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# Charge Carrier Transport in Phenazine

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The mode of charge carrier transport in Phenazine has been investigated in the light of existing theories. The effect of heteroatoms (nitrogen atoms) and the sensitivity of energy bands to crystal structure has been discussed. The mobilities of electrons and holes have been calculated under an anisotropic but constant relaxation time approximation. The anisotropic relaxation time reduces the anisotropy of the mobility tensor.

## 1 INTRODUCTION

Interest has recently been focussed on the theory of charge transport in organic molecular crystals. A search of the literature reveals that most of the studies have been on aromatic hydrocarbons and phthalocyanines. Various authors have adopted different approaches to understand the charge transport mechanism in aromatic hydrocarbons and phthalocyanines. One approach has been to calculate increasingly more reliable carrier band structure.[1–7] In these studies the electron-phonon interactions are introduced through a relaxation time parameter. The second approach considers the electron-phonon interactions explicitly. This approach, developed by Munn and Siebrand,[8,9] suggests three distinct transport mechanisms depending on the relative magnitudes of the electron-exchange, electron-phonon and phonon-dispersion energies:

a) *Slow-phonon coherent transport*, where electron-exchange energies dominate over phonon dispersion energies.

b) *Slow-phonon hopping*, where electron-exchange energies are small compared to electron-phonon energies but larger than the phonon-dispersion energies.

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c) *Slow-electron hopping*, where the electron-exchange energies are small compared to both the electron-phonon and phonon-dispersion energies.

Clearly, the calculation of conventional carrier band structure is valid only under the applicability of case (a).

The electron-exchange interactions depend on transfer integrals (TI's) between neighbouring molecules. The TI's in turn depend on interatomic resonance integrals. Since the spread of $2p_\pi$ orbitals is different for carbon and other heteroatoms (nitrogen, oxygen), the presence of heteroatoms in place of or in addition to carbon atoms should systematically effect the electron-exchange interactions. Since the electron-exchange interactions are known to effect the mode of transport, a study of heteroatomic molecular crystals may yield valuable information regarding the effect of heteroatoms on the mode of charge transport and hence on carrier mobilities. Mathur and Ramesh[10] have studied the energy bands of hydrogen phthalocyanines which belongs to the class of heteroatomic molecular crystals. They found that band theory is not applicable to $\beta$-hydrogen phthalocyanines. However, the limited studies on heteroatomic molecular crystals[11-14] show that they have larger conductivities, smaller activation energies and smaller photoconductive thresholds than their parent hydrocarbons. Since the applicability of the band model to hydrocarbons is more or less established, it is necessary to investigate the applicability of the band model to heteroatomic molecular crystals. The present communication deals with such studies on phenazine which belongs to the class of heteroatomic molecular crystals.

## 2 THEORY

Calculations based on either of the two approaches (Munn and Siebrand[8,9] approach or band approach[1-7]) involve an evaluation of two centre transfer integrals (TI's) of the type

$$E_n = \langle \phi_c(r - r_n) | V^{\text{neut}}(r - r_n) | \phi_c(r) \rangle$$

where $V^{\text{neut}}$ is the potential of the isolated molecule, $\phi_c$ the one-electron molecular orbital (MO) appropriate to the excess carrier (hole or electron) and $r_n$ locates the $n$th molecule.

Singh and Mathur[15] have done the detailed calculation of two centre transfer integrals (TI's) for hydrocarbon crystals belonging to the space group $P21/a \equiv C^52h$ and have obtained a closed-form analytical expression for them. The heteroatomic molecular crystal phenazine also belongs to this space group $P21/a$. Therefore, a similar approach for evaluating the TI's has been adopted.

The potential used in the present calculation is

$$V^{\mathrm{neut}} = \sum_{i=\mathrm{atoms}} (V_i - V_{2p_\pi}) + V_\pi,$$

where $V_i$ is the common G.M.S. neutral atom potential, $V_\pi$ is the potential of $\pi$ electrons in their respective orbitals and $V_{2p_\pi}$ is the potential of an electron missing from each $2p_\pi$ $AO$.

The final expression for the transfer integral has been found to be

$$E_n = \sum_{i,j} C_{ci}C_{cj}\left\{\langle i|V_i|j\rangle + (q_i - 1)\langle ii|\frac{1}{\gamma_{12}}|ij\rangle - \frac{q_i}{2}\langle ii|\frac{1}{\gamma_{12}}|ij\rangle\right\}$$

where $C_{ci}$ and $C_{cj}$ are the coefficients of $i$th $AO$ and $j$th $AO$ respectively in the MO describing the $c$th energy level of the molecule, and $|i\rangle$ is centered on the atom $i$ of the molecule 0 and $|j\rangle$ on the atom $j$ of the molecule $n$. The $q_i$'s are charge densities.

Following Mathur and Kumar,[7] the dependence of energy on the wave vector in the tight binding approximation and using a configuration interaction treatment is given by

$$E_\pm(\mathbf{k}) = \tfrac{1}{2}(H_{11} + H_{22}) \pm \{\tfrac{1}{4}(H_{11} - H_{22})^2 + |H_{12}|^2\}^{1/2}$$

To obtain the above expression Mathur and Kumar[7] considered the monoclinic base-centered crystal lattice (two non-equivalent molecules per unit cell) as being made up of the two interpenetrating simple monoclinic sublattices. The two sublattices correspond to two non-equivalent molecules in the crystal lattice. In the above equation $H_{11}$, $H_{12}$, $H_{22}$ are defined as

$$H_{ij}(\mathbf{k}) = \langle\psi_i(\mathbf{k})|H|\psi_j(\mathbf{k})\rangle, \qquad i, j = 1, 2$$

where $\psi_i(\mathbf{k})$ and $\psi_j(\mathbf{k})$ are two Bloch functions corresponding to two interpenetrating sublattices. The (+) and (−) signs give the two branches of bands corresponding to two nonequivalent molecules.

Phenazine is a base-centered monoclinic crystal. The atoms are in the position ($X$, $Y$, $Z$) and ($X + \tfrac{1}{2}$, $Y + \tfrac{1}{2}$, $Z$). The numbering of the molecules has been shown in Figure 1. Molecules have been numbered arbitrarily in order of decreasing $Z$, increasing $X$ and increasing $Y$ coordinates. Thus, the wave vector dependence of energy can be found out by substituting the values of $H_{11}$, $H_{12}$, $H_{22}$ in the above equation.

The highest occupied molecular orbital (HOMO) and lowest empty molecular orbital (LEMO) corresponding to the excess electron and the excess hole bands respectively are taken from Coulson and Streitwieser.[16]

Following Kuberev and Mikhailov,[17] the electron and hole mobilities have been calculated using the constant but anisotropic relaxation time approximation. According to these authors $(\tau_0)_{ij} \propto (1/w_{ij})$, where the $w_{ij}$'s

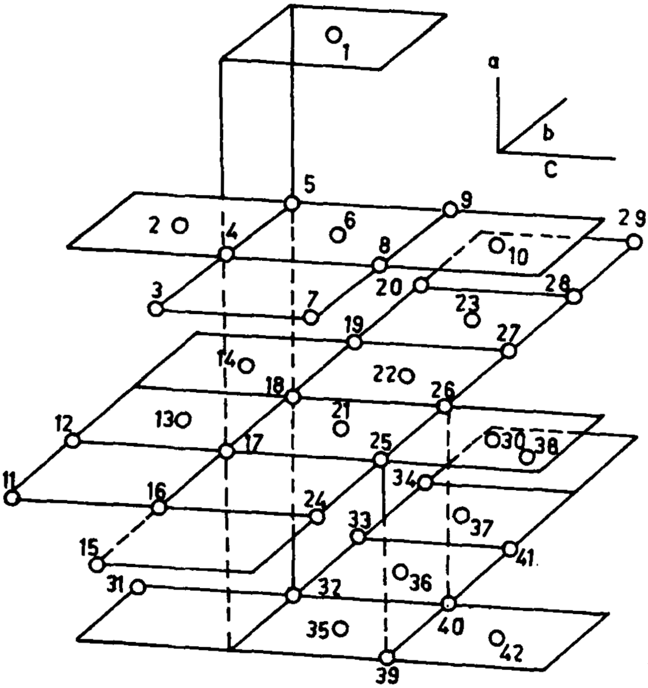

FIGURE 1 Schematic representation of the unit cell of Space group $P_{2_1}/a(z = 2)$ showing the numbering of the molecule.

are the band widths along the three crystallographic directions. The drift mobility tensor under the constant but anisotropic relaxation time approximation can be written as:

$$\mu = \beta\left\{\frac{1}{w_{ij}}\langle v_i v_j\rangle\right\}, \qquad \beta = \frac{e(\tau_0)_{ij}}{kT}$$

where $v_i$ is the $i$th component of the velocity vector. We have calculated the value of the expression within brackets for $a$, $b$ and $c'$ ($\perp ab$) directions.

## 3 CRYSTAL STRUCTURES

The phenazine molecule may be looked upon as an anthracene molecule whose 9,10 carbon atoms are replaced by nitrogen atoms. Both phenazine and anthracene are base-centered monoclinic crystals with space group $P21/a \equiv C^5 2h$, having two molecules per unit cell. For phenazine[18] $a{:}b{:}c$ is

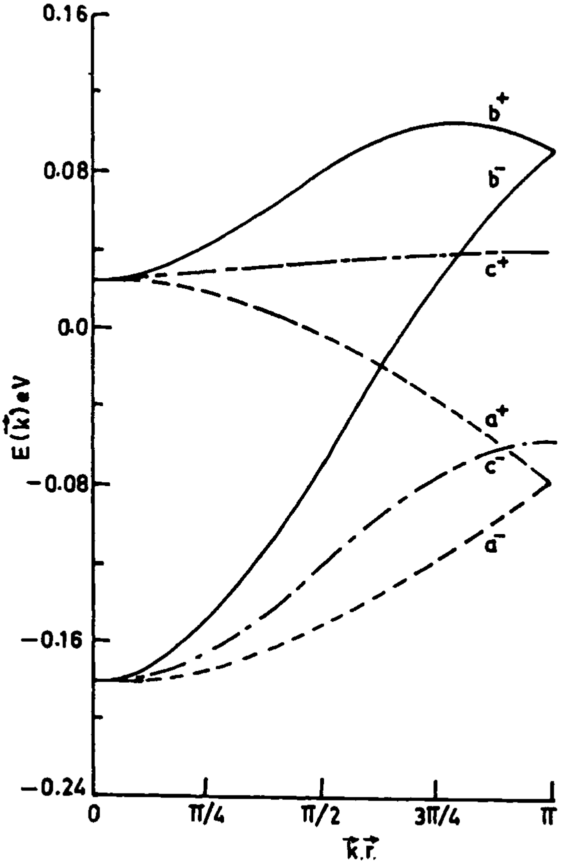

FIGURE 2 Shape of excess hole band of phenazine in the $a^{-1}$, $b^{-1}$ and $c^{-1}$ directions.

13.22:5.06:7.09, and for anthracene[19] $a{:}b{:}c$ is 8.562:6.038:11.184. The respective values of $\beta$ are 109° 13′ and 124° 42′. Thus we see that the $b$-axis in both the crystals is the shortest. The longest axis in phenazine is the $a$-axis, while the $c$-axis plays this role in anthracene. Therefore, the role of $a$- and $c$-axes in phenazine should correspond to the role of $c$- and $a$-axes respectively in anthracene.

## 4 RESULTS AND DISCUSSIONS

The intermolecular transfer integrals have been calculated for all molecules to within a distance of 10 Å from the reference molecule at the origin. The TI's obtained are presented in Table I. It has been found that the exchange

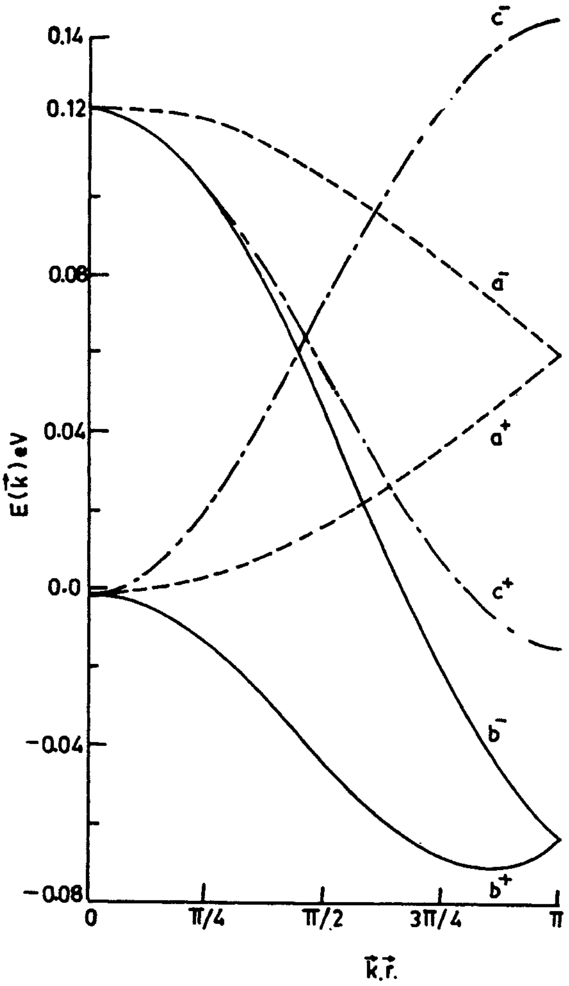

FIGURE 3 Shape of excess electron band of phenazine in the $a^{-1}$, $b^{-1}$ and $c^{-1}$ directions.

contribution is more significant than the contribution due to the G.M.S. potential. To save on space, contributions due to the G.M.S. potential, non-uniform charge distribution and the exchange potential have not been listed separately. Table I shows that non-equivalent molecules 4, 8, 5 and 7 differ not only in magnitude but in sign as well. Molecules 7, 9, 14 and 16 have large TI's and are therefore expected to dominate charge transport.

Singh and Mathur[15] have developed an approximate criterion for determining the mode of charge transport in aromatic hydrocarbons. According

TABLE I

Intermolecular transfer integrals (TI's) in units of $10^{-4}$ eV

| Molecule number | Position | | | Hole | Electron |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | Reference molecule | |
| 1 | $\frac{1}{2}$ | 0 | 2 | −0.149 | −0.019 |
| 2 | $-\frac{1}{2}$ | $\frac{1}{2}$ | 1 | −0.054 | 0.025 |
| 3 | −0 | $\frac{3}{2}$ | 1 | 0.005 | −0.003 |
| 4 | 0 | −2 | 1 | −0.057 | 0.022 |
| 5 | 0 | −1 | 1 | −10.994 | 1.827 |
| 6 | 0 | 0 | 1 | 19.086 | −2.361 |
| 7 | 0 | 1 | 1 | −179.89 | −14.351 |
| 8 | 0 | 2 | 1 | −2.135 | 0.314 |
| 9 | $\frac{1}{2}$ | $\frac{1}{2}$ | 1 | 69.150 | −177.54 |
| 10 | $\frac{1}{2}$ | $\frac{3}{2}$ | 1 | −0.397 | −0.001 |
| 11 | 1 | 0 | 1 | −0.105 | 0.022 |
| 12 | 1 | 1 | 1 | −0.260 | 0.309 |
| 13 | 1 | 2 | 1 | 0.0 | −0.002 |
| 14 | 0 | 1 | 0 | −226.06 | 320.75 |
| 15 | 0 | 2 | 0 | 1.258 | −4.116 |
| 16 | $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 195.36 | 21.497 |
| 17 | $\frac{1}{2}$ | $\frac{3}{2}$ | 0 | −3.119 | 1.107 |
| 18 | $\frac{1}{2}$ | $\frac{5}{2}$ | 0 | 0.022 | −0.005 |
| 19 | 1 | 1 | 0 | −0.061 | −0.003 |

to them the three limits given by Munn and Siebrand correspond to the following limits of the product $|E_n r_n|$:

i) $|E_n r_n| > 1{,}225 \times 10^{-4}$ ev-Å: slow-phonon coherent transport (band transport);

ii) $125 \times 10^{-4}$ ev-Å $< |E_n r_n| < 1{,}225 \times 10^{-4}$ *ev*-Å: slow-phonon hopping;

iii) $|E_n r_n| < 125 \times 10^{-4}$ ev-Å: slow-electron hopping;

Here $E_n$ is the inter-molecular transfer integral and $r_n$ is the distance of the *n*th molecule from the reference molecule 0. Physically the product $|E_n r_n|$ signifies that there may exist a situation where a relatively smaller transfer integral for a pair of molecules situated far apart may contribute more to mobility than a molecule situated closer to the reference molecule having a larger value of the transfer integral. On the basis of this criterion the likely mode of transport in various directions in a phenazine crystal is indicated in Table II. However, we cannot claim this classification of modes of transport in phenazine crystal to be very accurate as we have assumed the equivalence of electron-phonon interactions in this crystal with that in anthracene. Moreover, the limits to demarcating the three regions have been chosen on the basis of Munn and Siebrands assignment of transport mechanisms in

TABLE II

Values of the dominant contribution $|E_n r_n|$ to the mobilities and assignment of transport mechanism in phenazine crystal (Number within the parentheses 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).

| | $\lvert E_n r_n\rvert$ ($10^{-4}$ eV-Å) | | |
|---|---|---|---|
| | $a$ | $b$ | $c'(\perp ab)$ |
| Hole | 1291(16) | 1959(7) | 1205(7) |
| | B | B | PH |
| Electron | 759(9) | 1623(14) | 1189(9) |
| | PH | B | PH |

anthracene. The numerical values in the above criterion may be taken as a guideline rather than as sharp demarcations between various modes of transport. For example, though in Table II the transport along the $C'$-direction is shown to be occurring by slow-phonon hopping the description may well be in the slow-phonon coherent region. One may conclude this as the value of $|E_n r_n|$ is very close to the value demarcating the two modes of transport. Thus, the band theory may be taken to be the dominant mechanism of transport along all crystal directions except for the electron transport along the $a$-axis. The electron transport along the $a$-axis is clearly described by a slow-phonon hopping since $|E_n r_n|$ is well within the two limits set by Singh and Mathur.[15]

We know that a phenazine molecule is just an anthracene molecule whose 9,10 carbon atoms have been replaced by nitrogen atoms. We may find by calculating the overlap integrals ($S$) for different atom pairs that for fixed interatomic distances $S(\text{C—C}) > S(\text{C—N}) > S(\text{N—N})$. This follows from the fact that the spread of $2p_\pi$ orbitals of nitrogen is small compared to that of carbon. Also, the differences $[S(\text{C—C}) - S(\text{C—N})]$ and $[S(\text{C—C}) - S(\text{N—N})]$ increase with interatomic distance. Thus, one may expect that the introduction of nitrogen atoms in place of carbon atoms should decrease the intermolecular interactions and, hence, the mobility. However, experimental conductivity data on various heteroatomic crystals and their parent hydrocarbons contradict such a drastic conclusion. Hence, one should not expect a direct correlation between intermolecular transfer integrals of heteroatomic molecular crystals and their parent hydrocarbons.

It may be noticed by looking into the crystal data of various heteroatomic molecular crystals that in going from parent hydrocarbon crystals to heteroatomic molecular crystals, the crystal dimensions change drastically. For

TABLE III

Band widths and splitting (in eV)

| | Hole | Electron |
|---|---|---|
| $a_{+}^{-1}$ | 0.104 | 0.061 |
| $a_{-}^{-1}$ | 0.104 | 0.062 |
| $b_{+}^{-1}$ | 0.080 | 0.070 |
| $b_{-}^{-1}$ | 0.271 | 0.185 |
| $c_{+}^{-1}$ | 0.015 | 0.083 |
| $c_{-}^{-1}$ | 0.125 | 0.077 |
| $C^{-1}{}_{\text{splitting}}$ | 0.098 | — |

example, in going from anthracene to phenazine, the crystallographic $a$:$b$:$c$ axes change in the ratio 0.65:1.18:1.58. It may be that the substitution of heteroatoms in place of carbon atoms requires such a change in crystal dimensions. This may be needed for preserving the weak van der Waal binding between molecules held together. The above discussion suggests that there is some correlation between the crystal parameters and transport mechanism. This is consistent with the findings of Mathur and Kumar[7] who have established the structure sensitivity of energy bands and carrier mobilities of anthraquinone. Mathur and Mitra[20] have also highlighted the structure sensitivity of the energy bands of metal phthalocyanine crystals.

As expected from the crystal structure of phenazine, the bands are broadest along the $b$-direction and narrowest along the $a$-direction. The calculated band widths are collected in Table III. The hole bandwidths lie in the range 0.015 ev–0.271 ev and electron bandwidths range from 0.061 ev–0.185 ev. The bandwidths are much larger than $kT$ at room temperature. Only in the $a$-direction is the hole band quite narrow, and the band width is less than $kT$ at room temperature.

TABLE IV

Mobility anisotropies in the constant anisotropic relaxation time approximation and in the constant isotropic relaxation time approximation (within parentheses)

| Mobility anisotropy | Hole | Electron |
|---|---|---|
| $\frac{\mu_{aa}}{\mu_{bb}}$ | 1.073<br>(0.634) | 0.397<br>(0.193) |
| $\frac{\mu_{c'c'}}{\mu_{bb}}$ | 1.738<br>(0.691) | 0.725<br>(0.453) |

Using the relaxation time approximation we have calculated the carrier mobilities from the calculated band structure. The anisotropy of relaxation time has been taken into account following Kubarev and Mikhailov.[17] The mobility anisotropies thus obtained by using an isotropic relaxation time are also included in Table IV and the values are enclosed within round brackets. As may be seen from Table IV, the mobility anisotropies are considerably reduced on introducing the anisotropy of relaxation time. The anisotropies as shown in Table IV may represent a reasonably good prediction of mobility anisotropies except for $(\mu_{aa}|\mu_{bb})$ for electrons.

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