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Charge Transport Calculations in Anthraquinone

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Abstract—The excess electron and excess hole band structures of anthraquinone have been calculated at five different temperatures 293.5 K, 260.5 K, 201 K, 161 K and 103 K, using tight binding approximation, LCAO-MO's and SCF AO's. The calculated energy bands are highly anisotropic. The mobilities of electrons and holes are calculated in constant relaxation time (τ) approximation and their variation with temperature has been studied. The hole and electron mobilities decrease with increase in temperature following a relation $\mu \alpha T^{-n}$ except electron mobility along b axis which shows a slight increase with increasing temperature following a $\mu \alpha T^{0.06}$ dependence. Assuming anisotropic relaxation time the mobility anisotropies have been calculated.

1. Introduction

Recently considerable interest has developed in the theory of charge carrier transport in aromatic hydrocarbons. Following LeBlanc⁽¹⁾ several authors⁽²⁻⁸⁾ carried out energy band structure calculations for a variety of organic semiconductors. However, Munn and Siebrand⁽⁹⁾ argued that in organic semiconductors a possibility of electron phonon interaction dominating over electron-exchange interaction exists. Under these conditions the charge carrier transport will be in the hopping limit. The main success of their theory lies in the fact that they could explain the slight increase in the mobility of anthracene in c' ($\perp ab$) direction with increase in temperature.⁽¹⁰⁻¹⁴⁾

Earlier Chojnacki⁽¹⁵⁾ had tried to explain this increase in mobility by performing energy band structure calculations at two temperatures (95 K and 290 K) for which X-ray analysis of anthracene⁽¹⁶⁾ exists. Delacote⁽¹⁷⁾ questioned the result of Chojnacki who in turn⁽¹⁸⁾

recalled the values of transfer integrals reported in his earlier paper and suggested that inclusion of neutral hydrogen-atom potential and the exchange effect may give better agreement between theory and experiments.

Thus it was felt that more theoretical and experimental work should be done before a clear picture emerges about the charge carrier transport mechanism in organic semiconductors. While the arguments of Munn and Siebrand⁽⁹⁾ seem to be quite reasonable a possibility arises that the very slight increase in the electron mobility of anthracene referred above, may really be due to changes in crystal parameters. Unfortunately the X-ray analysis of anthracene is available only at two temperatures. Hence no sensible conclusions can be drawn on the basis of Chojnacki's calculations. For anthraquinone⁽¹⁹⁾ crystal structure is available at five different temperatures. We have, therefore, done excess electron and excess hole energy band structure calculations at all the five temperatures for which crystal structure is available. We hope experimental measurements of drift mobility in anthraquinone along with the present results can throw much light on the contribution of changes in crystal structure with temperature to the variation of mobility with temperature.

2. Theory

The theory of tight binding approximation for energy band structure calculations as applied to organic semiconductors has been described by many workers.⁽¹⁻⁸⁾ However we have deviated slightly in our approach. Below we give the main features of the calculations.

1) Anthraquinone crystal is a monoclinic, Space group $P2_1/a \equiv C_{2h}^5$ having two molecules per unit cell. One can look upon this crystal as being made of two interpenetrating sub-lattices. For these sub-lattices let the block function be $\psi_1(\kappa)$ and $\psi_2(\kappa)$.

Thus following the standard approach of constructing block functions we write

$$\psi_1(\boldsymbol{\kappa}) = 1/\sqrt{N} \sum_{n \atop \text{allunitcell}} \exp(ik \cdot \mathbf{r}_n)\phi_{1n} \tag{1}$$

$$\psi_2(\boldsymbol{\kappa}) = 1/\sqrt{N} \sum_{n \atop \text{allunitcell}} \exp[i\mathbf{k} \cdot (\mathbf{r}_n + \mathbf{r}_{12})]\phi_{2n} \tag{2}$$

where ϕ_{1n}, ϕ_{2n} are the orbitals for the two molecules in the n^{th} unit cell, $\mathbf{r}_{12}$ is radius vector between them.

Using the two block functions, a configuration interaction treatment gives

$$\begin{vmatrix} H_{11}-\epsilon & H_{12} \\ H_{12} & H_{22}-\epsilon \end{vmatrix} = 0$$

where

$$H_{ij}(\kappa) = \langle \psi_i(\kappa) \,|\, H \,|\, \psi_j(\kappa) \rangle; \quad i, j = 1, 2$$

with the periodic boundary conditions every molecule of type 1 is equivalent to every other molecule of type 2. So that κ is a good quantum number. The term H_{ij} refers to the whole crystal, and not to the individual molecules, solving the determinant we get

$$\mathscr{E}_{\pm}(\kappa) = \tfrac{1}{2}\{H_{11}(\kappa) + H_{22}(\kappa)\} \pm \sqrt{|H_{12}(\kappa)|^2 + \tfrac{1}{4}\{H_{11}(\kappa) - H_{22}(\kappa)\}^2} \tag{3}$$

values of H_{11} and H_{22} have the standard form

$$H_{ij} = e_0^{ij} + \sum_n e_n^{ij} + \sum_l e_l^{ij} \cos(\mathbf{k}\cdot\mathbf{r}_l) \tag{4}$$

The symbols appearing in the above equation are defined as below:

$$e_0^{ij} = \int \phi^* H^0 \phi \, \mathrm{d}\tau \tag{5}$$

$$e_n'^{ij} = \int \phi^*(r) V_n(r - r_n) \phi(r) \, \mathrm{d}\tau \tag{6}$$

$$e_l^{ij} = \int \phi^*(r - r_l) V_l(r - r_l) \phi(r) \, \mathrm{d}\tau \tag{7}$$

2) The potential used is

$$V_{\text{molecule}} = \sum_{i=\text{atoms}} (V_i - V_{2p\pi}) + V_\pi \tag{8}$$

where V_i is the common G.M.S. neutral atom potential,(20) V_π is the potential of π electrons on their respective orbital and $V_{2p\pi}$ is the potential of an electron missing on each $2p\pi$ AO.

3) The molecular orbitals used are LCAO-MO[21]

$$\phi_a = \sum_i C_{ai} U_i \tag{9}$$

where C_{ai} are the binding coefficients in the MO describing a^{th} energy level of the molecule and U_i are atomic orbitals.

The atomic orbitals used are self consistent field (SCF) AO's.(22) All electron interactions have been included following Mathur *et al.*(21) The highest occupied molecular orbital (HOMO) and lowest empty molecular orbital (LEMO) corresponding to the excess electron and the excess hole bands respectively are.

$$\begin{aligned}
(\mathrm{HOMO}) = & -0.04960\,(\psi_1+\psi_4-\psi_5-\psi_8)\\
& +0.31929\,(\psi_2+\psi_3-\psi_6-\psi_7)\\
& -0.34516\,(\psi_{11}+\psi_{12}-\psi_{13}-\psi_{14})\\
(\mathrm{LEMO}) = & -0.23753\,(\psi_1-\psi_4-\psi_5+\psi_8)\\
& -0.22721\,(\psi_2-\psi_3-\psi_6+\psi_7)\\
& \ \ 0.47582\,(\psi_9-\psi_{10})\\
& \ \ 0.18180\,(\psi_{11}-\psi_{12}-\psi_{13}+\psi_{14})\\
& -0.30769\,(\psi_{15}-\psi_{16})
\end{aligned} \tag{10}$$

4) It is clear from Eq. (4) that the entire **K** dependence of energy is contained in the third term on the right hand side of Eq. (4). Following Mathur and Singh⁽²³⁾ the transfer integrals e_n are given by

$$\begin{aligned}
e_n = & \sum_{ij} C_{ai} C_{aj} \{ \langle i | V_i | j \rangle + (q_i - 1) \langle ii | 1/r_{12} | ij \rangle \\
& - q_i/2 \langle ii | 1/r_{12} | ij \rangle
\end{aligned} \tag{11}$$

The closed form expressions obtained by Mathur and Singh⁽²³⁾ for the integrals $\langle i | V_i | j \rangle$ and $\langle ii | 1/r_{12} | ij \rangle$ have been used in the numerical calculations.

5) The mobility tensor has been calculated in the constant mean free time approximation i.e., $\tau_{ij}(\kappa) = (\tau_0)_{ij}$. The component of the mobility tensor in the above approximation is

$$\mu_{ij} = e(\tau_0)_{ij} \langle V_i\ V_j \rangle / \kappa T \tag{12}$$

where

$$\langle V_i V_j \rangle = \frac{\int \left\{ \frac{\partial E_+}{\partial \kappa_i} \frac{\partial E_+}{\partial \kappa_j} \exp[-\beta E_+(\kappa)] + \frac{\partial E_-}{\partial \kappa_i} \frac{\partial E_-}{\partial \kappa_j} \exp[-\beta E_-(\kappa)] \right\} d\kappa}{\hbar^2 \int \{ \exp[-\beta E_+(\kappa)] + \exp[-\beta E_-(\kappa)] \} d\kappa} \tag{13}$$

where

$$\beta = 1/\kappa T$$

All numerical calculations were carried out on an IBM 360 computer.

3. Results

The transfer integrals for the excess holes and excess electrons bands are collected in Tables 1 and 2 respectively. The temperatures

TABLE 1 Transfer integrals of holes for anthraquinone in units of 10^{-4} eV at different temperatures

Position	293.5 K	260.5 K	201 K	161 K	103 K
0 1 1	-9.020	-7.160	-6.740	-6.760	-5.260
0 1 0	-2841.9	-2802.1	-2879.1	-2804.2	-2790.3
0 -1 1	-1.860	-1.920	-2.000	-2.010	-2.070
0 0 1	26.410	30.150	32.570	33.900	39.160
0 2 1	-7.100	-7.940	-8.840	-8.820	-10.050
0 2 0	-2.210	-3.140	-3.360	-4.200	-4.340
0 -2 1	0.003	0.003	0.004	0.004	0.006
0 3 1	-0.092	-0.186	-0.210	-0.220	-0.230
$\frac{1}{2}$ $\frac{3}{2}$ 1	3.460	3.630	3.760	3.980	4.100
$\frac{1}{2}$ $\frac{3}{2}$ 0	0.320	0.380	0.450	0.470	0.530
$\frac{1}{2}$ $\frac{3}{2}$ -1	0.0	0.0	-0.0001	-0.0001	-0.0001
$\frac{1}{2}$ $\frac{1}{2}$ 1	-35.730	-35.150	-36.420	-35.960	-35.910
$\frac{1}{2}$ $\frac{1}{2}$ 0	-1.030	-0.940	-0.880	-0.800	-0.560
$\frac{1}{2}$ $\frac{1}{2}$ -1	0.0002	0.0002	-0.0002	-0.0002	-0.0002
$\frac{1}{2}$ $\frac{5}{2}$ 0	0.030	0.031	0.033	0.035	0.037
$\frac{1}{2}$ $\frac{1}{2}$ 2	—	—	—	-0.015	-0.016

TABLE 2 Transfer integrals of electron for anthraquinone in units of 10^{-4} eV at different temperatures

Position	293.5 K	260.5 K	201 K	161 K	103 K
0 1 1	140.17	145.50	161.47	164.93	182.01
0 1 0	-991.65	-903.96	-890.79	-825.11	-682.04
0 -1 1	8.270	9.090	9.580	9.870	10.560
0 0 1	-141.53	-152.98	-155.95	-157.42	-168.54
0 2 1	-10.540	-11.260	-12.150	-12.540	-13.380
0 2 0	-12.890	-13.250	-14.120	-14.880	-15.380
0 -2 1	-0.070	-0.068	-0.070	-0.180	-0.190
0 3 1	-0.130	-0.100	-0.110	-0.140	-0.110
$\frac{1}{2}$ $\frac{3}{2}$ 1	-0.500	-0.490	-0.490	-0.520	-0.470
$\frac{1}{2}$ $\frac{3}{2}$ 0	-1.680	-1.640	-1.760	-1.730	-1.690
$\frac{1}{2}$ $\frac{3}{2}$ -1	-0.002	-0.002	-0.002	-0.001	-0.001
$\frac{1}{2}$ $\frac{1}{2}$ 1	7.110	6.580	6.410	6.310	5.210
$\frac{1}{2}$ $\frac{1}{2}$ 0	-23.730	-24.260	-25.790	-26.720	-27.950
$\frac{1}{2}$ $\frac{1}{2}$ -1	0.002	0.002	0.003	0.004	0.004
$\frac{1}{2}$ $\frac{5}{2}$ 0	-0.041	-0.041	-0.042	-0.046	-0.045
$\frac{1}{2}$ $\frac{1}{2}$ 2	—	—	—	-0.008	-0.008

TABLE 3 Velocity components of hole for anthraquinone at different temperatures in constant τ approximation

Component	Constant τ (in units of 10^{10} cm^2/sec^2)				
	293.5 K	260.5 K	201 K	161 K	103 K
$\langle V_a^2 \rangle$	2.06	2.03	2.06	2.16	2.29
$\langle V_b^2 \rangle$	3072.94	2701.57	2506.96	2294.42	2208.11
$\langle V_{c'}^2 \rangle$	26.57	28.39	30.20	32.40	35.69
$\langle V_a V_{c'} \rangle$	−4.61	−5.21	−5.72	−6.21	−7.00

TABLE 4 Velocity components of electron for anthraquinone at different temperatures in constant τ approximation

Component	Constant τ (in units of 10^{10} cm^2/sec^2)				
	293.5 K	260.5 K	201 K	161 K	103 K
$\langle V_a^2 \rangle$	31.26	31.32	34.07	35.90	34.42
$\langle V_b^2 \rangle$	2152.08	1730.87	1485.81	1183.40	678.41
$\langle V_{c'}^2 \rangle$	29.68	34.08	26.56	23.60	23.74
$\langle V_a V_{c'} \rangle$	−7.42	−5.81	−3.87	−3.23	−3.71

TABLE 5 Band widths in eV

	Hole				
	293.5 K	260.5 K	201 K	161 K	103 K
a_+^{-1}	0.01	0.01	0.01	0.01	0.01
a_-^{-1}	0.01	0.01	0.01	0.01	0.01
b_+^{-1}	1.15	1.14	1.17	1.14	1.13
b_-^{-1}	1.12	1.11	1.14	1.11	1.11
c_+^{-1}	0.02	0.02	0.02	0.02	0.02
c_-^{-1}	0.03	0.03	0.03	0.03	0.03
	Electron				
	293.5 K	260 5 K	201 K	161 K	103 K
a_+^{-1}	0.01	0.01	0.01	0.01	0.01
a_-^{-1}	0.01	0.01	0.01	0.01	0.01
b_+^{-1}	0.35	0.31	0.30	0.27	0.21
b_-^{-1}	0.33	0.29	0.28	0.25	0.19
c_+^{-1}	0.004	0.005	0.006	0.007	0.008
c_-^{-1}	0.007	0.008	0.004	0.003	0.001

for which the transfer integrals are given are also included in the tables. The values of velocity components for holes and electrons at different temperatures are collected in Tables 3 and 4 respectively. The calculated band widths are given in Table 5. The shape of the energy bands along *a*, *b* and *c*′ ($\perp ab$) axes are shown in Fig. 1 (for

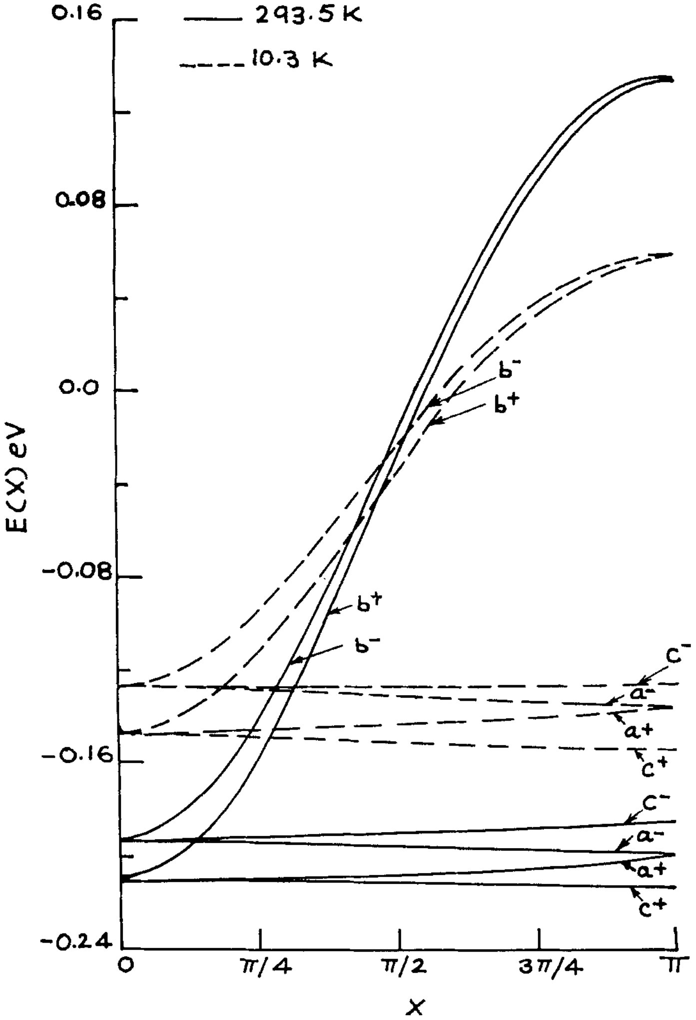

Figure 1. Shape of excess electron band of anthraquinone in the a^{-1}, b^{-1}, and c'^{-1} directions at temperatures 293.5 K and 103 K.

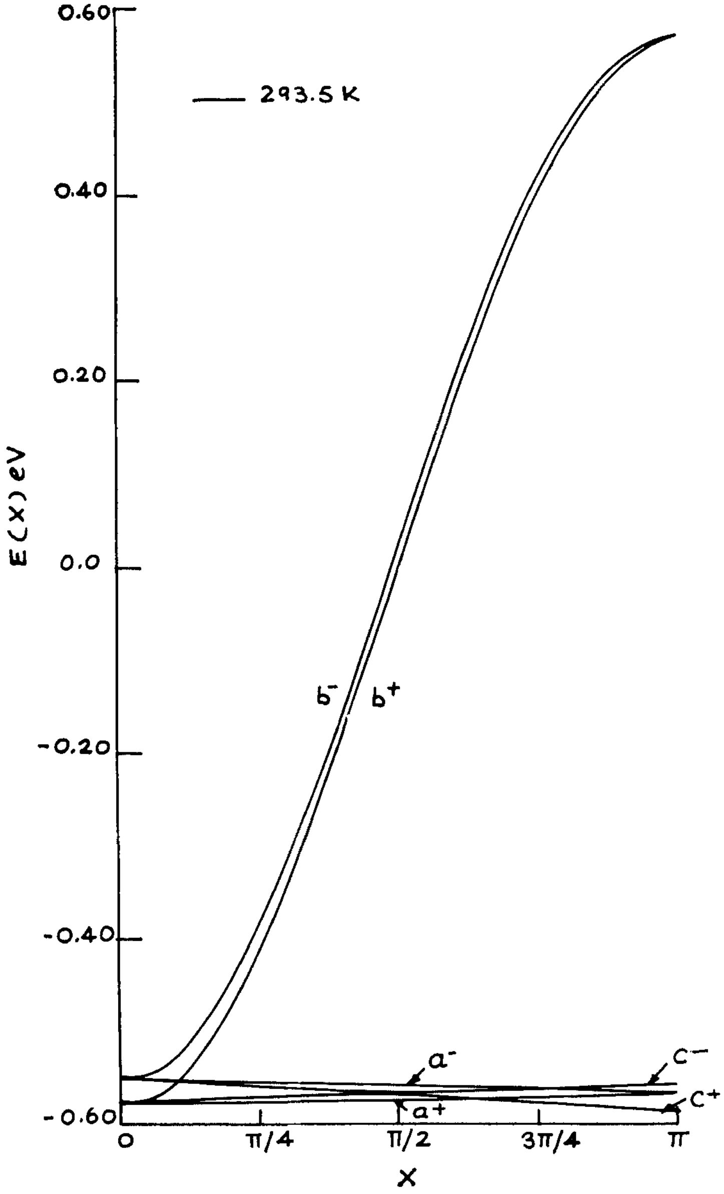

Figure 2. Shape of excess hole band of anthraquinone in the a^{-1}, b^{-1} and c'^{-1} directions at temperature 293.5 K.

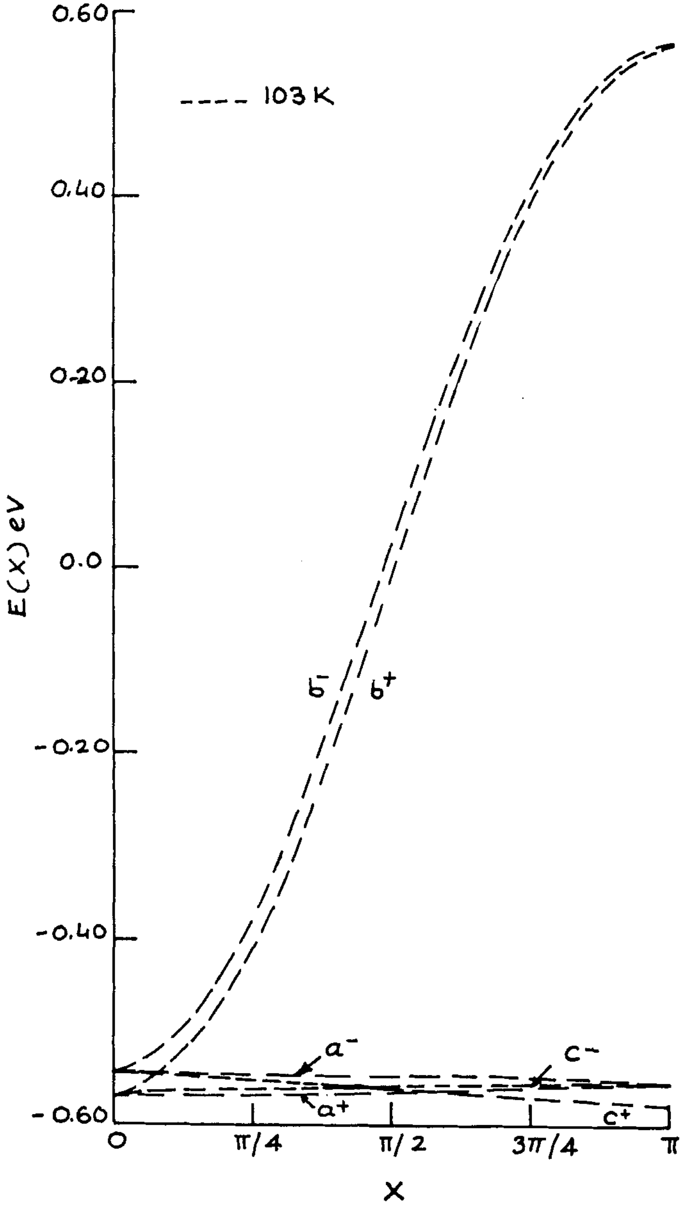

Figure 3. Shape of excess hole band of anthraquinone in the a^{-1}, b^{-1} and c'^{-1} directions at temperature 103 K.

excess electron), Figs. 2 and 3 (for excess holes), only at the highest (293.5 K) and the lowest (103 K) temperatures to avoid overcrowding. The energy bands at intermediate temperatures lie between these two. Figures 4 and 5 are $\log \mu$ vs. $\log T$ plots. In the figures the calculated points are shown by circles and the solid line represents the least square fits. The calculated values of mobility anisotropies for holes as well as electrons are given in Table 7.

4. Discussion

The values of transfer integrals given in Tables 1 and 2 include the contributions from the G.M.S. potential, nonuniform charge distribution over the molecule and exchange potential. These are not listed separately to save on space. From Tables 1 and 2 one can see that the transfer integrals vary as the crystal parameter change at different temperatures. It may be mentioned here that the molecule pairs ($\frac{1}{2}$, 3/2, 1) and ($\frac{1}{2}$, −3/2, 1); ($\frac{1}{2}$, 3/2, 0) and ($\frac{1}{2}$, −3/2, 0);

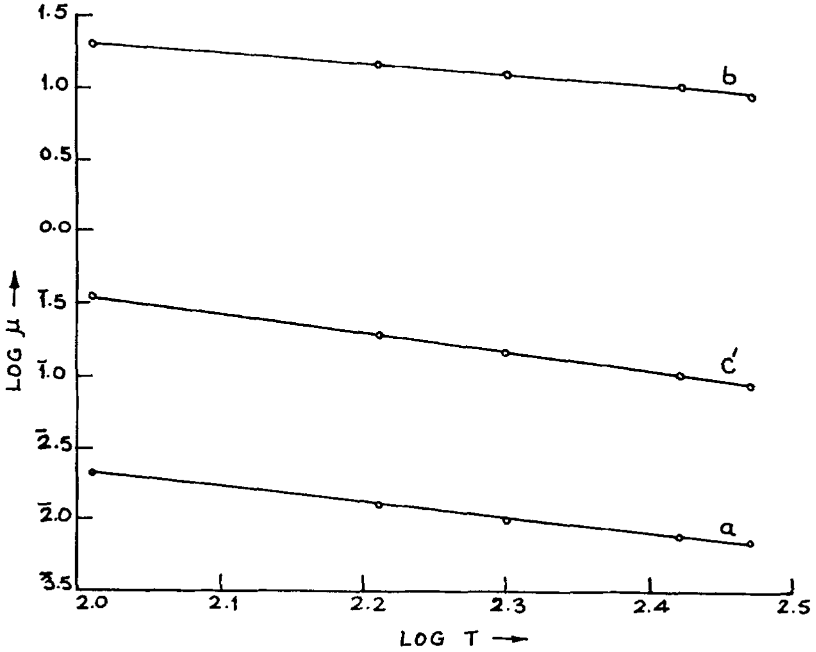

Figure 4. Temperature variation of hole mobility.

$(\frac{1}{2}, 3/2, -1)$ and $(\frac{1}{2}, -3/2, -1)$; $(\frac{1}{2}, \frac{1}{2}, 1)$ and $(\frac{1}{2}, -\frac{1}{2}, 1)$; $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, -\frac{1}{2}, 0)$; $(\frac{1}{2}, \frac{1}{2}, -1)$ and $(\frac{1}{2}, -\frac{1}{2}, -1)$; $(\frac{1}{2}, 5/2, 0)$ and $(\frac{1}{2}, -5/2, 0)$; $(\frac{1}{2}, \frac{1}{2}, 2)$ and $(\frac{1}{2}, -\frac{1}{2}, 2)$ are taken to be equivalent in agreement with the earlier workers. But in contrast to earlier workers the equivalence of molecule pairs $(0, 1, 1)$ and $(0, -1, 1)$; $(0, 2, 1)$ and $(0, -2, 1)$ etc. is not assumed. The Bloch functions $\psi_1(\kappa)$ and $\psi_2(\kappa)$ are by themselves not crystal wave functions, but a proper linear combination of the two can be made to have correct symmetry properties, hence the configuration interaction treatment.

The calculated bands are highly anisotropic. The bands are degenerate at $\kappa \cdot \mathbf{a} = \kappa \cdot \mathbf{b} = \pi$, but they show splitting in c'^{-1} direction. The calculated band widths in Table 4 range from 0.01–1.17 eV for holes and 0.001–0.35 eV for electrons. For excess hole as well as excess electron bands the calculated band widths are maximum for $\kappa \parallel b^{-1}$ and minimum for $\kappa \parallel a^{-1}$. The band widths do not show any appreciable change with temperature except in the $\kappa \parallel b^{-1}$ direction of electron band. These band widths increase with increase in temperature. As expected from the values of transfer integrals and

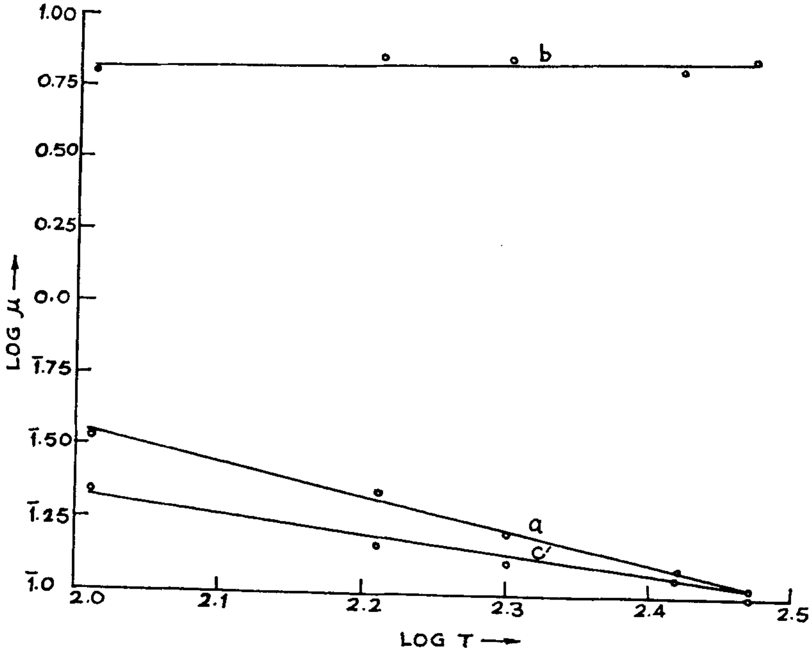

Figure 5. Temperature variation of electron mobility.

TABLE 6

	Electron			Holes		
Crystal direction	*a*	*b*	*c′*	*a*	*b*	*c′*
Exponent *n*	− 1.15	0.06	− 0.67	− 1.09	− 0.71	− 1.27

band widths, the calculated mobilities for holes and for electrons are maximum along crystallographic *b* direction and minimum along *a*-axis. Figures 4 and 5 show the variation of mobility with temperature. For holes as well as for electrons the mobility decreases with increasing temperature following a relation of the type $\mu \alpha T^{-n}$. The values of *n* are given in Table 6. However the Electron mobility along *b* direction is an exception to this rule. Along the *b*-axis the electron mobility follows the relation $\mu \alpha T^{0.06}$ giving a slight increase in mobility with increasing temperature. Therefore it will be interesting to measure the drift mobility in anthraquinone along the *b*-axis at various temperatures from 100 K to 300 K. An experimental

TABLE 7 Anisotropy of the mobility in anthraquinone at different temperatures

	Hole				
	293.5 K	260.5 K	201 K	161 K	103 K
$\frac{\mu_{aa}}{\mu_{bb}}$	0.0505 (0.0006)	0.0846 (0.0007)	0.0943 (0.0008)	0.1129 (0.0010)	0.1155 (0.0011)
$\frac{\mu_{c'c'}}{\mu_{bb}}$	0.3923 (0.0086)	0.4730 (0.0105)	0.5563 (0.0120)	0.6358 (0.0141)	0.7243 (0.0162)
	Electron				
	293.5 K	260.5 K	201 K	161 K	103 K
$\frac{\mu_{aa}}{\mu_{bb}}$	0.4953 (0.0145)	0.5424 (0.0181)	0.6650 (0.0229)	0.7891 (0.0303)	1.0155 (0.0508)
$\frac{\mu_{c'c'}}{\mu_{bb}}$	0.7837 (0.0138)	1.1805 (0.0197)	1.0361 (0.0179)	1.0396 (0.0200)	1.3997 (0.0350)

examination of our predicted values of mobility along the *b* direction will certainly go a long way in testing the applicability of band model to anthraquinone.

The calculated mobility ratios for holes as well as electrons are collected in Table 7. The mobility ratios are calculated using anisotropic relaxation time approximation following Kuberav *et al.*(24) The values in parenthesis correspond to isotropic relaxation time. For holes $\mu_{bb} > \mu_{c'c'} > \mu_{aa}$ and for electrons $\mu_{bb} > \mu_{aa} > \mu_{c'c'}$. The calculated mobility anisotropies for holes as well as electrons show an increase with increase in temperature. The relaxation times τ_a, τ_b and $\tau_{c'}$ along the three orthogonal axes are assumed to be inversely proportional(24) to the band widths *Wa*, *Wb* and *Wc′* along *a*, *b* and *c′* directions respectively. The mobility anisotropies for holes as well as electrons reduce by considering anisotropic relaxation time. However, the trend of variation of anisotropies with temperature remains unchanged.

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