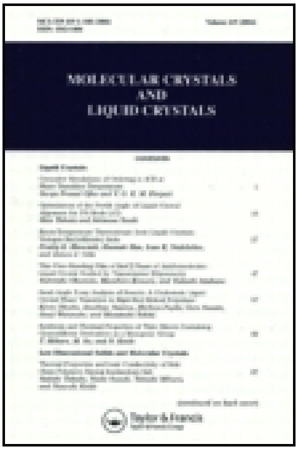

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# A study of electron transport in bispyrazolopyridine derivatives

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# A STUDY OF ELECTRON TRANSPORT IN BISPYRAZOLOPYRIDINE DERIVATIVES

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*In bispyrazolopyridine derivatives dispersed into polystyrene, transient currents have been studied using a conventional time-of-flight method. A field dependent electron drift mobility, in the range of* $4\times10^{-7}-2\times10^{-5}\ cm^2/(Vs)$ *at an electric field of* $(0.6–7.0)\times10^5$ *V/cm, has been found. The correlation between chemical structure and measured mobility is found to fit the correlated disorder model reasonably when the charge transport is represented in terms of the one-electron transfer between frontier molecular orbitals. Optimisation of molecule configuration and calculation of the orbital energy and wave-function decay constant have been computed by the semi-empirical methods. The PM3 approach is shown to approximate experimental data more better than the AM1.*

*Keywords*: electron mobility; bispyrazolopyridine; time-of-flight; semi-empirical computing

## INTRODUCTION

An enormous interest in searching for novel electron transport organic materials has been stimulated by the recent development of organic electroluminescent devices and many other types of optoelectronic devices. In our work [1], a new class of organic electron transporting material pyrazolo[3,4-b]quinoline derivatives was reported. The pyrazoloquinoline

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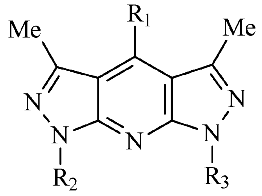
doped polystyrene films have electron drift mobility in the range of $1 \times 10^{-6} - 4 \times 10^{-5}\,\mathrm{cm}^2/(\mathrm{V\,s})$ in an electric field of $(1–7) \times 10^5$ V/cm. These materials were also found to be suitable for use in electroluminescent devices [2].

Bispyrazolopyridine (PAP) derivatives are a close family of pyrazoloquinolines. In the present work, the electron transporting properties of bispyrazolopyridine derivatives have been studied. Further computing has been carried out to compare with the experimental data.

## EXPERIMENTAL

The general structure of PAP derivatives is shown in Figure 1. A brief description of the preparation of 4-phenyl-1,3,5,7-tetramethyl-1,7-dihydrodipyrazolo[3,4-*b*;4′,3′-*e*′]pyridine (PAP1) and other details can be found in reference [2]. Polystyrene used in the experiment was from BDH and had a number average molecular weight of 120,000.

The specimen for electron drift mobility measurement was prepared by uniformly dispersing PAP in a polystyrene matrix as a dopant at a level of 8 wt%. Layered sandwich specimens (3–8 μm in thickness) were prepared for TOF experiment as previously described [1]. The drift mobility $\mu$ was determined from the expression $\mu = d/(F \cdot t_T)$, where $F$ is the applied field and $d$ is the thickness of carrier transporting layer. In our experiments, the observed transient currents had a non-dispersive profile with a short initial



| | R1 | R2 | R3 |
|---|---|---|---|
| PAP1 | Ph | Me | Me |
| PAP2 | Ph | Ph | Ph |
| PAP3 | Ph-O-Me | Ph | Ph |
| PAP4 | Py | Ph | Ph |
| PAP5 | Ph-NMe$_2$ | Ph | Ph |

**FIGURE 1** Molecular structure of bispyrazolopyridine (PAP) derivatives.

spike, then a well-defined plateau followed by a tail of the transient. The time for the current to decay to half of its plateau value was chosen as $t_T$ in our calculation of mobility. Geometries of molecules and radical anions, the parameters of their frontier molecular orbitals (MOs) were calculated using the semi-empirical PM3 or AM1 through a HyperChem computation program (Hypercube, Inc.).

## RESULTS AND DISCUSSION

From all specimens, the $F^{1/2} - \lg\mu$ plot yields straight lines within the error of experiments of 15% (Fig. 2). The results in Figure 2 show that the mobility increases as field increases. The field dependent mobility of PAP2 was then further investigated at different temperature as seen in Figure 3 and the mobility increases as the temperature is raised.

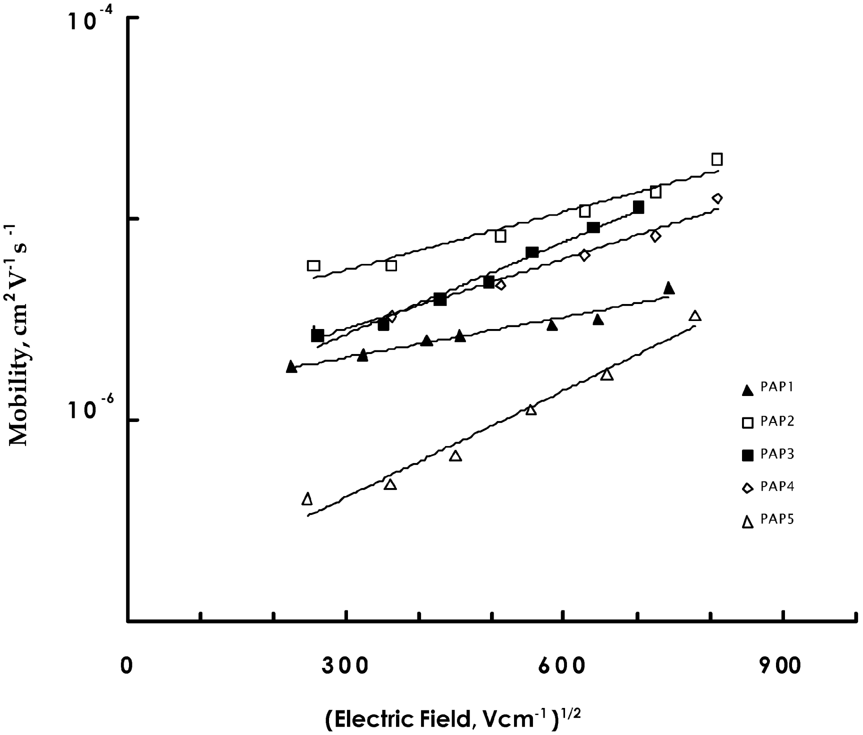


**FIGURE 2** Field dependence of electron drift mobility in polystyrene films doped with 8 wt.% of the PAP derivatives at room temperature.

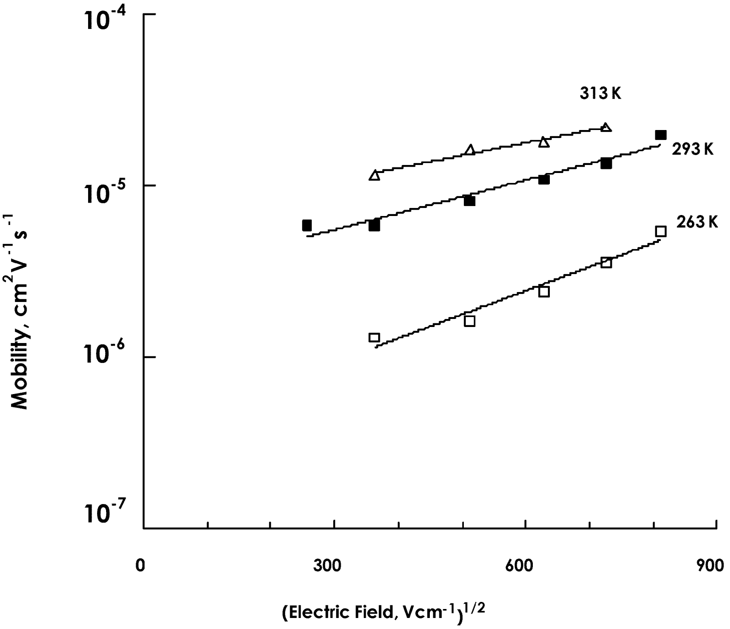


**FIGURE 3** Field dependence of electron drift mobility in polystyrene films doped with 8 wt.% PAP2 at different temperatures.

It has been demonstrated that the correlated disorder model (CDM) [3] appeared to be a suitable model to describe the dependence of mobility on the applied electric field from our previous study [1]. The CDM takes into account the dipole nature of the medium and leads to the following relationship describing non-dispersive mobility [3]:

$$\mu = \mu_0 \exp\left[-\left(\frac{3\sigma}{5kT}\right)^2 + C_0\left(\left(\frac{\sigma}{kT}\right)^{3/2} - \Gamma\right)\sqrt{\frac{eRF}{\sigma}}\right] \tag{1}$$

where $C_0 = 0.78$, $\Gamma = 2$, $\mu_0$ is the pre-exponential factor, $R$ is the distance between transport sites. $\sigma$ is the root mean square width of the dipolar energetic disorder, a key parameter of the model is determined by dipoles existing in the system, and it has a relation to material parameters as $\sigma = 2.35\, ep/(\varepsilon a^2)$, in which $p$ is the permanent dipole moment of molecule, $a$ is the dipole-dipole distance and $\varepsilon$ is the dielectric constant of the medium.

In Figure 2, the linear relation between $lg\mu$ and $F^{1/2}$ agrees with Eq. (1) in all systems studied. The CDM predicts that the larger the dipole moment, the lower the zero-field mobility $\mu(F = 0)$, provided that the pre-exponential factor is equal and all other factors are unchanged in Eq. 1.

Such a correlation was not observed in our previous work [1,4]. However, it is important to see how this will fit to our current PAP system. A tentative estimation gives small values for $\sigma$ which are only in the range of 0.015–0.032 eV when $\varepsilon$ is equal to 2.4 and calculated values for $p$ are in the range of 0.5–4.4 D. In order to find a correlation between the individual features and transport properties of a molecule, the $\mu(F = 0)$ data measured are compared with the data calculated from the CDM with the molecule energy characteristics being taken into account in a similar way to our previous work [1,4].

Generally, electron transport is seen as a chain of redox reactions consisting of one-electron transfer from the single occupied molecular orbital (SOMO) of the radical anions to the lowest unoccupied orbital (LUMO) of the neutral molecules. In the process of moving from the radical anion to the neutral molecule, the electron occupies the LUMO energy level, which rearranges at the moment of transfer and becomes equal in value to the energy of SOMO for the radical anion at the geometry which is optimal for the neutral molecule. So an electron transport efficiency is defined by the energy gap $\Delta$ between the SOMO of the radical anion at its optimal geometry and the SOMO of the radical anion at the optimal geometry of the neutral molecule. For the drift mobility of equation [1], the pre-exponential factor can be expressed as

$$\mu_0 \propto R^2 \exp(-2R/r_0) \exp(-\Delta/kT) \tag{2}$$

where $r_0$ is the wave-function decay constant. In combination of Eqs. (1) and (2) zero-field mobility is given by

$$\mu(F = 0) \propto R^2 \exp\left(-\frac{2R}{r_0}\right) \cdot \exp\left(-\frac{\Delta}{kT}\right) \cdot \exp\left[-\left(\frac{3\sigma}{5kT}\right)^2\right] \equiv A \tag{3}$$

Assuming one transporting site per molecule, $R$ can be replaced with the approximate average intermolecular distance which can be calculated using formula $R = [M/(N_A \rho c)]^{1/3}$, where $M$ is the molecular weight, $\rho$ is the density of the solid, $c$ is the weight concentration of transport molecules and $N_\mathrm{A}$ is the Avogadro number. For PAPs, values of $r_0$ and $\Delta$ were computed with both the PM3 and AM1 semi-empirical methods. The calculated results are shown in Table I. The $\mu(\mathrm{F} = 0)$ values were obtained by extrapolation of the straight line to zero field in Figure 1.

One may conclude that for the PAP molecules the values of the energy gap and particularly wave-function decay constant calculated by the PM3 are more credible than those by the AM1. The highest and the lowest zero field mobility in PAPs measured are related to their permanent dipole moments, the smallest for PAP2 and the biggest for PAP5. This can also be explained from their chemical structure. PAP2 has a relatively symmetric

**TABLE I** Zero-field Electron Mobility and Computed Parameters

| | Dipole moment, D | | A, (Eq. 3) | | $\mu(F=0)$, $cm^2 V^{-1} s^{-1}$ $10^{-6}$ |
|---|---|---|---|---|---|
| | PM3 | AM1 | PM3 | AM1 | |
| PAP1 | 1.6 | 1.3 | $1.8 \cdot 10^{-21}$ | $1.2 \cdot 10^{-23}$ | 1.3 |
| PAP2 | 2.0 | 1.6 | $2.1 \cdot 10^{-20}$ | $2.1 \cdot 10^{-30}$ | 2.8 |
| PAP3 | 2.3 | 2.2 | $1.2 \cdot 10^{-21}$ | $2.0 \cdot 10^{-31}$ | 0.8 |
| PAP4 | 0.5 | 1.0 | $7.5 \cdot 10^{-22}$ | $1.0 \cdot 10^{-39}$ | 1.3 |
| PAP5 | 4.4 | 3.6 | $1.1 \cdot 10^{-22}$ | $1.4 \cdot 10^{-37}$ | 0.1 |

structure with no polar substituent group and hence the dipole moment will be small. PAP5 has a strong dipole amine substituent and it can introduce a larger dipole moment.

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