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Study on the influence of methyl groups and their location on properties of triphenylamino-based charge transporting hydrazones

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Abstract Methyl substituent effects on the HOMO and LUMO energy levels, and the ability to transport charge and form stable molecular glasses of 4-(diphenyl-amino)benzaldehyde phenylhydrazones were investigated. Thermal properties, HOMO and LUMO energy levels, and hole mobility values are dependent on the number of methyl substituents and their position in the investigated transporting materials. Surprisingly, however, the presence of methyl groups at any position negatively affects the hole drift mobility of the molecularly doped polymers containing those hydrazones.

Keywords Charge transport · Hydrazones · Ionization potential · Substituent effects

Introduction

Charge transport materials are employed in various fields such as electrophotography (photoreceptors of copying machines, laser printers and modern fax machines), displays (organic light emitting diodes), power generation (solar cells), memory devices (field effect transistors), etc. The first industrial scale application of organic semiconductors was xerography [1]. Of many technologies that led

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to the evolution of xerography, charge transport materials played a major role [2]. In recent years, several families of hole transporting materials have been increasingly studied [3]. High photosensitivity, good enough charge-transporting properties for technical applications, simple synthesis and low cost are the main advantages of aryl aldehyde hydrazones compared to other classes of charge transport materials [4]. Numerous investigations are being carried out aimed at enhancement of hole drift mobility; however, until now only a few concrete recommendations have been made with regard to molecular structure modification. Only limited data are available concerning the influence of alkyl substituents on the qualitative parameters of charge transporting layers (CTL). The importance of these groups can be seen while constructing the frame of an effective photoconductor using N,N,N',N'-tetraarylbenzidine derivatives [5]. In our previous paper [6] we reported on the thermal and photophysical properties of N,N,N',N'-tetraarylphenylenediamine derivatives. The introduction of methyl groups into the N-substituted phenyl moiety in all cases increases the photosensitivity and reduces the residual potential considerably. On the other hand, the presence of alkyl substituents enhances the stability of the glassy state of such π -electron-conjugated systems. In addition, the highest mobility was observed in transporting materials (TM) containing methyl groups at the para positions of the side benzene rings and at the central ring of these π -electron starburst molecules [7].

In this paper we present a study on the influence of methyl groups and their location on HOMO and LUMO energy levels, ability to transport charge and form stable molecular glasses in hydrazones bearing a triphenylamine moiety. The 4-(diphenylamino)benzaldehyde phenylhydrazones were chosen as they are among the most usable and effective organic hole transporting materials [4]. Methyl

S. Urnikaite \cdot M. Daskeviciene \cdot T. Malinauskas \cdot

groups were selected because of the commercial availability of the starting materials; moreover, there is a very slight difference between methyl and ethyl groups in regard to the charge transport ability [5].

Results and discussion

The synthesis of 4-(diphenylamino)benzaldehyde phenylhydrazones **1–6**, possessing different numbers and positions of methyl substituents, is shown in Scheme 1. The general synthetic procedure for all of these derivatives involves the well-known reaction of suitable aldehydes with the corresponding phenylhydrazines, followed by Nalkylation reaction with iodomethane in the presence of a base.

Formation of the glassy state was confirmed by differential scanning calorimetry (DSC) analysis. The melting points ($T_{\rm m}$) and glass transition temperatures ($T_{\rm g}$) of the investigated TMs are presented in Table 1.





Table 1 Thermal, photophysical and optical properties of 1-6

Typical DSC analysis curves of 2 are presented in Fig. 1. Melting temperatures, tendency to crystallize and formation of the glassy state are noticeably influenced by the position and amount of the methyl substituents. The synthesized charge transporting materials exhibit a relatively stable glassy state; they do not undergo crystallization after melting and subsequent cooling.

Introduction of the methyl group at the *p*-phenyl position of triphenylamine or N-phenylhydrazone fragments results in a 9 °C decrease in melting temperature in comparison with 1. This slight decrease can be attributed to a plasticizing effect of the aliphatic group. Glass transition temperatures, however, remain almost unchanged. Methyl groups at the o- or m-position affect the conformation of the molecule more substantially, thus increasing the number of conformers and changing the way of packing of the molecules. $T_{\rm m}$ of the hydrazone **3** decreases by 30 °C with respect to unsubstituted compound 1, and 4 is already an amorphous material. Glass transition temperatures are also affected somewhat more substantially, i.e., T_{g} decreases by ca. 3 and 11 °C for 3 and 4 accordingly. It is interesting to note that the presence of para substituents in both triphenylamine and N-phenylhydrazone fragments (6) increases $T_{\rm m}$ by ca. 8 °C compared with 2 and 5. Most likely the molecule of hydrazone 6 assumes a more planar conformation, thus allowing more tight packing of the molecules.

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 hole transporting hydrazones **1–6**. Comparison of electron absorption bands of 4-(diphenylamino)benzaldehyde phenylhydrazones **1–6**, possessing methyl substituents in different locations (Fig. 2), reveals that they are similar, except for 4-(diphenylamino)benzaldehyde *N*-methyl-*N*-(2-methylphenyl)hydrazone (**4**).

The latter acts somewhat unusually—the hypsochromic shift of its extinction maximum is by ca. 14 nm in comparison with other hydrazone derivatives. This indicates that the methyl group at *o*-position restricts π -electron

Compound	$T_{\rm m}$ (°C)	$T_{\rm g}$ (°C)	I _p (eV) (HOMO)	EA (eV) (LUMO)	$\begin{array}{l}S_0 - S_1\\ (\text{eV})\end{array}$	$\mu_0 \ (\mathrm{cm}^2 \ \mathrm{V}^{-1} \ \mathrm{s}^{-1})$	$\mu (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$	FL λ_{\max} (nm) ²
1	153	35	5.46	2.36	3.10	4.5×10^{-6}	1.2×10^{-4}	422
2	144	36	5.40	2.31	3.09	2.0×10^{-6}	3.8×10^{-5}	421
3	123	32	5.45	2.37	3.08	2.2×10^{-6}	4.0×10^{-5}	423
4	-	24	5.47	2.22	3.25	1.5×10^{-7}	5.0×10^{-6}	402
5	144	35	5.40	2.31	3.09	3.2×10^{-6}	6.0×10^{-5}	419
6	152	36	5.38	2.25	3.13	3.0×10^{-6}	6.0×10^{-5}	421

^a $\lambda_{ex} = 360$ nm (4), $\lambda_{ex} = 380$ nm (for the rest)



Fig. 1 DSC curves of 2 (heating rate 10 °C min⁻¹)



Fig. 2 Light absorption spectra of 1–6 in THF ($c = 10^{-4}$ M)

conjugation in this molecule. Obviously, the *o*-substituent hinders formation of the flat stereo structure and thus prevents π -electrons from joining a common system. In addition, a small bathochromic shift (4 nm) was observed for the hydrazone **6**, possessing two methyl groups in *p*-phenyl positions of both triphenylamine and *N*-phenylhydrazone fragments. This can be explained by σ - π conjugation and a consequent electron density delocalization [5]. On the other hand, this effect was not observed in the case of other hydrazones **2**, **3** and **5**.

It is known that materials used for optoelectronic devices have to meet certain HOMO and LUMO energy level requirements; therefore, it is important to measure these parameters. The ionization potential I_p (HOMO) was measured by the electron photoemission in air method, the HOMO–LUMO energy band gap ($S_0 - S_1$) was



Fig. 3 Estimation of HOMO–LUMO energy band gap (S_0-S_1) of compound 1 from intersection of normalized UV–Vis and fluorescence spectra

determined from intersection of normalized UV–Vis and fluorescence spectra (as shown in Fig. 3), and electron affinity (LUMO) values were calculated using Eq. 1. Estimated values are presented in Table 1.

$$LUMO = I_{p} - (S_{0} - S_{1})$$
(1)

From the data presented in Table 1 it can be stated that $I_{\rm p}$ of 2 and 5, possessing methyl substituents at the pphenyl positions of triphenylamine or N-phenylhydrazone fragments, is lower by ca. 0.06 eV as compared to the hydrazone 1. Addition of two methyl groups leads to a further $I_{\rm p}$ value decrease down to 5.38 eV in the TM 6, which means better hole injection conditions. Hydrazones 3 and 4, containing methyl groups at ortho or meta positions, do not demonstrate such behavior, and their ionization potentials are close to that of unsubstituted compound 1. Furthermore, the values of ionization potential change depend on the position of the methyl substituents: p - < m - < o. It is clear from this data that charge carriers in p-phenyl based TMs must be excited more easily. The LUMO levels follow pretty much the same pattern as $I_{\rm p}$ except for *ortho* substituted hydrazone 4. Its LUMO energy level is noticeably lower (2.22 eV) compared to derivatives 1-3. Obviously, the o-substituent significantly hinders formation of the flat stereo structure. The magnitudes of the HOMO-LUMO gap for 1-6correlate with the observed absorption and emission properties. Thus, the most blue-shifted compound 4 shows the highest HOMO-LUMO gap of 3.25 eV, and the most red-shifted **3** corresponds to a gap of 3.08 eV.

Low-molecular-weight TMs containing hydrazone moieties are usually crystalline materials not capable of

forming thin neat homogenous layers, and are used in combination with polymeric hosts in a mass proportion of 1:1 [2]. The hole drift mobilities of the molecular mixtures of the investigated hydrazones with polycarbonate-Z (PC-Z) were estimated by xerographic time of flight (XTOF) technique. XTOF measurements revealed that small charge transport transients are Gaussian with well-defined transit time on linear plots in all the investigated samples (Fig. 4). Figure 5 shows the room temperature dependencies of the hole drift mobility on the electric field in hydrazones **1–6**. The values of the hole drift mobility μ and μ_0 found by extrapolation of the experimental dependencies to the values of the electric field $E = 10^6$ V cm⁻¹ and E = 0 V cm⁻¹ accordingly are given in Table 1.

The hole mobility is dependent on the number of methyl substituents and their position in the TM. Higher mobility was observed in compounds 5 and 6 containing methyl groups at the *p*-phenyl position of the triphenylamine



Fig. 4 XTOF transients for 3 composition with PC-Z (1:1). *Insert* shows a typical transient curve in linear plot



Fig. 5 The electric field dependencies of the hole drift mobility in the CTL of hydrazones 1-6 doped in PC-Z (50 wt.%)

fragment. Interestingly, however, an additional methyl group in p-position of the hydrazone fragment (6) did not yield further positive effects. Slightly worse results were obtained when methyl substituents are located at the m- or p-positions of the hydrazone fragment (2, 3). And the lowest mobility was observed in compound 4 containing a methyl group in the ortho position. Surprisingly, however, the best results were observed in hydrazone 1 with no additional methyl groups. It is obvious that the total conjugation and HOMO, LUMO energy levels of the TM molecules are not an obligatory precondition for a more effective charge transport, because of other effects taking place in the charge transporting layer. One of the reasons could be less efficient arrangement of the molecules in the molecularly doped polymers. This, in turn, means larger distances between charge hopping sites and decreased mobility values.

In conclusion, we have presented a study on the influence of methyl groups and their location on HOMO and LUMO energy levels, the ability to transport charge and form stable molecular glasses in hydrazones bearing a triphenylamine moiety. The presence and position of the substituents influence melting temperature and, to a smaller extent, glass transition temperature. A methyl group at *o*-position of the hydrazone fragment alters the conformation of the molecule quite significantly in turn affecting thermal, optical and photophysical properties of the compound. Substituents located at *p*-position of the triphenylamine or hydrazone fragments effectively reduce the ionization potential. Surprisingly, however, the presence of methyl groups at any position negatively affects the hole drift mobility of the molecularly doped polymers containing those hydrazones.

Experimental

The ¹H NMR spectra were taken on a Varian Unity Inova (300 MHz) spectrometer. Elemental analyses (C, H, N) were conducted using the Elemental Analyser Exeter Analytical CE-440; their results were found to be in good agreement ($\pm 0.2\%$) with the calculated values. The UV spectra were recorded on a Spectronic Genesys 8 spectrometer in THF. A 10⁻⁴ M solution of the investigated TM and a microcell with an internal width of 1 mm were used. IR spectroscopy was performed on a Perkin Elmer Spectrum BX II FT-IR System using KBr pellets. Fluorescence emission and excitation spectra were recorded with a Hitachi MPF-4 luminescence spectrometer. Melting points were determined in capillary tubes using an Electrothermal MEL-TEMP capillary melting point apparatus. The course of the reactions was monitored by TLC on ALUGRAM® SIL/UV254 plates and development with UV light. Silica gel (grade 62, 60-200 mesh, 150 Å, Aldrich) was used for column chromatography.

Thermal properties for **1–6** were examined by using a Netzsch STA 409 PC Luxx apparatus under inert atmosphere. The samples were prepared by placing 5 mg of neat hydrazone derivative into an aluminum sample pan and crimping the upper lid to produce a hermetically sealed sample for DSC testing. The results were normalized on a per unit mass basis. During the first heating the melting points were measured. After melting, the samples were cooled with the same rate. The resulting glasses were heated again under the same conditions to measure the glass transition temperatures. A scan rate for all DSC cycles was 10 °C min⁻¹.

Samples for the charge carrier mobility measurements were prepared by casting the solutions of mixtures of investigated compounds with binder material PC-Z (Iupilon Z-200 from Mitsubishi Gas Chemical Co.) at a mass proportion of 1:1 in THF. The substrate was a polyester film with an Al layer. After coating, the samples were heated at 80 °C for 1 h. The thickness of the CTL varied in the range of 7-11 µm. The hole drift mobility was measured by XTOF technique [8]. Positive corona charging created an electric field inside the TM layer. The charge carriers were generated at the layer surface by illumination with pulses of a 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 the 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 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 and U_0 the surface potential at the moment of illumination.

Samples for the ionisation potential measurement were prepared by dissolving the TM in THF and coating on Al plates pre-coated with a ~0.5 μ m methylmethacrylate and methacrylic acid copolymer sub-layer. The thickness of the TM layers was 0.5–1 μ m. The ionization potential I_p was measured by the electron photoemission in air method, similar to the one used in [9] and described in [10].

All chemicals were purchased from Aldrich and used as received without further purification, except for 4-(*N*-(4-methylphenyl)-*N*-phenylamino)benzaldehyde, which was synthesized by the well-known Vilsmeier-Haack reaction [11].

General method for the preparation of arylaldehyde phenylhydrazones

To arylaldehyde (22 mmol) dissolved in 25 cm³ toluene the corresponding arylhydrazine (26 mmol) or arylhydrazine hydrochloride (53 mmol) dissolved in 50 cm³ methanol

was added. The mixture was refluxed until the arylaldehyde disappeared (TLC control). At the end of the reaction, the mixture was cooled to room temperature. The crystals formed upon standing were filtered off and washed with a mixture of ethyl acetate and *n*-hexane (1:1) to give the corresponding phenylhydrazone, which was subjected to the reaction with iodomethane without further purification.

General method for the preparation of hole transporting hydrazones **1–6**

Method A

A mixture of the corresponding arylaldehyde phenylhydrazone (22 mmol), benzyltriethylammonium chloride (2 mmol), iodomethane (132 mmol) and a catalytic amount of potassium iodide was stirred at room temperature in 36 cm³ toluene for 0.5 h. Then aqueous 50% KOH (154 mmol) was added, and the obtained mixture was refluxed until the starting arylaldehyde phenylhydrazone disappeared. After the termination of the reaction (TLC, acetone: n-hexane = 3:22), the reaction mixture was treated with toluene and washed with distilled H₂O. The organic layer was dried over anhydrous MgSO₄ and filtered. After removal of the solvent and excess of iodomethane, the residue was dissolved in toluene and allowed to stand at 5 °C for 12 h. The obtained crystals were filtered off and washed with 2-propanol. Compound 3 was purified by column chromatography (eluent: acetone: n-hexane = 2:23).

Method B

To a refluxing mixture of the corresponding arylaldehyde phenylhydrazone (22 mmol) and 80 cm³ iodomethane 85% powdered KOH (85 mmol) and anhydrous Na₂SO₄ (8 mmol) were added in three equal portions every 1 h. After the termination of the reaction (TLC, acetone: *n*-hexane = 1:4) the desired products were isolated by column chromatography according to the procedure described above.

4-(Diphenylamino)benzaldehyde

N-methyl-N-phenylhydrazone (1, C₂₆H₂₃N₃)

Synthesized according to Method A. The yield of **1** was 76%; m.p.: 156–157 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.65$ (d, J = 8.7 Hz, 2H, *p*-subst. Ph of triphenylamine), 7.54 (s, 1H, CH=N), 7.47–7.29 (m, 8H, Ar), 7.23–7.07 (m, 8H, Ar), 6.98 (t, J = 7.0 Hz, 1H, 4-H Ph), 3.47 (s, 3H, CH₃) ppm; IR (KBr): $\bar{\nu} = 3,057, 3,023$ (CH_{ar}), 2,930, 2,899, 2,813 (CH_{al}), 827, 756, 748, 727, 701, 696, 688 (CH=CH of mono- and 1,4-disubst. benzene) cm⁻¹.

4-(Diphenylamino)benzaldehyde

N-methyl-N-(4-methylphenyl)hydrazone (2 , $C_{27}H_{25}N_{3}$) Synthesized according to Method A. The yield of 2 was 70%; m.p.: 147–149 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.64$ (d, J = 8.7 Hz, 2H, *p*-subst. Ph of triphenylamine), 7.50 (s, 1H, CH=N), 7.39–7.04 (m, 16H, Ar), 3.44 (s, 3H, N-CH₃), 2.37 (s, 3H, CH₃) ppm; IR (KBr): $\bar{\nu} =$ 3,084, 3,058, 3,032 (CH_{ar}), 2,934, 2,902, 2,854, 2,813 (CH_{al}), 839, 833, 812, 752, 737, 694 (CH=CH of monoand 1,4-disubst. benzene) cm⁻¹.

4-(Diphenylamino)benzaldehyde

N-methyl-N-(3-methylphenyl)hydrazone ($\mathbf{3}$, $\mathbf{C}_{27}\mathbf{H}_{25}\mathbf{N}_{3}$)

Synthesized according to Method A. The yield of **3** was 59%; m.p.: 124–126 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.55$ (d, J = 8.6 Hz, 2H, *p*-subst. Ph of triphenylamine), 7.42 (s, 1H, CH=N), 7.27–6.92 (m, 15H, Ar), 6.73–6.69 (m, 1H, Ar), 3.35 (s, 3H, N–CH₃), 2.33 (s, 3H, CH₃) ppm; IR (KBr): $\bar{\nu} = 3,086, 3,062, 3,033$ (CH_ar), 2,993, 2,896, 2,811 (CH_al), 768, 748, 729, 694 (CH=CH of mono-and 1,4-disubst. benzene) cm⁻¹.

4-(Diphenylamino)benzaldehyde

N-methyl-N-(2-methylphenyl)hydrazone (**4**, $C_{27}H_{25}N_3$) Synthesized according to Method B. The yield of **4** was 43%; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.46$ (d, J = 8.6 Hz, 2H, *p*-subst. Ph of triphenylamine), 7.33–6.93 (m, 17H, Ar, CH=N), 3.29 (s, 3H, N-CH₃), 2.32 (s, 3H, CH₃) ppm; IR (KBr): $\bar{\nu} = 3,058,3,023$ (CH_{ar}), 2,924, 2,860 (CH_{al}), 825, 753, 722, 694 (CH=CH mono- and 1,2-, 1,4-disubst. benzene) cm⁻¹.

$\label{eq:2.1} \begin{array}{l} \textit{4-(N-(4-Methylphenyl)-N-phenylamino)benzaldehyde} \\ \textit{N-methyl-N-phenylhydrazone} \ (\textbf{5}, \ C_{27}H_{25}N_3) \end{array}$

Synthesized according to Method B. The yield of **5** was 79%; m.p.: 144–146 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.54$ (d, J = 8.7 Hz, 2H, *p*-subst. Ph of triphenylamine), 7.45 (s, 1H, CH=N), 7.38–7.18 (m, 6H, Ar), 7.18–6.94 (m, 9H, Ar), 6.88 (t, J = 7.0 Hz, 1H, 4-H Ph), 3.37 (s, 3H, N-CH₃), 2.31 (s, 3H, CH₃) ppm; IR (KBr): $\bar{\nu} = 3,061, 3,024$ (CH_{ar}), 2,921, 2,902, 2,813 (CH_{al}), 827, 820, 727, 716, 698, 689 (CH=CH mono- and 1,4-disubst. benzene) cm⁻¹.

4-(N-(4-Methylphenyl)-N-phenylamino)benzaldehyde

N-methyl-*N*-(4-methylphenyl)hydrazone (**6**, $C_{28}H_{27}N_3$) Synthesized according to Method B. The yield of **6** was 75%; m.p.: 155–157 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.54$ (d, J = 8.7 Hz, 2H, *p*-subst. Ph of triphenylamine), 7.40 (s, 1H, CH=N), 7.31–7.17 (m, 4H, Ar), 7.15–6.93 (m, 11H, Ar), 3.34 (s, 3H, N–CH₃), 2.31 (s, 3H, CH₃), 2.28 (s, 3H, CH₃) ppm; IR (KBr): $\bar{\nu} = 3,061,3,024$ (CH_{ar}), 2,915, 2,856, 2,810 (CH_{al}), 817, 797, 756, 732, 714, 696, 678 (CH=CH mono- and 1,4-disubst. benzene) cm⁻¹.

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