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Journal of Photochemistry and Photobiology A: Chemistry 151 (2002) 39–43

Journal of Photochemistry and Photobiology A:Chemistry

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Hole-drift mobility in phenylenediamine derivatives possessing methyl substituents

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Received 7 January 2002; accepted 15 January 2002

Abstract

Substituent effects on the hole-drift mobility of *N,N,N′,N′*-tetraarylphenylenediamine derivatives have been investigated. The hole mobility values are dependent on the number of methyl substituents and their position in the investigated transporting materials (TM). The highest mobility was observed in the TM containing methyl groups at the *para* positions of the side benzene rings and at the central ring. On the other hand, the priority of the *m*-phenylenediamine derivative against the *p*-phenylenediamine homologue was proved.

Keywords: Conducting materials; Hole-drift mobility; Substituent effects; Phenylenediamines

1. Introduction

Photo- and electroactive organic materials have been the subject of recent attention, including organic photoactive materials for solar cells, organic non-linear optical materials, photo- and electrochromic organic materials, resist materials, liquid crystals, and others [1]. Among them, the π-electron starburst molecules as charge transporting materials (TM) are intensely synthesised and investigated during past decades [2]. In addition, a variety of π-conjugated molecules, involving carbazole [3–5], phenothiazine [6], thiophene [7–9], diphenylamine and triphenylamine [10–13], oxadiazole and quinoxaline [14–16] and other moieties have been investigated. They ensure rapid charge transporting ability, high photosensitivity and durability of the charge transporting layers (CTL). Meanwhile, numerous investigations are being carried out aiming to enhance hole-drift mobility, however until now only few concrete recommendations have been made with regard to the molecular structure modification. Only limited data are available concerning the influence of the presence and location of alkyl substituents on the qualitative parameters of CTL. The importance of these groups in *N,N,N′,N′*-tetraarylbenzidine derivatives while constructing the frame of an effective photoconductor has been demonstrated [17]. In our previous paper [18] we reported on the electrophotographic properties and stability of amorphous state of *N,N,N′,N′*-tetraarylphenylenediamine derivatives. The introduction of methyl groups into *N*-substituted phenyl moiety in all the cases increases the photosensitivity and reduces the residual potential considerably. On the other hand, the presence of alkyl substituents enhances the stability of glassy state of such π-electron-conjugated systems.

In this paper, we report on the influence of methyl groups and their location on the hole-drift mobility in *N,N,N′,N′*-tetraarylphenylenediamine derivatives, which have been recently mentioned among the most effective TM in various electro-optical applications [19,20].

2. Experimental details

2.1. Materials

Triphenylamine from Aldrich was used as received. The synthesis (Scheme 1) of *N,N,N′,N′*-tetraarylphenylenediamine derivatives **1a**, **2a–f** have been reported earlier [18].

Preparation of 1,4-bis(3,3′-dimethyldiphenylamino) benzene (**1b**). 7.57 g (0.07 mol) of 1,4-phenylenediamine, 76.31 g (0.35 mol) of 3-iodotoluene, 48.30 g (0.35 mol) of powdered anhydrous potassium carbonate, 4.44 g (0.07 mol) of electrolytic copper powder and 2 g (3.78 mmol) of 18-crown-6 were refluxed in 50 ml of *o*-dichlorobenzene

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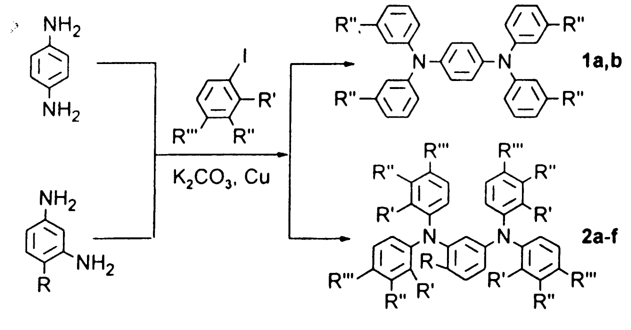
PII: S1010-6030(02)00013-8



	1a	1b	2a	2b	2c	2d	2e	2f
R	-	-	H	H	H	H	CH_3	H
R'	-	-	H	CH_3	H	H	H	H
R''	H	CH_3	H	H	CH_3	H	H	CH_3
R'''	-	-	H	H	H	CH_3	CH_3	CH_3

Scheme 1. Synthesis route of *N,N,N′,N′*-tetraarylphenylenediamine derivatives **1a**,**b**, **2a**–**f**.

under argon for 24 h. The copper and inorganic salts were then removed by filtration of the hot reaction mixture. The solvent was distilled under reduced pressure and the crude product was purified by column chromatography with silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) using *n*-hexane: 1,2-dichloroethane (vol. ratio 5:1) as eluent. The yield of **1b** was 19.6 g (60%), m.p. 176.5–178 °C (from *n*-hexane). ^1H NMR (100 MHz) spectrum: 7.3–6.5 (20H, m, Ar); 2.2 (12H, s, $4CH_3$). IR spectrum (cm^{-1}): 3040 (CH_{arom}); 2940 (CH_{aliph}); 830, 770, 690 (=C–H of 1,3- and 1,4-disubstituted benzenes). Found (%): C 86.91; H 6.71; N 6.17. $C_{34}H_{32}N_2$. Calculated (%): C 87.14; H 6.88; N 5.98.

2.2. Measurement

The ^1H NMR spectrum was taken on a JEOL-FX 100 (100 MHz) spectrometer in $CDCl_3$. The chemical shifts are expressed in ppm, downfield from haxamethyldisiloxane (HMDS), used as internal standard. The IR spectrum was taken in KBr pellet on a Specord M-80. The UV spectra were recorded on a Spectronic Genesys 8 spectrometer in acetonitrile. 10^{-4} M solution of investigated TM and microcell with an internal width of 1 mm was used.

The samples for the charge carrier mobility measurements were prepared by casting the solutions of the TM **1b**, **2b**–**f** or solutions of mixtures of these compounds with binder material polycarbonate Z at a mass proportion of 1:1 in THF. The substrates were glass plates with a conductive SnO_2 layer or a polyester film with an Al layer. After coating, the samples were heated at 80 °C for 1 h, thus the CTL of the samples were prepared. The thickness of the CTL varied in the range 2–9 μm.

The hole-drift mobility was measured by time of flight technique [21]. Positive corona charging created electric field inside the TM layer. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in linear or double logarithmic scale. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness, U_0 the surface potential at the moment of illumination.

The samples for the ionisation potential measurement were prepared dissolving TM in THF and coating on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer (MKM) sub-layer. The thickness of the TM layers was 0.5–1 μm.

The ionisation potential I_p was measured by the electron photoemission in air method, similar to the used in [22] and described in [23,24].

Electron affinity for compounds was estimated from the position of HOMO and LUMO states according to Eq. (1) [25]. The determined values of ionisation potential were equated with HOMO values. After determining the starting value of long-wave absorption λ_{min}, which was evaluated in eV, the electron affinity (error is due to relaxation) was estimated according to formula (1).

$$\chi \approx I_p - h\nu_{min} \qquad (1)$$

3. Results and discussion

N,N,N′,N′-Tetraarylphenylenediamines **1a**,**b**, **2a**–**f** were synthesised by the Ullmann reaction [26] of 1,3-, 1,4-phenylenediamines and 2,4-toluenediamine with corresponding iodoarenes in nitrobenzene or 1,2-dichlorobenzene at reflux in the presence of catalyst—copper powder and anhydrous potassium carbonate (the latter combines with the liberating hydrogen iodide).

Since π-electrons are very important for the charge transporting process in conjugated TM structures, their state was explored from the light absorption spectra of *N,N,N′,N′*-tetraarylphenylenediamines **1a**,**b**, **2a**–**f**. Electron transitions to the higher energy states in the investigated derivatives give two main photon absorption maxima (Figs. 1 and 2) at 190–200 nm ($\log(\varepsilon_1) \approx 5$) and 290–310 nm ($\log(\varepsilon_2) \approx 4.7$). Comparison of these results with the extinction of benzene electrons [27] (λ_{max1} = 204 nm/$\log(\varepsilon_1)$ = 3.9, λ_{max2} = 256 nm/$\log(\varepsilon_2)$ = 2.3) shows that the second absorption band is bathochromically shifted by 40–50 nm and is hyperchromically intensified due to the π-electron conjugation through the lone electron pair at the nitrogen atom. As seen from the comparison of UV absorption spectra (Fig. 1) of triphenylamine, 1,4-bisdiphenylaminobenzene (**1a**) and 1,3-bisdiphenylaminobenzene (**2a**), *p*-phenylenediamine derivative **1a** (λ_{max} = 308 nm) distinguishes itself by the strongest conjugation. Comparison of electron

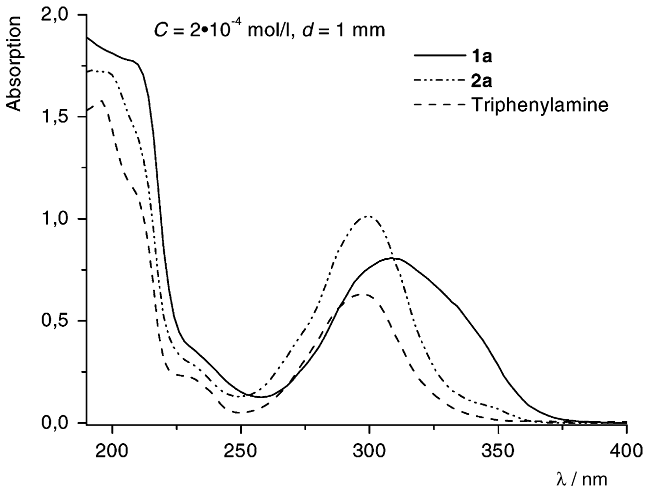


Fig. 1. Light absorption spectra of triphenylamine and *N*,*N*,*N*′,*N*′-tetraarylphenylenediamine derivatives **1a**, **2a**.

absorption bands of tetraaryl *m*-phenylenediamines, possessing methyl substituents in the different locations (Fig. 2) reveals that they are similar, except that for 1,3-bis(2,2′-dimethyldiphenylamino)benzene (**2b**). The latter acts somewhat unusually—hypsochromic shift of its extinction maximum is by ca. 8 nm in comparison with *m*-phenylenediamine derivatives, possessing methyl substituents in *m*-, *p*-, both *m*- and *p*-positions, and in the central ring: 1,3-bis(3,3′-dimethyldiphenylamino)benzene (**2c**), 1,3-bis(4,4′-dimethyldiphenylamino)benzene (**2d**), 1,3-bis(4,4′-dimethyldiphenylamino)-4-methylbenzene (**2e**), 1,3-bis(3,3′,4,4′-tetramethyldiphenylamino)benzene (**2f**). In addition, n → π* transitions give a weak band at the long wavelength side of the second absorption in UV spectrum of **2b**, while strong bathochromic and hyperchromic effects of π → π* transitions are completely obscure this band in phenylenediamine derivatives **2c**–**f**. This shows that methyl groups at *o*-position restrict π-electron conjugation in the molecule. Obviously, the *o*-substituent hinders formation of the flat stereo structure and thus prevents π-electrons from joining a common system.

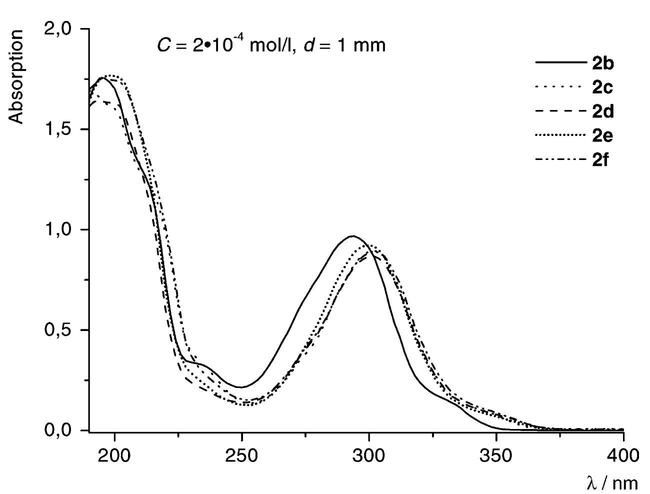


Fig. 2. Light absorption spectra of *N*,*N*,*N*′,*N*′-tetraarylphenylenediamine derivatives **2b**–**f**.

The selection of solely 1,3-phenylenediamine derivatives, possessing methyl substituents, for further investigations on hole-drift mobility was made after the results of differential scanning calorimetry analysis of *N*,*N*,*N*′,*N*′-tetraarylphenylenediamine derivatives obtained from 1,2-, 1,3- and 1,4-phenylenediamines. As was mentioned earlier [18], *m*-phenylenediamine derivatives are more plastic than *o*-, *p*-derivatives and namely due to these properties CTL of good homogeneity can be obtained from both in the mixture with polymeric binder and without it.

Fig. 3 shows the room temperature dependencies of hole-drift mobility on electric field in *N*,*N*,*N*′,*N*′-tetraarylphenylenediamines **1b**, **2b**–**f**. The values of hole-drift mobility μ and μ_0 found by extrapolation of the experimental dependencies to the values of electric field $E = 10^6$ and $0\,\mathrm{V\,cm^{-1}}$ are given in Table 1. The hole mobility values are dependent on the number of methyl substituents and their position in the TM. The highest mobility was observed in the compound **2e** containing methyl groups at the *para* positions of the side benzene rings and at the central ring. The lowest mobility was observed in the compound **2b** containing methyl groups in the *ortho* positions at the side benzene rings. In addition, there is no distinct difference on the results of drift mobility between *m*- and *p*-substituents. Thus, consistent patterns of the influence of drift mobility and photosensitivity reported early [18] are very similar, however mobility is influenced more by the central substituent.

According to the obtained hole mobility data and light absorption spectra, mobility of charge carrier increases with the increasing π-electron conjugation. Therefore, it can

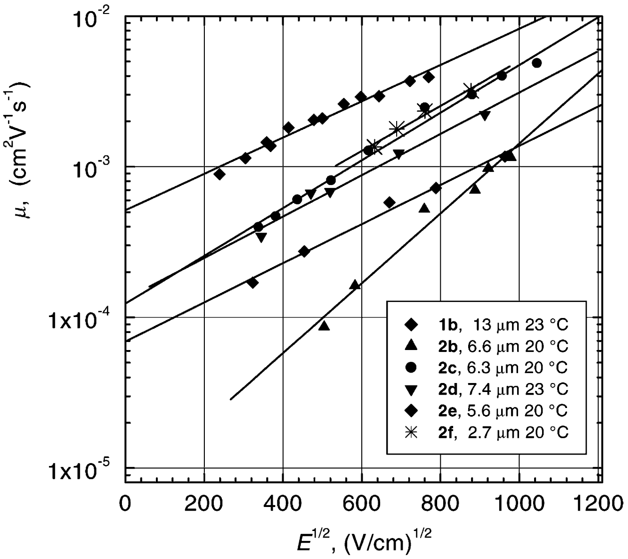


Fig. 3. The electric field dependencies of the hole-drift mobility in amorphous films of *N*,*N*,*N*′,*N*′-tetraarylphenylenediamine derivatives **1b**, **2b**–**f**.

Table 1
Quantum and charge carrier transportation parameters for *N*,*N*,*N*′,*N*′-tetraarylphenylenediamine derivatives **1a**,**b**, **2a**–**f**

Compound	I_p (eV)	$h\nu_\mathrm{min}$ (eV)	χ (eV)	μ (cm^2 V^{-1} s^{-1}), $E = 10^6$ V cm^{-1}	μ_0 (cm^2 V^{-1} s^{-1}), $E = 0$ V cm^{-1}
1a	5.34	3.33	∼2.0		
1b	5.17	3.32	∼1.85	1.4×10^{-3}	7.0×10^{-5}
2a	5.65	3.44	∼2.2		
2b	5.65	3.54	∼2.1	1.4×10^{-3}	8.0×10^{-6}
2c	5.58	3.43	∼2.15	4.6×10^{-3}	1.2×10^{-4}
2d	5.44	3.45	∼2.0	3.0×10^{-3}	1.3×10^{-4}
2e	5.53	3.41	∼2.1	8.0×10^{-3}	5.0×10^{-4}
2f	5.37	3.39	∼2.0	5.0×10^{-3}	1.5×10^{-4}

be concluded that *p*-phenylenediamine derivatives should be most suitable ones. In order to check this assumption, tetraarylated *p*-phenylenediamine derivative forming an amorphous state was synthesised. As the influence of *m*-substituents on the stability of amorphous state is the strongest [18], 1,4-bis(3,3′-dimethyldiphenylamino)benzene (**1b**) was prepared. As expected, layers of high quality were obtained from **1b** both in the mixture with polycarbonate (PC) and without polymeric binder. However, our assumption was proven to be wrong. Comparison of mobility of layers from tetraarylated phenylenediamine derivatives with methyl groups at *p*- and *m*-positions, and the new *p*-phenylenediamine derivative **1b** in the mixture with PC reveals that mobility of the latter compound is the lowest (Fig. 4). In addition, mobility of the layer from the neat substance is inferior to those obtained from *m*-phenylenediamine homologue (Fig. 3). Meanwhile, the priority of the *p*-substitution on the hole mobility was proved here.

In order to explain the results of hole mobilities of *N*,*N*,*N*′,*N*′-tetraarylphenylenediamines **1a**,**b**, **2a**–**f** ionisation potential was determinate from the curves of electron photo emission spectra in air and the electron affinity was calculated. The values of I_p and χ are presented in Table 1. From the data presented in Table 1 it can be stated that I_p **2d**, possessing methyl substituents at the *para* positions of the side benzene rings, is lower as compared to the **2b**,**c** containing the methyl groups at *ortho* or *meta* positions. Furthermore, the values of ionisation potential increase depending on the position of methyl substituents: $p\text{-} < m\text{-} < o\text{-}$. Addition of two methyl groups leads to further I_p value decrease down to 5.37 eV in the TM **2f**. Meanwhile, the ionisation potential of *p*-phenylenediamine derivative **1b** is considerably lower as compared to the last, which means better hole injection conditions as compared with the *m*-phenylenediamine based TM. The electron affinity for investigated TM, possessing the methyl substituents in different positions, is very similar, except for *p*-phenylenediamine derivative **1b**. The electron affinity is considerably lower (1.85 eV) as compared to the *m*-phenylenediamine derivatives **2b**–**f**. It is obvious from these dates, that charge carriers in *p*-phenylenediamine-based TM must be excited easier.

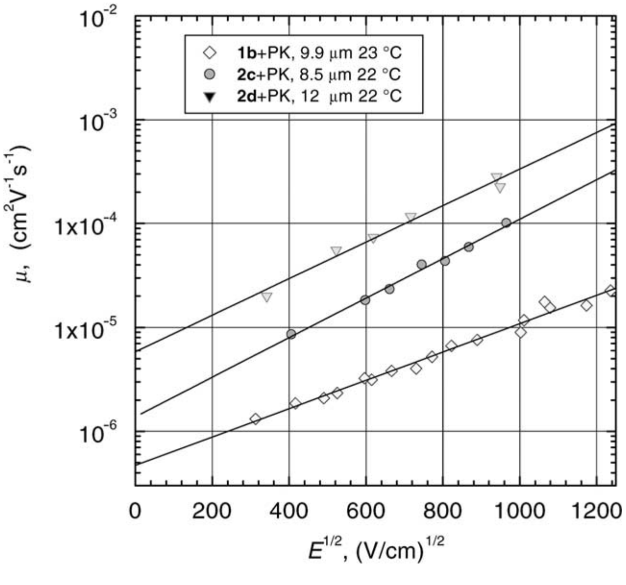


Fig. 4. The electric field dependencies of the hole-drift mobility in the CTL of *N*,*N*,*N*′,*N*′-tetraarylphenylenediamine derivatives **1b** and **2c**,**d** doped in polycarbonate Z (50 wt.%).

As was mentioned earlier, the hole-drift mobility of the layer from **1b** is inferior to those obtained from *m*-phenylenediamine homologues despite the lowest value of ionisation potential and electron affinity. Apparently, the total π-conjugation of TM molecule is not an obligatory precondition for effective charge transport in *N*,*N*,*N*′,*N*′-tetraarylphenylenediamine derivatives because of other unknown effects. It was noticed during recording of NMR spectra, that a molecule of compound **1b** gets oriented in strong magnetic field. It is, however, difficult to relate this fact to low mobility in this compound.

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