
Biphenyl	0.08	0.09	0.20	0.04	0.06	0.19	–
p-Terphenyl	0.02	0.03	0.14	0.09	0.08	0.06	–
p-Quaterphenyl	0.001	0.006	0.14	0.13	0.07	0.02	–
	Electron						
Naphthalene	0.10	0.11	0.06	0.15	0.02	0.02	0.18
Anthracene	0.22	0.21	0.09	0.34	0.01	0.02	0.43
β-Perylene	0.11	0.11	0.16	0.07	0.08	0.15	0.15
Biphenyl	0.17	0.17	0.05	0.35	0.08	0.05	0.21
p-Terphenyl	0.15	0.16	0.07	0.35	0.03	0.05	0.22
p-Quaterphenyl	0.17	0.18	0.10	0.42	0.01	0.04	0.29

TABLE 6

Components in the constant τ Approximation in Units of 10^{10} cm^2/sec^2 and in the Constant λ Approximation (within parentheses) in Units of 10^5 cm/sec.

Crystal	a^2	b^2	c'^2	ac'
	Hole			
Naphthalene	107.6	1214.2	293.4	−19.6
	(2.6)	(25.0)	(6.7)	(−0.6)
Anthracene	386.1	1399.8	727.5	−131.1
	(7.4)	(24.0)	(13.6)	(−1.9)
β-Perylene	10.2	4525.9	1005.3	−21.2
	(0.1)	(44.8)	(17.8)	(−0.5)
Biphenyl	130.0	963.6	2931.3	186.2
	(2.7)	(17.8)	(36.2)	(1.7)
p-Terphenyl	181.1	911.0	3521.5	−550.3
	(3.3)	(15.8)	(42.5)	(−6.2)
p-Quaterphenyl	186.5	1070.7	2990.3	−561.1
	(3.1)	(18.1)	(38.8)	(−6.9)
	Electron			
Naphthalene	557.0	231.4	41.1	−18.1
	(16.6)	(7.6)	(1.9)	(−0.4)
Anthracene	1670.7	501.6	4.3	−1.1
	(31.6)	(9.4)	(0.1)	(−0.0)
β-Perylene	1163.5	239.8	2897.4	141.8
	(17.1)	(4.5)	(40.0)	(1.0)
Biphenyl	432.8	1129.6	358.4	69.7
	(9.0)	(21.4)	(8.9)	(1.1)
p-Terphenyl	313.0	1368.0	89.1	−30.7
	(7.4)	(25.9)	(2.2)	(−0.6)
p-Quaterphenyl	343.7	1782.6	83.4	11.8
	(7.8)	(29.5)	(2.2)	(−0.3)

tions about transport mechanism in Table 4, the bandwidths are also largest along b^{-1} and smallest along a^{-1} for holes and along c^{-1} for electrons. In general, (2) bands are found to be wider than (1) bands except for holes along the b direction.

The velocity components calculated at 300°K in the constant τ and the constant λ approximations are collected in Table 6. Numerical calculations were carried out by dividing the integration range along each axis into three equal intervals and then applying a four-point Gauss quadrature formula[22] to each interval. Velocity components again follow the pattern of bandwidths. In a monoclinic crystal, the *b*-axis is a principal axis of the mobility tensor, hereas *a* and *c*' are not. Therefore, the off-diagonal components μ_{ab} and μ_{bc}' should be zero. This condition is not exactly 10Å apart, but does hold numerically to within 1 part in 10^6.

In Table 7, we have calculated the mobility anisotropies and compared them with the experimental values where available. Although both the constant τ and the constant λ approximations tend to exaggerate the mobility anisotropy, the constant τ approximation does it to a somewhat greater degree. This is in agreement with LeBlanc's observation[23] that for conduction in narrow bands, mean free path is constant rather than the mean free time.

As the band theory is not applicable to any of the crystals in all the directions, we cannot hope for a quantitative agreement, but the qualitative picture provided by the calculations must still be true. This is indeed the case for electrons, but for holes only the direction of the highest mobility could be correctly predicted. Experimental observations on naphthalene and anthracene show the holes to be more mobile along *a* than along *c*, whereas calculations predict otherwise. We suspect that the discrepancy may be because of an

TABLE 7

Mobility Ratios in Various Aromatic Hydrocarbon Crystals in the Constant τ and the Constant λ (within parentheses) Approximations

	Hole		Electron	
Crystal	μ_a/μ_b	$\mu_{c'}/\mu_b$	μ_a/μ_b	$\mu_{c'}/\mu_b$
Naphthalene	0.09 (0.10)	0.24 (0.27)	2.41 (2.17)	0.18 (0.25)
Exptl. [a]	0.65	0.35	1.08	0.83
Anthracene	0.28 (0.31)	0.52 (0.57)	3.33 (3.36)	0.01 (0.01)
Exptl. [b]	0.5	0.37	1.36	0.36
β -Perylene	0.002 (0.003)	0.22 (0.40)	4.85 (3.84)	12.08 (8.99)
Biphenyl	0.13 (0.15)	3.04 (2.04)	0.38 (0.42)	0.32 (0.41)
p-Terphenyl	0.20 (0.21)	3.87 (2.69)	0.23 (0.29)	0.06 (0.09)
p-Quaterphenyl	0.17 (0.17)	2.79 (2.14)	0.19 (0.26)	0.05 (0.07)

[a] Average of M. Silver, J.R. Rho, D. Olness and R. C. Jarnagin, *J. Chem. Phys. 38*, 3030 (1963) and D. H. Spielberg, A. I. Korn and A. C. Damask, *Phys. Rev.* B3, 2012 (1971).

[b] Average of a large number of data; quoted from Ref. (8).

assumed isotropic relaxation time as pointed out by Kubarev and Mikhailov.[24,25] They suggest the relaxation time in a particular direction to be inversely proportional to the bandwidth in that direction. If that be the case, then smaller hole bandwidth along a^{-1} will make the relaxation time and hence the mobility along a-axis larger than along c'-axis.

No experimental data exist on the mobility anisotropy of β-perylene or any of the polyphenyls, but for *p*-terphenyl, Szymanski and Labes[26] have found both the hole and the electron mobilities to be very small ($\sim$0.001 cm^2 V^{-1} sec^{-1}) along c'. However, their data was taken for an amorphous film and is not really characteristic of a single crystal. Also severe trapping was present for electrons. An earlier estimate by Mark and Helfrich[27] puts the hole mobility somewhere near 0.03 cm^2 V^{-1} sec^{-1}.

The aromatic hydrocarbons studied here include members from two homologous series – naphthalene, anthracene from polyacenes and biphenyl, *p*-terphenyl, *p*-quaterphenyl from polyphenyls – hence it is not out of place to say something about the effect of molecular size on semiconduction. From a comparison of $|E_n \gamma_n|$ values in Table 4, it is obvious that the applicability of band theory generally increases with the increasing size of the molecule except in the c' direction where it decreases. This is so because the c'-axis gets increasingly larger to accommodate the increasing size of the molecule, which results in a weakening of the electron-exchange interactions in this direction. On the other hand, the a and b axes remain almost constant or even decrease slightly so that because of the increased size of the molecule the overlap and hence the electron-exchange interactions increase in these directions. A similar trend is exhibited by the bandwidths also (Table 5). As the molecular size increases, the hole mobility along a and the electron mobility along b increases whereas the electron mobility along c' decreases (Table 6). Hole mobilities become less anisotropic as the molecule gets increasingly larger, but the anisotropy in the electron mobilities increases (Table 7).

Finally we should stress the strong need of experimental data on mobility anisotropies and the variation of mobilities with temperature. Predictions made here about the mobility anisotropies should be very helpful in planning future experiments as many earlier attempts at measuring the drift mobilities in organic solids are known to have ended in failure because of an unfavourable choice of the crystal direction dictated by the shape of the available crystals. Results of such experiments in conjunction with the present predictions should provide a much better understanding of charge transport in aromatic hydrocarbons.

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