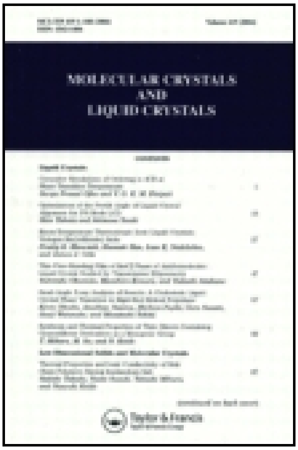

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Charge-Carrier Drift Mobility in Perylene Single Crystals

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Abstract—The electron and hole drift mobilities in highly pure perylene single crystals were measured using a conventional time-of-flight method. Observed values were 0.017 ± 0.001 cm²/V sec for electrons and 0.02 ± 0.003 cm²/V sec for holes at room temperature. The mobilities increased with the temperature between 296°–353 °K with an activation energy of 0.20 eV for electrons. Taking a fluctuation of transfer integrals and a stabilization of electron energy due to the excimer-like excess electron state into consideration, the fairly good agreement between the calculated and measured values of mobility has been obtained.

1. Introduction

The electron or hole mobilities in organic molecular crystal have been measured by several workers using the time-of-flight method originally introduced by LeBlanc for an anthracene crystal.(1) The observed values for the drift mobilities are in the range of 10^{-1} to 10^{0} cm²/V sec and its temperature dependence is roughly proportional to T^{-n}; $n = 1$–2, both of which have a corresponding anisotropy with the directions along the crystal axis.

The qualitative and also quantitative interpretations for the observed results have been proposed in terms of a band model(2) or a hopping model.(3) Although the recent approach to this problem

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carried out by Munn and Siebrand(4) seems to be rather general and attractive, it may be still quite difficult to establish the explicit picture in the intermediate region(4) relevant to the real system.

We will report in this paper that the carrier drift mobility in the perylene single crystal was so small and also its activation energy obtained from its temperature dependence was rather so high that a naive application of hopping scheme would be possible.

The effect of " dimeric structure " in the unit cell of a perylene crystal(5) for the results stated above will be also discussed.

2. Experimental

Highly pure perylene was synthesized from acenaphthene(6) and crystallized from its toluene solution as a golden-yellow disk-plate in size of ~3 mm × ~3 mm × ~0.3 mm (in the thickness).

Nearly the same measuring system as reported previously(7) in the case of anthracene was employed. Electrons or holes were created at the one surface of the crystal via singlet-excitons formed by the photo-excitation (~450 nm) through a tin oxide transparent electrode using an air-gap-discharge light pulser with a proper filter (Toshiba VB-46).

The temperature at the mobility cell was varied in the range of 296–353 °K by an electric heater and the corresponding changes in a mobility-pulse width were measured.

3. Results

The typical photocurrent pulses observed are shown in Fig. 1 on the specified conditions in its caption. Although these pictures are very different from those of the ideal current, the point of an abrupt change in the slope after a flat on top could be recognized, at which the transit time of carriers was determined. A rather long tail of the pulse may be due to the defects of the crystals used which were obtained from a solution.

The drift velocity was proportional to the electric-field up to $\sim 4 \times 10^4$ V/cm and its dependence at several temperatures was measured as shown in Fig. 2.

The mean values of the drift mobility in c'-direction were 0.017 ±

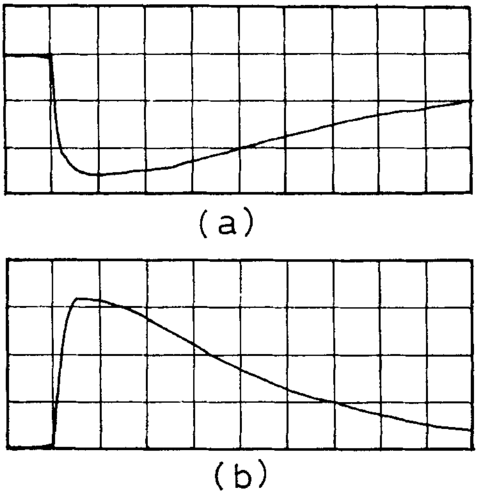

Figure 1. Typical photocurrent vs. time curves: (a) Electron current, (b) Hole current, at 345 °K, 50 μsec/division (abscissa).

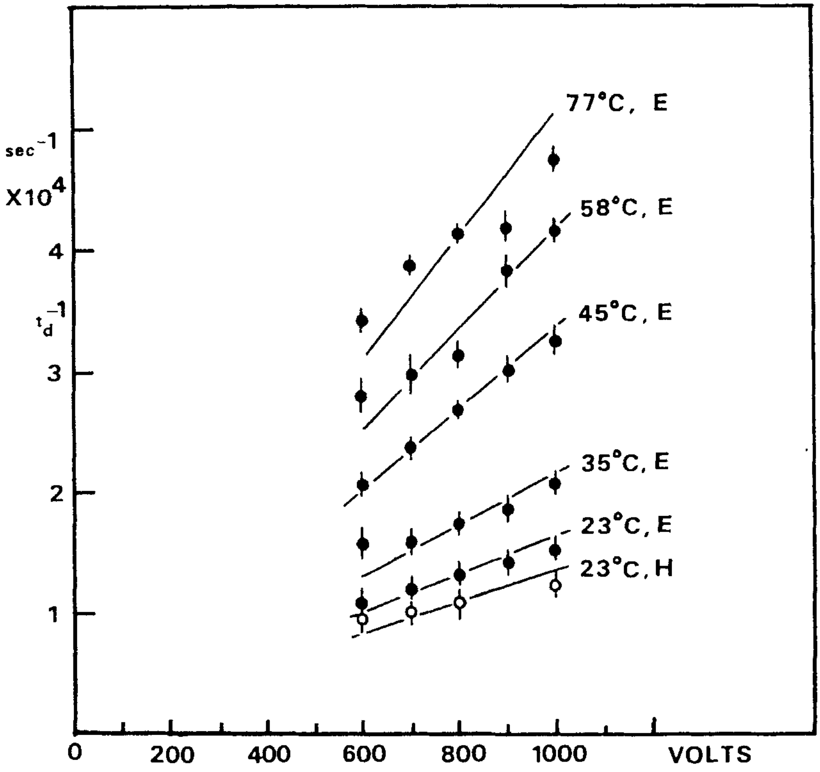

Figure 2. (Transit time, $t_d)^{-1}$ vs. applied voltage at various temperatures. *E* is for electron current and *H* for hole current.

0.001 cm^2/V sec for electrons and 0.02 ± 0.003 cm^2/V sec for holes at room temperature (296 °K). The pulse shape of a hole current was not so good as that of an electron one.

The electron mobility increased with the temperature between 296–353 °K. Plots of the logarithm of the mobility versus T^{-1} in Fig. 3 show an almost straight line with an activation energy of 0.20 eV in this temperature range. The hole mobility also showed similar temperature dependence. We found, however, it rather difficult to determine the change in the transit time within the same accuracy as that in an electron current, because of the increasing ambiguity in determination of the inflection point on a pulse with temperature.

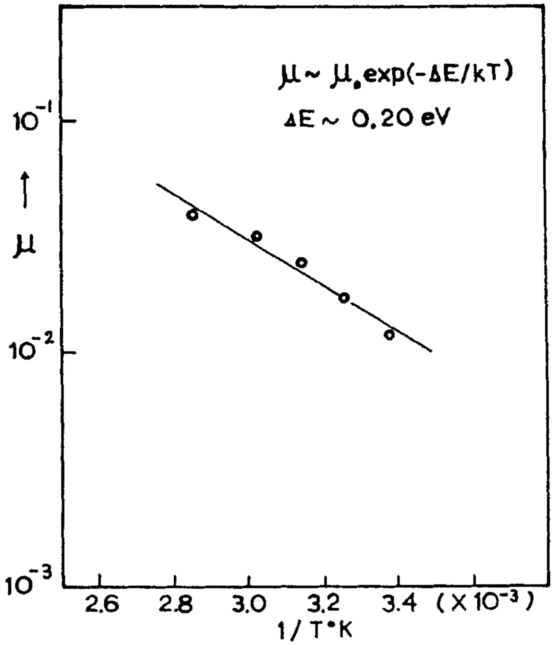

Figure 3. Temperature dependence of electron drift mobility.

4. Discussion

The drifting behavior of the charge carriers in organic molecular crystals may be determined mainly by the intermolecular resonance integrals or transfer integrals, which can be evaluated from the molecular wavefunctions taking the crystal structure into consideration.

The crystal structure of perylene was analyzed by Robertson *et al.*(8) and also by Tanaka.(5) The crystals used in this experiment have four molecules in a unit cell, that is, are " dimeric in structure " or " α-form " in Tanaka's nomenclature.

The transfer integrals for each pair of molecules in a perylene crystal were calculated using the Hückel-type molecular orbitals in which a single Slater orbital exponent, 3.08×10^8 cm^{-1} was employed. Only the two center integrals were considered and other procedures in calculation were almost the same as those of Katz *et al.*(9)

In Table 1 we display the transfer integrals calculated between the molecule at Position 1 and the several neighboring molecules of which numbering is shown in Fig. 4.

TABLE 1 Intermolecular transfer integrals in units of 10^{-4} eV

Molecule number	Electron	Hole
2	-58.9	-25.7
3	19.6	17.8
4	9.72	9.15
5	19.6	17.8
6	-11.4	0.82
7	9.73	9.15
8	-3.57	2.52
9	0.01	0.03
10	-0.04	0.13
11	0.84	1.17
12	0.01	0.11
13	0.13	0.17

In order to elucidate the experimentally obtained characteristics of the electron drift mobility in c'-direction, we display the relevant transfer integral values in Table 2, in comparison with the corresponding ones in an anthracene crystal. The latter were selected from Katz's Table(9) within the same order of approximation as the present calculation.

The largest value in c'-direction, 3.57×10^{-4} eV (1 and 8), in perylene is fairly larger than that in anthracene, 0.67×10^{-4} eV.

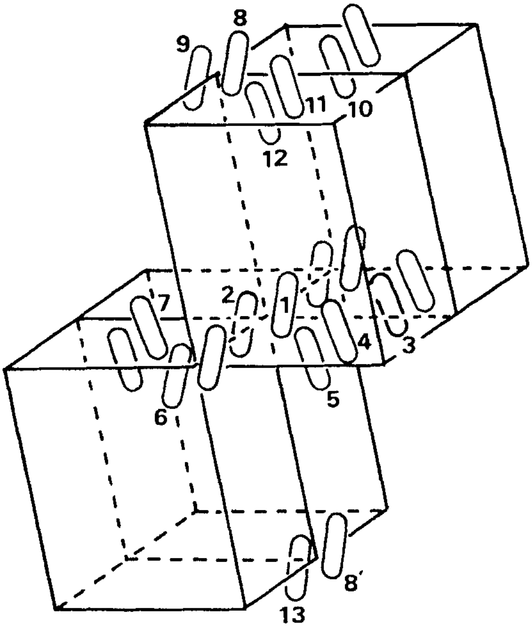

Figure 4. Schematic representation of the perylene unit cells, showing the numbering of the molecules used in this paper.

TABLE 2 The comparison of the electron transfer integrals in c'-direction in a perylene crystal with those in an anthracene crystal.

Molecule-pairs	Perylene	Anthracene
1–8	3.57[a]	0.38[a]
1–11	0.84	0.67
1–13	0.13	0.38

[a] In units of 10^{-4} eV.

Nevertheless, the observed drift mobility in perylene, 0.017 cm^2/V sec, was so small compared with that in anthracene, 0.4 cm^2/V sec, that we have to consider an alternate mechanism for the carrier transport in a perylene crystal.

The significant fluctuations of the transfer integrals should generally determine the drift mobility value. Gosar and Choi(10) found out that the fluctuation of polarization energy through the electron–phonon (lattice phonon) interaction was most important, and obtained fairly good agreement between the calculated and measured values of mobility in an anthracene crystal using the Kubo linear-response formulation.

In the perylene crystal, an excess electron on a dimeric point may be somewhile localized through the formation of an excimer-like electronic state between two molecules. The excimer-state in perylene crystals is known to be located at ~0.4 eV below the mutually independent molecular excited states.(11) The relative displacement between dimeric molecules due to an excimer formation was also estimated to be ~ − 0.2 Å in a pyrene crystal by Birks.(11) Then, the same order of stabilization in energy and displacement between two molecules could be assumed on the case of an " excess-electron-dimeric state " in a perylene crystal, and these effects might result in the fluctuation of transfer integrals and also the activation process in the electron transport procedure.

Within the physical picture mentioned above, we can estimate the drift mobility using the following equation deduced by Gosar and Choi,(10)

$$\mu^0 = \frac{\pi e}{\hbar kT} \sum_j (r_j - r_i)(r_j - r_i)[\omega(i,j)^2/\alpha(i,j)], \tag{1}$$

where μ^0 is a tunneling mobility, r_i and r_j are position vectors of molecule i and j, $\omega(i,j)$ denotes a transfer integral between i and j, and $\alpha(i,j)$ the fluctuation of $\omega(i,j)$. The decreasing in the distance between dimer molecules will cause the fluctuation of transfer integral between 1 and 8 (Fig. 4). The fluctuation, $\Delta\omega$, may be calculated by the equation;

$$\Delta\omega = \frac{d\omega}{dr} \Delta r. \tag{2}$$

The value of $|\Delta\omega|$ is found 0.893×10^{-4} eV assuming 0.2 Å for Δr in Eq. (2).† Applying this $|\Delta\omega|$ for $\alpha(i,j)$ and 3.57×10^{-4} eV ($j = 8$) for $\omega(i,j)$ in Eq. (1), we obtain 1.45×10^2 cm^2/V sec at 296 °K for $\mu^0_{cc'}$, the electron tunneling mobility in c'-direction.

In order to estimate the true mobility taking the activation process into consideration, we have to multiply μ^0_{cc} by a factor of $\exp(-\Delta E/kT)$;

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† The fluctuation due to lattice phonons should be smaller than this value.

$$\mu_{cc} \sim \mu_{cc}^{0} \cdot \exp(-\Delta E/kT) \qquad (3)$$

where ΔE means an activation energy. Then, μ_{cc} was roughly evaluated to be ~ 0.015 cm^2/V sec for electrons at 296 °K inserting the observed activation energy, 0.20 eV, into ΔE in Eq. (3). The fairly good agreement between the calculated (0.015 cm^2/V sec) and measured (0.017 cm^2/V sec) values has been suggestive of the validity of the proposed electron transport mechanism.

Further confirmation could be obtained by comparing the present results with the drift mobility measurement in " β-form "(5) perylene crystals. We should also carry out quite careful measurement of drift mobilities in pyrene dimeric crystals.(12)

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