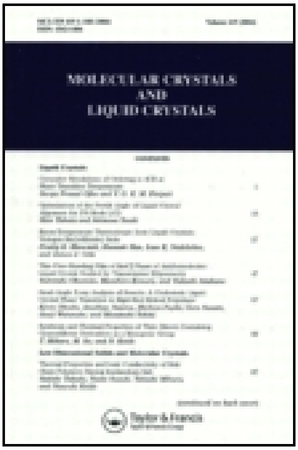

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Charge Transport Properties of Arylaldehyde Hydrazones in Their Glassy States - Single Component and Doped Systems

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CHARGE TRANSPORT PROPERTIES OF ARYLALDEHYDE HYDRAZONES IN THEIR GLASSY STATES – SINGLE COMPONENT AND DOPED SYSTEMS

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Abstract For the purpose of elucidating charge transport in disordered organic materials, hole transport in the glassy state of 4-diphenylaminobenzaldehyde diphenylhydrazone (DPH), 4-diphenylaminobenzaldehyde methylphenylhydrazone (DPMH), and DPH doped with a small amount of 4-diethylaminobenzaldehyde diphenylhydrazone (DEH) has been studied. The hole drift mobility in the DPMH glass was approximately one-fifth of that in the DPH glass; this was attributed to a higher activation energy in terms of the Arrhenius formalism or to an increased width of the Gaussian density of states based on the site energy disorder model for the DPMH glass. The introduction of less than 1 mol% DEH into DPH resulted in a significant increase in activation energy or in the Gaussian width of the site energy distribution, which increased with increasing concentration of the dopant.

Keywords: 4-diphenylaminobenzaldehyde diphenylhydrazone, 4-diphenylaminobenzaldehyde methylphenylhydrazone, 4-diethylaminobenzaldehyde diphenylhydrazone, mobility, charge transport, Poole Frenkel, photoconductivity, trapping

INTRODUCTION

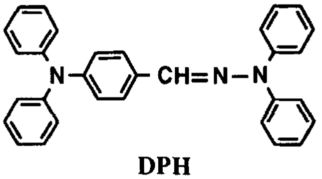
Charge transport in organic disordered systems, particularly molecularly doped polymer systems where low-molecular-weight organic compounds are dispersed into polymer binders, has been a subject of recent extensive studies in relation to their practical application as photoreceptor materials in electrophotography.[1-5] It has been understood that charge transport in disordered organic systems, which is a thermally activated process, takes place by a hopping mechanism. A few models have been proposed to explain temperature and electric-field dependencies of charge carrier drift mobilities in organic disordered systems, which include the Poole-Frenkel model,[6] small polaron model,[2,3] and energy disorder model.[7,8] The former two models follow the temperature dependence of the Arrhenius form, while the energy disorder model is described by a non-Arrhenius temperature dependence.

It has recently been revealed that charge transport in molecularly doped polymer systems, where the binder polymer was thought to be inert for charge transport, is greatly affected by the binder polymer.[9-12] In fact, hole drift mobilities in a few moleculary doped polymer systems have been shown to vary by two orders of magnitude depending upon the binder polymer. Ion-dipole interactions between the molecule radical cation and the binder polymer are thought to be responsible for this phenomenon.

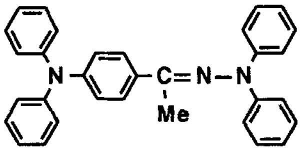
In order to elucidate intrinsic properties of charge transport in disordered organic materials, it is necessary to study charge transport in the amorphous glassy state of low-molecular-weight organic materials without the binder polymer. However, very few studies have been made of charge transport in the amorphous glassy state of low-molecular-weight organic materials,[13-15] since there have been known very few examples of low-molecular-weight organic compounds that form stable glasses with glass-transition temperatures above room temperature.

We have found that a series of arylaldehyde and arylketone hydrazones constitute a family of amorphous molecular materials that form stable amorphous glasses on cooling from the melt.[13] We have shown that hole drift mobilities in the glassy state of 4-diphenylaminobenzaldehyde diphenylhydrazone (DPH) and 4-diphenylamino-acetophenone diphenylhydrazone (M-DPH) are over one order of magnitude greater than those in 50 wt% moleculary doped polycarbonate systems, and that the two or three fold higher hole mobilities in DPH than those in M-DPH are attributed to a lower activation energy. The steric effect by the methyl substituent in M-DPH, which affects the intermolecular overlap of π-electrons, may be responsible for the higher activation energy.[14]

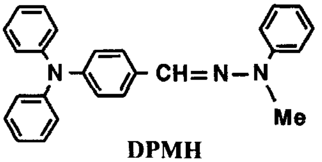
In the present study, we have investigated hole transport in the glassy state of 4-diphenylaminobenzaldehyde methylphenylhydrazone (DPMH), where one phenyl group in DPH is replaced by a methyl group, in order to elucidate how the electronic effect will affect the charge transport in these materials. In addition, in order to gain information on thermal activation energies for hopping transport or trapping of charge carriers in amorphous molecular materials without the polymer matrix, hole transport in DPH doped with a small amount of DEH having a lower oxidation potential has been studied.



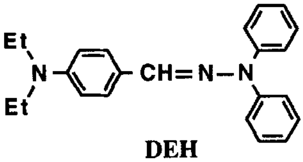
DPH



M-DPH



DPMH



DEH

EXPERIMENTAL

Materials

The arylaldehyde hydrazones, DPH, DPMH and DEH, were prepared by the reaction of 4-diphenylaminobenzaldehyde or 4-diethylaminobenzaldehyde with diphenylhydrazine or with methylphenylhydrazine in ethanol, and purified by recrystallization from benzene/ethanol. The amorphous films of DPH, DPMH and DPH/DEH systems were prepared either by coating from a dichloromethane solution using a glass bar or on cooling from the melt sample.

Measurements

The hole drift mobilities were measured by a time-of-flight method for a layered device consisting of a charge carrier generation layer (CGL) and a charge carrier transport layer (CTL). A thin film (thickness: less than 1 μm) of X-type metal-free phthalocyanine dispersed into poly(ethylene-co-vinylchloride) was coated on an aluminum substrate to make a CGL. A thicker film (thickness: 10-20 μm) of the amorphous glass of the hydrazones as a CTL was coated on to the CGL. Then, a semitransparent gold electrode was vapor deposited on the top of the CTL. The photocurrent, obtained by irradiation with pulsed light from a xenon stroboscopic lamp (pulse duration time: *ca.* 1-4 μs), was monitored using a digital storage scope, KDS-102 (Kawasaki Electronica).

RESULTS AND DISCUSSION

Single Component systems

Both DPH and DPMH form spontaneously stable amorphous glasses *via* supercooled liquid states when the melt samples are cooled on standing in air, as characterized by differential scanning calorimetry (DSC) and X-ray diffraction. The films prepared by coating from a solution were also confirmed to be amorphous glasses. The glass-transition temperatures of DPH and DPMH are *ca.* 50°C and 30°C, respectively, as determined by DSC.

The transit time (τ_t) was observed as a cusp in the trace of photocurrent (i_{ph}) as a function of time (t), which was almost in accord with the value determined from the plot of log i_{ph} *vs.* log t based on the Scher-Montroll theory.[16] The hole drift mobility was calculated from the transit time, according to the expression $\mu = L^2/\tau_t V$, where L is the sample thickness and V the applied voltage.

Table I lists the values of hole drift mobilities (μ_h) and intersite distances (ρ) for the

DPH and DPMH glasses. The results show that the hole drift mobility in the DPMH glass is approximately one-fifth of that in the DPH glass.

TABLE I Hole drift mobilities[a)] and intersite distances.[b)]

Material	$\mu_h/cm^2V^{-1}s^{-1}$	ρ/Å
DPH	2.2×10^{-4}	8.6
DPMH	4.9×10^{-5}	8.2

a) Measured at an electric field of 2.0×10^5 Vcm^{-1} and at 20°C
b) Calculated from $\rho=(M/Ad)^{1/3}$, where M is the molecular weight, A the Avogadro's number, and d the density

Electric-field and temperature dependencies of hole drift mobilities in the DPMH glass were analyzed both by the empirical equation (eq. 1) proposed by Gill,[6] which takes into account the Poole-Frenkel model, and by the site energy disorder model (eq. 2) of Bässler *et al.* [7,8]

$$\mu=\mu_0\exp[-(E_0-\beta_{PF}E^{1/2})/k_BT_{eff}] \qquad (1)$$
$$T_{eff}^{-1}=T^{-1}-T_0^{-1}$$

where E_0 is the activation energy at the zero electric field, β_{PF} the Poole-Frenkel coefficient, k_B Boltzmann's constant, E the electric field, T_0 the temperature at which extrapolated data of Arrhenius plots at various electric fields intersect with one another, and μ_0 the mobility at T_0.

$$\mu=\mu_0\exp[-(T_0/T)^2]\exp(\beta E^{1/2}) \qquad (2)$$

where T_0 is proportional to the Gaussian width σ ($\sigma=(3/2)kT_0$) of the site energy distribution and μ_0 the mobility in a hypothetical energy disorder-free system extrapolated to $T \rightarrow \infty$.

As observed for DPH, hole drift mobilities of the DPMH glass were found to follow the electric-field dependence of $\exp(\beta E^{1/2})$, as shown in Figure 1.

As was the case for DPH, temperature dependence of hole drift mobilities in the DPMH glass was found to fit both to the Arrhenius form in eq. 1 and to $\exp[-(T_0/T)^2]$ in eq. 2. Figure 2 shows Arrhenius plots of hole drift mobilities in DPMH at different electric fields. The zero-field activation energy (E_0) in eq. 1 was determined by the extrapolation of the plots of apparent activation energies (E_{act}) *vs.* $E^{1/2}$ to the zero electric field, as shown in Figure 3.

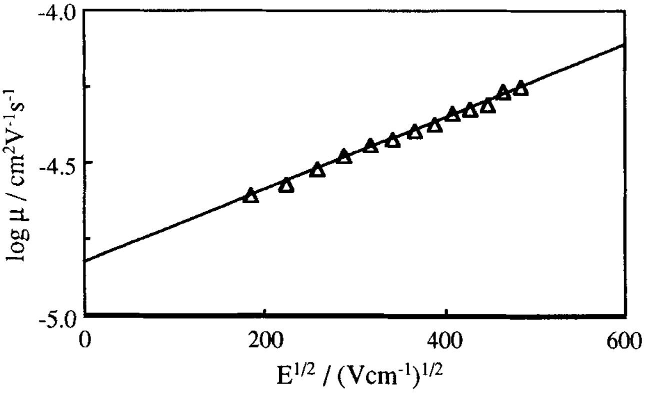


FIGURE 1 Electric-field dependence of hole drift mobilities in the DPMH glass at 20°C.

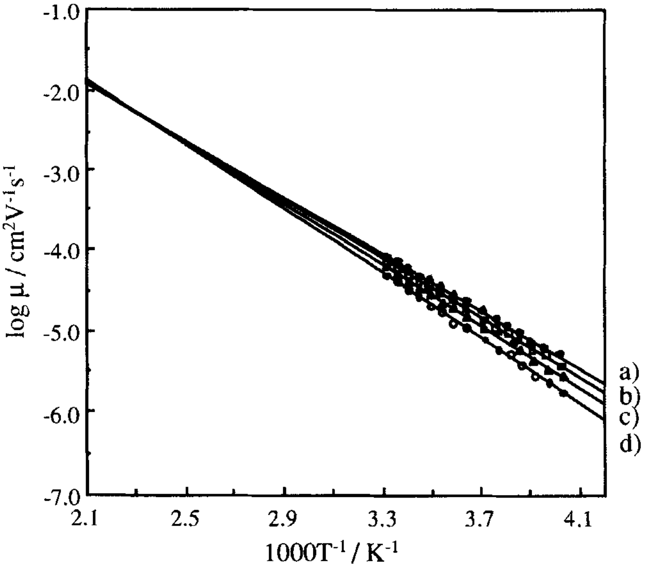


FIGURE 2 Arrhenius plots of hole drift mobilities in the DPMH glass at different electric fields; a) 2.5×10^5, b) 2.0×10^5, c) 1.5×10^5, and d) 1.0×10^5 Vcm^{-1}.

The hole transport parameters in eq. 1, μ_0, E_0 and T_0, which were determined from Figs. 2 and 3, are summarized in Table II. The results for the DPH glass are also included in the Table for comparison.

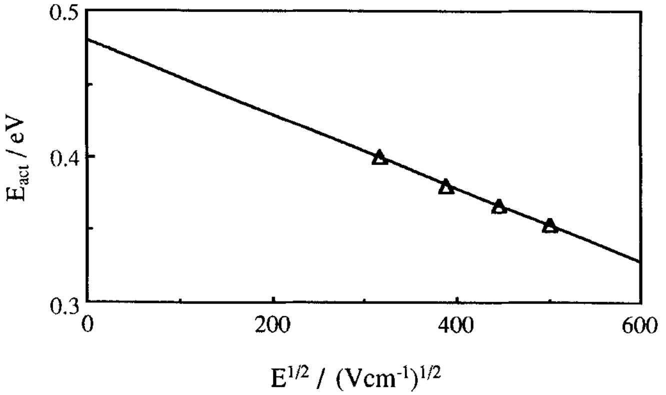


FIGURE 3 Apparent activation energies (E_{act}) *vs.* $E^{1/2}$ for the DPMH glass.

Figure 4 shows the plots of log $\mu(E=0)$ *vs.* T^{-2} for the DPMH glass. The hole transport parameters in eq. 2, T_0 and μ_0, which were obtained from the slope and the intersect of the linear plot extrapolated to T → ∞, respectively, are listed in Table III, together with the values for the DPH glass.

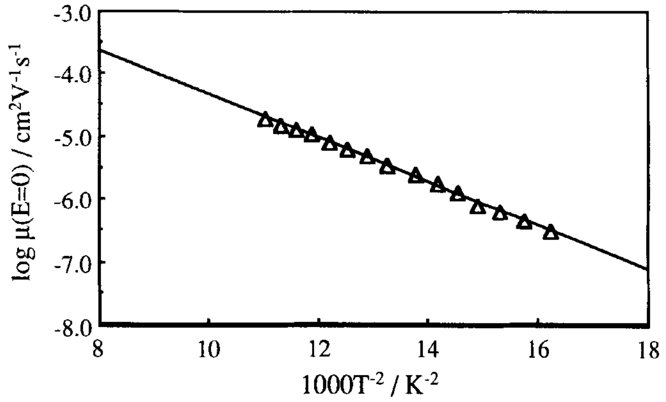


FIGURE 4 Logarithms of hole drift mobilities in the DPMH glass at the zero electric field *vs.* T^{-2}.

The results listed in Tables II and III show that the lower hole mobility in the DPMH glass relative to the DPH glass (Table I) is attributed mainly to a higher thermal activation energy in terms of the Arrhenius form or to an increased width of the Gaussian density of states based on the energy disorder model, for the DPMH glass relative to the

DPH glass. It is thought that the electronic effect due to the replacement of one phenyl group in DPH by the methyl group causes changes in the molecular dipole moment, intermolecular aggregation, or intermolecular overlap of π-electrons; these may be responsible for an increased zero-field activation energy (E_0) according to eq. 1 and for an increased Gaussian width of the site energy distribution based on eq. 2.

TABLE II Hole transport parameters based on eq. 1.

Material	μ_0/cm^{2}V^{-1}s^{-1}	E_0/eV	T_0/K	β_{PF}/eV(Vcm^{-1})$^{-1/2}$
DPH	4.2×10^{-3}	0.39	420	3.1×10^{-4}
DPMH	4.3×10^{-3}	0.48	424	2.5×10^{-4}

TABLE III Hole transport parameters based on eq. 2.

Material	μ_0/cm^{2}V^{-1}s^{-1}	T_0/K (σ/eV)
DPH	2.1×10^{-1}	849 (0.11)
DPMH	1.5×10^{-1}	901 (0.12)

Doped Systems

A few studies have been made of charge transport in organic disordered materials doped with another material in the amorphous polymer matrix.[17-19] It has been shown that charge transport in the disordered system doped with another molecule having a lower ionization potential is trap-controlled. Investigation of charge transport in a mixed system of two different materials is expected to distinguish between the hopping models.[19] In order to gain information on the thermal activation energy for hopping transport or trapping of charge carriers in amorphous molecular materials, hole transport in the DPH glass doped with a small amount of DEH having a lower oxidation potential was studied.

The oxidation potentials ($E_{1/2}$) of DPH and DEH in dichloromethane were determined to be 0.47 and 0.29 V *vs.* Ag/Ag$^+$(0.01mol dm^{-3}), respectively. Table IV shows hole drift mobilities in undoped DPH and DPH doped with varying concentrations of DEH. The hole drift mobility was found to decrease with increasing concentration of DEH.

The logarithms of hole drift mobilities in the doped systems were proportional to the square root of the electric field. Temperature dependence of hole drift mobilities in the doped systems was found to fit to the Arrhenius form and to T^{-2}. The zero-field activation energy (E_0) for the doped systems based on eq. 1 was determined from the plots of E_{act} *vs*. $E^{1/2}$, as shown in Figure 5.

TABLE IV Hole drift mobilities in DPH doped with DEH.[a)]

Material	μ_h/cm^{2}V^{-1}s^{-1}
DPH 100%	2.2×10^{-4}
DPH:DEH=148:1	1.0×10^{-4}
DPH:DEH= 63:1	2.5×10^{-5}
DPH:DEH= 40:1	6.0×10^{-6}

a) Measured at an electric field of 2.0×10^5 Vcm^{-1} and at 20°C

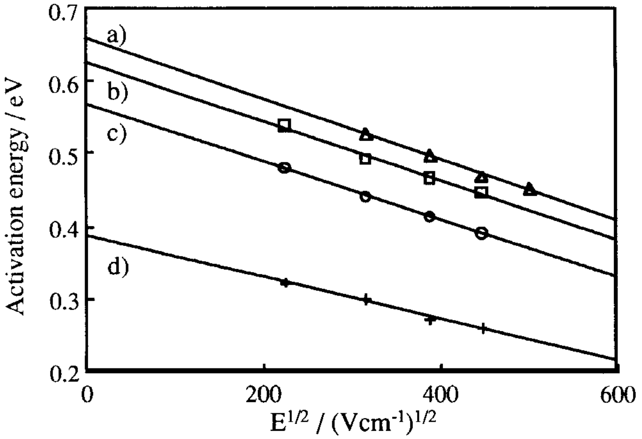


FIGURE 5 Activation energies *vs*. $E^{1/2}$;
a) DPH:DEH=40:1, b) DPH:DEH=63:1,
c) DPH:DEH=148:1 and d) DPH 100%.

Figure 6 shows the plots of log $\mu(E=0)$ *vs*. T^{-2}. Hole transport parameters based on eq. 1 and eq. 2 are summarized in Table V. The introduction of less than 1 mol% DEH into DPH resulted in a significant increase in activation energy in terms of eq. 1 and an increase in the Gaussian width of the site energy distribution. The difference of 0.18 eV in the activation energy between undoped DPH and the DPH:DEH (mole ratio 148:1) system corresponds to the difference in the oxidation potential between DPH and DEH. It is understood that DEH acts as a hole trap, and hence charge transport in the doped system is trap-controlled. However, the activation energy was found to increase further with increasing concentration of DEH. Likewise, the Gaussian width of the site energy distribution increased with increasing concentration of the dopant molecule DEH, while the mobility in a hypothetical energy disorder-free system (μ_0) was shown to be almost the same for the doped and undoped systems. In a trap-controlled model, the activation energy should not exceed the difference in the redox potential between the host and dopant molecules. It is suggested that the introduction of the dopant DEH into DPH increases the disorder in the material, and that both trap-controlled transport and site energy disorder should be considered for the doped system.

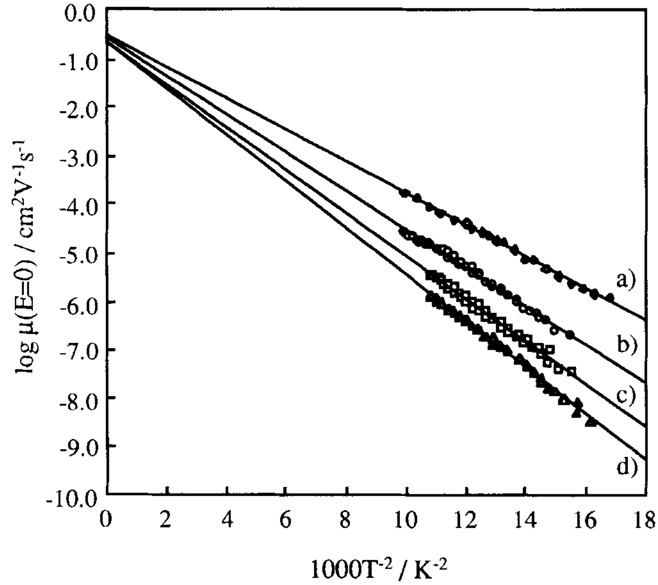


FIGURE 6 Logarithms of hole drift mobilities at zero electric field *vs.* T^{-2}; a) DPH 100%, b) DPH:DEH=148:1, c) DPH:DEH=63:1 and d) DPH:DEH=40:1.

TABLE V Hole transport parameters for undoped DPH and DPH doped with DEH.

Material	$E_0/eV^{a)}$	$\mu_0/cm^2V^{-1}s^{-1b)}$	$T_0/K\,(\sigma/eV)^{b)}$
DPH 100%	0.39	2.5×10^{-1}	849 (0.11)
DPH:DEH=148:1	0.57	2.7×10^{-1}	961 (0.12)
DPH:DEH= 63:1	0.63	2.2×10^{-1}	1024 (0.13)
DPH:DEH= 40:1	0.66	2.2×10^{-1}	1048 (0.14)

a) Based on eq.1 b) Based on eq.2

SUMMARY

Charge transport in the glassy state of DPH and DPMH has been investigated. The results were analyzed both by the empirical equation and by the site energy disorder model, and discussed in relation to the molecular structure. The lower mobility in DPMH relative to DPH was attributed to a higher activation energy or to an increased Gaussian width of the site energy distribution. Hole transport in the DPH glass doped with a small amount of DEH having a lower oxidation potential has also been studied. The results suggest that both trap-controlled transport and site energy disorder should be considered for the doped system.

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