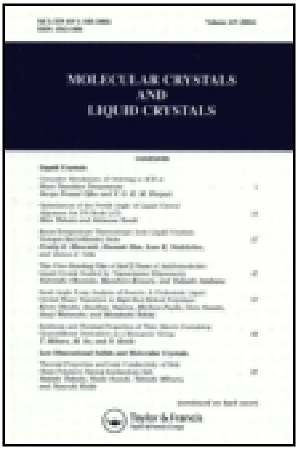

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Glass-Forming Hole-Transporting Triphenylamine-Based Hydrazones with Reactive Functional Groups

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Glass-Forming Hole-Transporting Triphenylamine-Based Hydrazones with Reactive Functional Groups

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Synthesis and the properties of a series of triphenylamine-based hydrazones are reported. The dependence of their thermal and glass-forming properties on their chemical structure is discussed. The ionization potentials of the synthesized hydrazones measured by the electron photoemission technique range from 5.16 to 5.32 eV. Hole-drift mobilities of some derivatives molecularly dispersed in bisphenol Z polycarbonate exceed 10^{-4} $cm^2V^{-1}s^{-1}$ *at high electric fields* (10^6 *V/cm), at room temperature.*

Keywords: Hole-drift mobility; Hydrazone; Ionization potential; Triphenylamine

INTRODUCTION

Aromatic hydrazones of the general formula $RCH{=}N{-}NR_2$, where R are aromatic, heteroaromatic, or aliphatic groups, are widely studied as organic hole-transport materials [1–3]. Hydrazones as well as aromatic amines, such as *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) [4] and 1,1-bis(di-4-tolylaminophenyl) cyclohexane (TAPC) [5], are widely used in electrophotography. Most of the modern organic electrophotographic photoreceptors have a

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dual-layer configuration. The main advantage of this configuration is the possibility of separate optimization of the two layers. The charge-generation layer usually consists of a dye such as titanyl phthalocyanine dispersed in a polymer binder [*e.g.*, poly(vinylbutyral)]. The charge transport layer is usually prepared by embedding an organic hole-transport material into a polymer matrix (*e.g.*, polycarbonate). A charge-transport layer has to contain a large amount (up to 50%) of the active material to ensure effective transport of holes. Introduction of such a large amount of low-molar-mass charge-transport compound into the polymer matrix can lead to crystallization. Morphological stability of charge-transported layers can be increased either by using charge-transport compounds that do not readily crystallize (molecular glasses) or using (photo)polymerizable or (photo)-cross-linkable charge-transport materials.

Triphenylamine-containing hydrazones described in the literature exhibit relatively high hole-drift mobilities [6]. Most of triphenylamine-based hydrazones reported contain only one hydrazine moiety per molecule. Such molecules are rather small, and their inclination to crystallize is rather high. In this work, we report on the properties of triphenylamine-based dihydrazones with the functional hydroxyl and epoxypropyl groups. When we designed these molecules, we expected that an increase of the molar mass of the triphenylamine-based hydrazones would reinforce the inclination of the molecules to form glasses and that the enlarged system of conjugated π-electrons would allow enhanced charge-carrier mobilities. The presence of reactive functional groups should make them useful in prepartion of polymeric or cross-linked charge-transport layers.

EXPERIMENTAL

Materials

The starting compounds 4-iodoanisole, triphenylamine, boron tribromide, *N*,*N*-diphenylhydrazine hydrochloride, *N*-methyl-*N*-phenylhydrazine, epichlorohydrin, and 4,4′-thiobisbenzenethiol were purchased from Sigma-Aldrich. 3-Bromomethyl-3-methyloxetane was bought from Chemada Fine Chemicals (Israel). All the starting compounds were used as received. All the required auxiliary chemicals [i.e., 18-crown-6, potassium carbonate, copper powder, phosphorus oxychloride, sodium sulphate, benzyltrimethylammonium chloride, magnesium sulphate, sodium hydride, and triethylamine (TEA)] were purchased from Aldrich. Organic solvents were purified and dried by standard methods [7]. Silica gel was used for column chromatography.

N-(4-Methoxyphenyl)-N-phenylbenzenamine (1)

Diphenylamine (10 g, 59 mmol), 4-iodoanisole (18.02 g, 77 mmol), powdered potassium carbonate (27.6 g, 200 mmol), copper powder (7.5 g, 118 mmol), and 18-crown-6 (0.56 g, 2.1 mmol) were refluxed in 50 ml of *o*-dichlorobenzene under nitrogen for 36 h. Copper and inorganic salts were filtered off. The solvent was removed by distillation. The product was crystallized from methanol, filtered, and dried. Yield: 13.42 g (83%) of $C_{19}H_{17}NO$ (mp: 104°C). FW = 275 g/mol. MS(APCI$^+$, 20 V), m/z (%): 276 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3053, 3003 (CH_{ar}), 2909 ($CH_{aliphatic}$), 1585, 1507, 1490 ($C{=}C_{ar}$), 1246 (C−O−C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.65 (s, 3H, $-OC\underline{H}_3$), 6.67–7.06 (m, 14H, $-C\underline{H}_{ar}$).

Di(4-formylphenyl)-4-methoxyphenylamine (2)

$POCl_3$ (10.11 ml, 110 mmol) was added dropwise to dry dimethylformamide (10.13 ml, 131 mmol) at 0°C under an N_2 atmosphere. Then the solution of *N*-(4-methoxyphenyl)-*N*-phenylbenzenamine (**1**) (3 g, 11 mmol) in 15 ml of *o*-dichlorobenzene was added stepwise to the reaction flask. The reaction mixture was stirred at 85°C until the starting compound was reacted. Then the reaction mixture was cooled down to the room temperature, poured into ice water, and neutralized with sodium acetate until pH = 6–8. The crude product was extracted with chloroform several times. The chloroform solution was washed with water, dried with anhydrous sodium sulphate, and filtered, and the solvent was removed. The product was purified by silica-gel column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 3:1. Yield: 2.41 g (67%) of $C_{21}H_{17}NO_3$ (FW = 331 g/mol). MS(APCI$^+$, 20 V), m/z (%): 332 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3062, 3008 (CH_{ar}), 2835 ($CH_{aliphatic}$), 1687 (CHO), 1583, 1561 ($C{=}C_{ar}$), 1247 (C−O−C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.70 (s, 3H, $-OC\underline{H}_3$), 6.77–7.17 (m, 8H, $-C\underline{H}_{ar}$), 7.80–7.84 (m, 4H, $-C\underline{H}_{ar}$), 9.66 (s, 2H, −CHO).

Di(4-formylphenyl)-4-hydroxyphenylamine (3)

Di(4-formylphenyl)-4-methoxyphenylamine(**2**) (2 g, 6 mmol) was dissolved in dry dichloromethane (45 ml) at room temperature and cooled to −80°C (acetone/dry ice). Then 30 ml of 1 M solution of boron tribromide (30 mmol) in dichloromethane was added slowly. The homogeneous mixture obtained was stirred at −80°C for 30 min and was then allowed to warm slowly to room temperature overnight. The reaction mixture was poured into water (200 ml), stirred for 30 min, and extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$, filtered, and concentrated under vacuum. The product was purified by silica-gel column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 4:1. Yield: 1.55 g (81%) of $C_{20}H_{15}NO_3$ (FW = 317 g/mol). MS(APCI$^+$, 20 V), m/z (%): 318 ($[M+H]^+$, 100). IR (in KBr) ν/cm^{-1}: 3279 (OH), 3065, 3030 (CH$_{ar}$), 2823 (CH$_{aliphatic}$), 1691 (CHO), 1585, 1504 (C=C$_{ar}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 4.95 (s, 1H, −OH), 6.95–7.30 (m, 8H, $-C\underline{H}_{ar}$), 7.76–7.80 (m, 4H, $-C\underline{H}_{ar}$), 9.88 (s, 2H, $-C\underline{H}O$).

Hydrazones **4** and **5** (1–2 g) were prepared by condensation of dialdehyde **3** and the derivatives of hydrazine by the following general procedure.

A solution of *N*, *N*-diphenylhydrazine hydrochloride (or *N*-methyl-*N*-phenylhydrazine) in methanol was added dropwise to a solution of di(4-formylphenyl)-4-hydroxyphenylamine (**3**) in methanol by stirring in a molar ratio of 2 mol of hydrazine to 1 mol of formyl group. The reaction mixture was refluxed for 1 h. Then it was cooled down to the room temperature. The product was purified by column chromatography (silica gel, eluent acetone–hexane, 1:2). The compound **5** was recrystallized from methanol. The compound **4** was isolated as amorphous powders after column chromatography.

Di((4-(diphenylamino)iminomethyl)phenyl)-4-hydroxyphenylamine (4)

Yield: 1.56 g (76%) of $C_{44}H_{35}N_5O$ (FW = 649 g/mol). MS(APCI$^+$, 20 V), m/z (%): 650 ($[M+H]^+$, 27). IR (in KBr) ν/cm^{-1}: 3424 (OH), 3060, 3033 (CH$_{ar}$), 2953, 2922 (CH$_{aliphatic}$), 1596 (C=N), 1506, 1493 (C=C$_{ar}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 4.94 (s, 1H, $-O\underline{H}$), 7.03–7.49 (m, 32H, aromatic protons and 2H, $Ph-C\underline{H}$=N-).

Di((4-(methylphenylamino)iminomethyl)phenyl)-4-hydroxyphenylamine (5)

Yield: 1 g (68%) of $C_{34}H_{31}N_5O$ (FW = 525 g/mol). MS(APCI$^+$, 20 V), m/z (%): 526 ($[M+H]^+$, 17). IR (in KBr) ν/cm^{-1}: 3320 (OH), 3065, 3023 (CH$_{ar}$), 2950, 2904, 2882 (CH$_{aliphatic}$), 1593 (C=N), 1536, 1493 (C=C$_{ar}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 3.40 (s, 6H, $-C\underline{H}_3$), 5.01 (s, 1H, −OH), 6.95–7.34 (m, 22H, aromatic protons and 2H, $Ph-C\underline{H}$=N−).

The synthesis of hydrazones bearing epoxy groups **6** and **7** was carried out according to the following general procedure.

The corresponding hydrazone (2 mmol), 20 ml of epichlorohydrin, and 0.02 g of benzyltrimethylammonium chloride were placed in a 100 ml, round-bottomed flask. The mixture was heated at 80°C for 2 h. The excess of epychlorohydrin was removed at reduced pressure, and the resin obtained was dissolved in CH_2Cl_2, washed several times with water, and dried over magnesium sulphate. The solvent was evaporated under vacuum, and the product was purified by silica-gel column chromatography (silica gel, eluent hexane–chloroform, 4:1), followed by recrystallization of compound **7** from methanol. Compound **6** was isolated as amorphous powder after column chromatography.

Di((4-(diphenylamino)iminomethyl)phenyl)-4-(2,3-epoxypropyl)oxyphenylamine (6)

Yield: 0.67 g (62%) of $C_{47}H_{39}N_5O_2$ (FW=705 g/mol). MS(APCI$^+$, 20 V), m/z (%): 706 ($[M+H]^+$, 66). IR (in KBr) ν/cm^{-1}: 3059, 3045 (CH_{ar}), 2967, 2825 ($CH_{aliphatic}$), 1599 (C=N), 1506, 1493 ($C{=}C_{ar}$), 1245 (C−O−C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 2.80 (dd, 1H, in oxirane ring), 2.82 (dd, 1H, in oxirane ring), 3.40 (m, 1H, $-OC\underline{H}-$), 3.97 (dd, 1H, ortho to $-OC\underline{H}_2-$), 4.00 (dd, 1H, para to $-OC\underline{H}_2-$), 6.90–7.54 (m, 32H, aromatic protons and 2H, $Ph-C\underline{H}{=}N-$).

Di((4-(methylphenylamino)iminomethyl)phenyl)-4-(2,3-epoxypropyl) Oxyphenylamine (7)

Yield: 0.5 g (43%) of $C_{37}H_{35}N_5O_2$ (FW = 581 g/mol). MS(APCI$^+$, 20 V), m/z (%): 582 ($[M+H]^+$, 84). IR (in KBr) ν/cm^{-1}: 3055, 3032 (CH_{ar}), 2950, 2904, 2882 ($CH_{aliphatic}$), 1600 (C=N), 1536, 1493 ($C{=}C_{ar}$), 1240 (C−O−C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 2.82 (dd, 1H, in oxirane ring), 2.90 (dd, 1H, in oxirane ring), 3.40 (m, 1H, $-OC\underline{H}-$), 3.51 (s, 3H, $-C\underline{H}_3$), 4.0 (dd, 1H, ortho to $-OC\underline{H}_2-$), 4.2 (dd, 1H, para to $-OC\underline{H}_2-$), 6.93–7.62 (m, 22H, aromatic protons and 2H, $Ph-C\underline{H}{=}N-$).

Di((4-(diphenylamino)iminomethyl)phenyl)-4-((3-methyloxetan-3-yl)methoxy) Phenylamine (8)

Compound **4** (0.2 g, 0.3 mmol) was dissolved in 10 ml of ethylmethylketone, and 3-bromomethyl-3-methyloxetane (5 ml) was added dropwise. After adding of 0.09 g (3.6 mmol) of NaH, the reaction was carried out at 60°C for 2 h. The excess of 3-bromomethyl-3-methyloxetane was removed at reduced pressure, and the resin obtained was dissolved in ethyl acetate, washed several times with water, and dried over magnesium sulphate. The solvent was evaporated under vacuum, and the product was purified by silica-gel column chromatography using an eluent mixture of hexane and acetone in a volume ratio of 3:1. Yield: 0.17 g (73%) of $C_{49}H_{43}N_5O_2$ (FW = 733 g/mol). MS(APCI$^+$, 20 V), m/z (%): 734 ($[M+H]^+$, 56). IR (in KBr) ν/cm^{-1}: 3049, 3033 (CH_{ar}), 2977, 2845, 2840 ($CH_{aliphatic}$), 1583 (C=N), 1500, 1495 ($C{=}C_{ar}$), 1243 (C−O−C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.49 (s, 3H, $-C\underline{H}_3$), 4.06 (s, 2H, $-OC\underline{H}_2$), 4.50 (ds, 2H, in oxetane ring), 4.68 (ds, 2H, in oxetane ring), 6.91–7.50 (m, 32H, aromatic protons and 2H, Ph$-$C$\underline{\text{H}}$=N$-$).

Di(4-(4-(di((4-(diphenylamino)iminomethyl)phenyl)amino)-phenyl)oxy-2-hydroxypropylthio)phenylsulfide (9)

Compound **6** (0.5 g, 0.77 mmol) and 0.1 g (0.38 mmol) of 4,4′-thiobisbenzenethiol were dissolved in 10 ml of ethylmethylketone. The reaction was catalyzed by adding of 0.2 ml of TEA at 80°C. After 24 h, the reaction was terminated by precipitation into methanol. The precipitated product was filtered off and purified by silica-gel column chromatography using an eluent mixture of hexane and chloroform in a volume ratio of 1:2. Yield: 0.41 g (64%) of $C_{106}H_{88}N_{10}O_4S_3$. IR (in KBr), ν/cm^{-1}: 3426 (OH), 3065, 3034 ($CH_{ar.}$), 2923, 2882, 2867 ($CH_{aliphatic}$), 1586 (C=N), 1593, 1512, 1482 (C=$C_{ar.}$). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 2.69–2.85 (m, 2H, $-CH_2-C\underline{H}-CH_2-$), 3.30 (m, 4H, $-SC\underline{H_2}$), 4.07 (s, 4H, $-OC\underline{H_2}$), 4.14 (s, 2H, $-\underline{OH}$), 6.84–7.52 (m, 72H, aromatic protons and 4H, Ph$-$C$\underline{\text{H}}$=N$-$).

Measurements

^{1}H NMR spectra of deuterated chloroform solutions were taken on a Gemini-2000 [300-MHz (^{1}H)] spectrometer. IR spectra were recordered using a Perkin-Elmer FT-IR system. The spectra of solid compounds were performed in a form of KBr pellets. Electron-impact mass spectra were obtained on a Waters 2Q 2000. The UV spectra were recorded on a Spectronic Genesys^{TM} 8 spectrometer. A 10^{-5} M solution of an investigated compound in THF was placed into a microcell with an internal width of 1 mm.

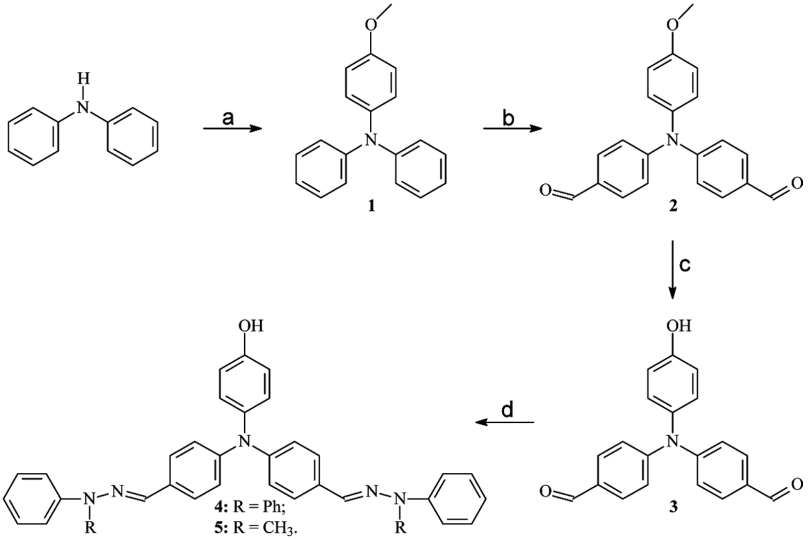
Differential scanning calorimetry (DSC) measurements were carried out with a Mettler DSC-821e at 10°C min^{-1} heating rate under a nitrogen atmosphere. The glass-transition temperatures (T_g) were determined from second heating scans. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA 851e at a 10°C min^{-1} heating rate under a nitrogen atmosphere.

The ionization potentials (I_p) of the films of the synthesized compounds were measured by electron photoemission in the air method as described before [8,9]. The standard error in the mean to 95% confidence for the values of ionization potential was 0.04 eV.

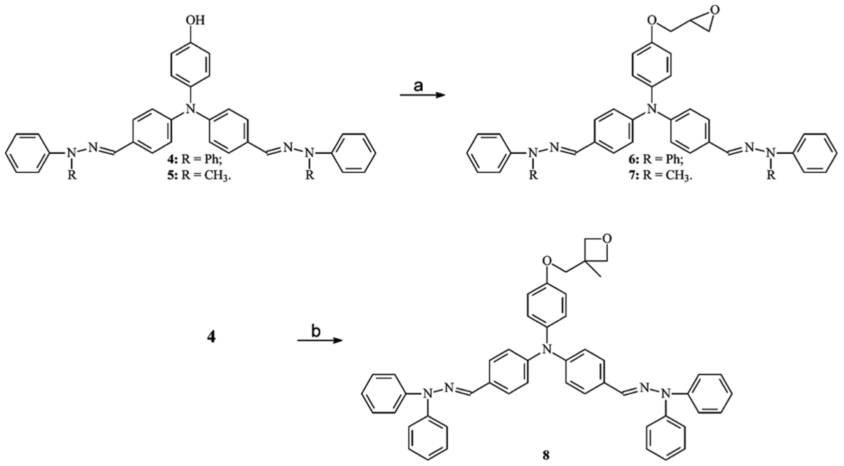
Hole-drift mobilities were measured by the xerographic time of flight (XTOF) technique [10,11]. Positive corona charging created an electric field inside the charge transport layer. Charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1–5% of the initial potential before illumination. The capacitance probe that was connected to the wide-frequency-band electrometer measured the rate of the surface potential decrease, dU/dt. The transit time t_t was determined by the kink on the transient curve in a linear 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 is the surface potential at the moment of illumination. The samples for the measurements were prepared by casting the solutions of the molecular mixtures of the synthesized compounds with bispenol Z polycarbonate at mass proportion 1:1 or 1:1.6 in THF. The substrates were polyester films with an Al layer.

RESULTS AND DISCUSSION

Compounds **4** and **5** were prepared as described in Scheme 1 by a multistep synthetic route involving Ullmann coupling of diphenylamine with 4-iodoanisole, Vilsmeyer formylation of *N*-(4-methoxyphenyl)-*N*-phenylbenzenamine **1** with $POCl_3$/DMF complex, demethylation of methoxy group of diformyl compound **2**, and condensation of compound **3** with differently substituted hydrazines.



SCHEME 1 Reagents and conditions: (a) 4-iodoanisole, Cu, 18-crown-6, K_2CO_3, *o*-dichlorobenzene, reflux, 36 h; (b) $POCl_3$/DMF complex, *o*-dichlorobenzene, 85°C, 24 h; (c) BBr_3, CH_2Cl_2, 24 h; (d) methanol, *N,N*-diphenylhydrazine hydrochloride for **4** and *N*-methyl-*N*-phenylhydrazine for **5**, reflux, 1 h.



SCHEME 2 Reagents and conditions: (a) benzyltrimethylammonium chloride, epichlorohydrine for **6** and **7**, 80°C, 2 h; (b) 3-bromomethyl-3-methyloxetane, NaH, ethylmethylketone, 60°C, 2 h.

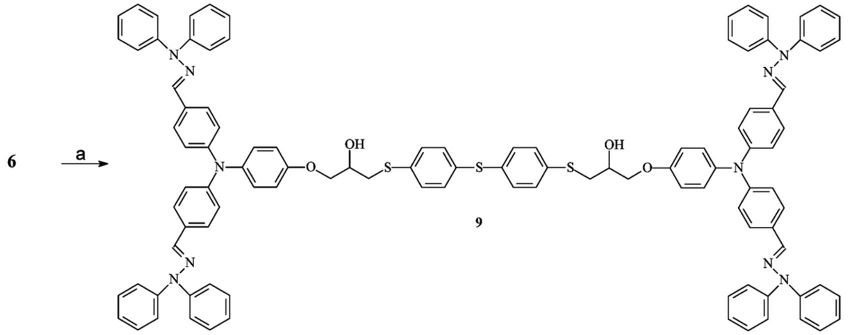
Hydrazones containing reactive epoxy groups (**6–8**) were synthesized by alkylation of the corresponding hydroxyl substituted hydrazones (**4**,**5**) with epychlorohydrin. Hydrazone with reactive oxetanyl group was prepared by alkylation of compound **4** with 3-bromomethyl-3-methyloxetane in the presence of NaH (Scheme 2).

With the purpose of demonstrating how the reactive functional groups can be employed in further synthesis, we have synthesized the twin-like molecule **9**. The increase of molecular size and especially the presence of hydroxyl groups capable of hydrogen bonding can improve morphological stability of molecular glasses [2,3]. Compound **9** was synthesized by the condensation of hydrazone **6** with 4,4′-thiobisbenzenethiol in the presence of TEA as a catalyst (Scheme 3).

The structures of the newly synthesized triphenylamine-based hydrazones were confirmed by IR, ^{1}H NMR, and mass spectrometries.

The synthesized compound can be used for the preparation of cross-linked charge-transport layers. Compound **9** can be cross-linked with polyisocianates as cross-linking agents, as was reporterd earlier for similar systems [12]. Both monomers **6–8** and compound **9** can also be incorporated into a polymer network by the methods used for hardening epoxy resins.

Thermal properties of the triphenylamine-based dihydrazones were examined by DSC and TGA under a nitrogen atmosphere. The triphenylamine-based hydrazones having diphenyl substituents at



SCHEME 3 Reagents and conditions: (a) 4,4′-thiobisbenzenethiol, TEA, ethylmethylketone, 60°C, 24 h.

the hydrazine N atom (**4**, **6**, **8**, and **9**) were obtained as amorphous substances as confirmed by DSC. When the samples of **4**, **6**, **8**, and **9** were heated, the glass transitions were observed in range 64–109°C, and no peaks due to crystallization and melting appeared. Cooling down and repeated heating revealed only the glass transitions again. The methylphenyl-substituted hydrazones **5** and **7**, which were isolated as crystalline compounds, show melting only in the first DSC heating scan and form glasses upon cooling from the melt. The second heating scan reveals only glass transition at 87°C for **5** and 65°C for **7** and no signals due to crystallization and melting. DSC curves of compound **5** are given in Fig. 1 for an illustration.

The glass-transition temperatures (T_g), melting temperatures (T_m), and temperatures at which initial loss of mass (5%) was observed (T_{ID}) are summarized in Table 1. Hydrazones having hydroxyl groups (**4**,**5**) show T_g by more than 20°C higher than the corresponding alkylated derivatives (**6–8**). This observation can hardly by explained by introduction of short alkyl chains and epoxide or oxetane cycles into the molecules of **6–8**. Apparently, hydrogen bonding predetermines higher T_g of compounds **4** and **5**. Compound **9** shows the highest T_g among the compounds synthesized. This observation can also by explained by hydrogen bonding as well by increased molecular size. The comparison of the values of T_g of *N*,*N*-diphenyl-substituted hydrazones (**4**, **6**) and *N*-methyl-*N*-phenyl-substituted hydrazones (**5**, **7**) shows that the T_g values of the former compounds are higher only by 2°C than those of the later derivatives.

The data presented in Table 1 show that the thermal stability of the synthesized hydrazones is comparable with that of other aromatic hydrazones reported earlier [13]. A 5% mass loss for compounds **4**, **6**,

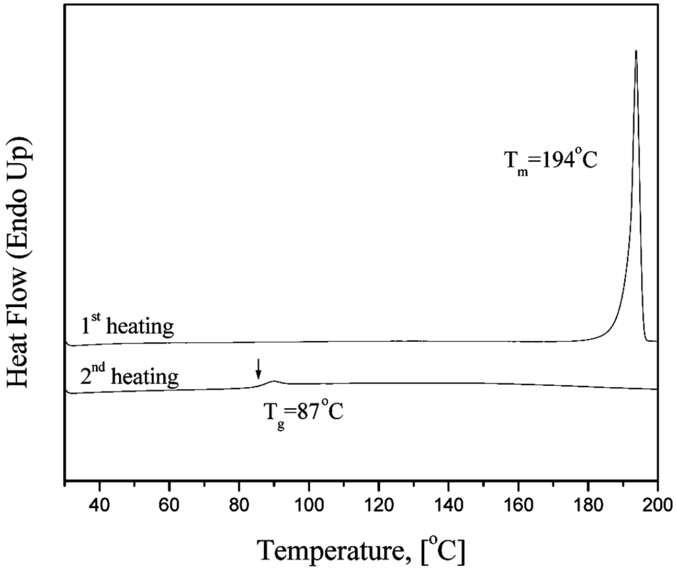


FIGURE 1 DSC curves of dihydrazone **5**, at the heating/cooling rate of 10°C/min, N_2 atmosphere.

and **8**, having diphenyl-substituted hydrazine nitrogen atoms, is observed at 255°C, whereas compounds **5** and **7**, containing methylphenyl-substituted nitrogen atoms, show a corresponding mass loss at 292°C. It is evident that the substituents at the hydrazine N atom affect the 5% mass loss temperature and consequently the thermal stability of the synthesized compounds. This observation corroborates the earlier observation that the thermal degradation of aromatic hydrazones starts from the degradation of the hydrazone moiety [13]. The nature

TABLE 1 Thermal Characteristics of the Triphenylamine-Based Dihydrazones

Compound	T_g(°C)	T_m(°C)	T_{ID}(°C)
4	89	—[a]	255
5	87	194[b]	292
6	67	—[a]	255
7	65	162[b]	292
8	64	—[a]	255
9	109	—[a]	265

[a] Obtained as an amorphous material.
[b] First heating only.

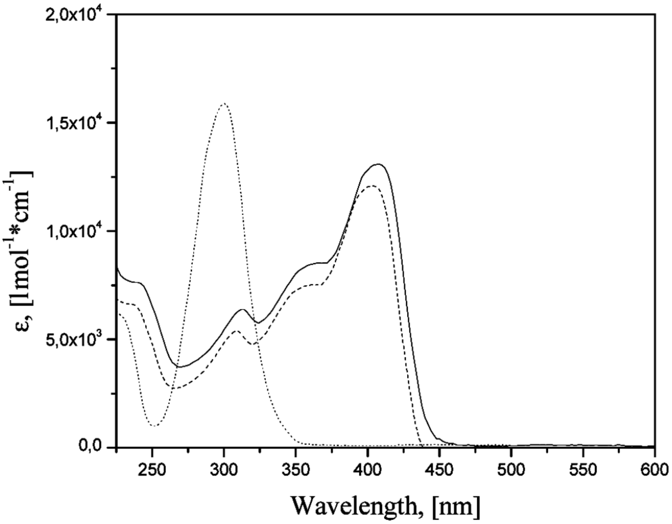


FIGURE 2 UV-vis absorption spectra of dilute THF solutions (10^{-5} mol l^{-1}) of **4** (solid line), **5** (dashed line), and triphenylamine (dotted line).

of the substituents at the phenyl group of the tripenylamine moiety seems not to have influence on the thermal stability of the materials. The 5% mass-loss temperatures for hydroxyl-, epoxypropyl-, and oxetanyl-substituted derivatives **4**, **6**, and **8** is the same (*i.e.*, 255°C).

The synthesized hydrazones absorb electromagnetic radiation in the 240 to 450-nm region. The absorption spectra of all compounds **4–9** are similar, due to their similar structure. As an example, the UV-vis absorption spectra of hydrazones **4** and **5** are shown in Fig. 2. For comparison, the spectrum of triphenylamine is given. The spectra of the hydrazones **4** and **5** exhibit a strong bathochromic shift with respect to the spectrum of triphenylamine. This shows that the π-electron conjugation system in compounds **4** and **5** is extended. Moreover, UV spectra of diphenyl-substituted hydrazones exhibit higher values of molar extinction coefficient and small bathochromic shifts with respect of the spectra of methylphenyl-substituted hydrazones.

The fluorescence emission spectra of dilute THF solutions of compounds **4** and **5** are shown in Fig. 3. The bands of fluorescence spectra of hydrazones are shifted toward the long wavelength region in comparison with those of triphenylamine. The emission from diphenyl-substituted hydrazones is bathochromically shifted relative to that from methylphenyl-substituted hydrazones. This observation is consistent with the UV spectroscopy data.

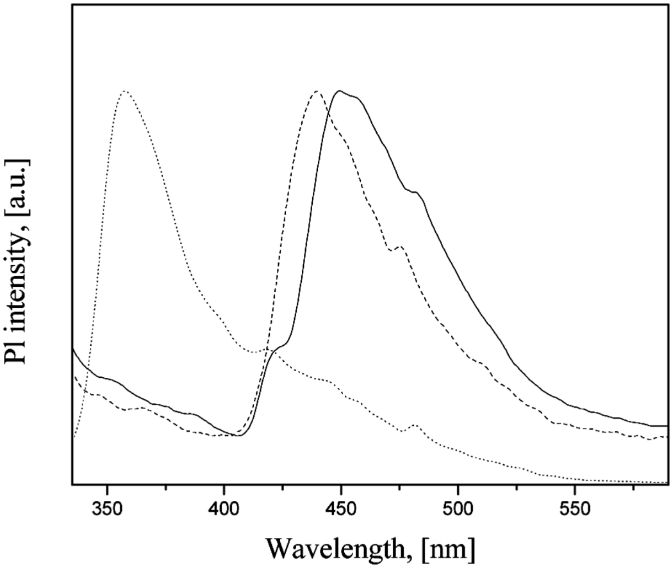


FIGURE 3 Normalized fluorescence spectra of dilute THF solutions (10^{-5} mol l^{-1}) of hydrazones **4** (solid line), **5** (dashed line), and triphenylamine (dotted line). For **4** and **5** $\lambda_{max} = 310$ nm; for triphenylamine $\lambda_{max} = 290$ nm.

The red shift of UV-Vis absorption and fluorescence spectra can be interpreted as the extended conjugation of π-electrons. Therefore, the new derivatives should show lower values of ionization potential (I_p) than that of triphenylamine derivatives.

The newly synthesized triphenylamine-based hydrazones are soluble in common organic solvents such as chloroform, acetone, and tetrahydrofuran. Amorphous thin films on the substrate can be prepared by casting or spin-coating techniques from all hydrazones reported in this presentation. The stabilities of the films with thicknesses of 0.5 to 1 μm were fully sufficient for ionization potential (I_p) measurements. Figure 4 shows electron photoemission spectra of the amorphous films of compounds **4–9**. The intersection point of the straight lines drown with the absciss axis gives the values of the ionization potential, which are summarized in Table 2. The I_p values of the synthesized hydrazones are more than 0.3 eV lower than those of 4-methyltriphenylamine, which was reported to be 5.64 eV [14].

The typical time-of-flight transients for the molecular mixtures of the synthesized hydrazones with bisphenol Z polycarbonate (PC-Z) are presented in Fig. 5. Nondispersive hole transport is characteristic of most of the investigated molecular mixtures. The transit time t_t was

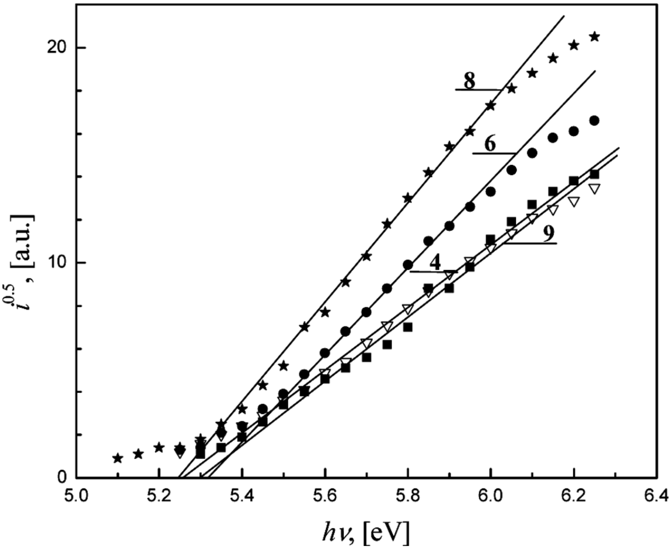


FIGURE 4 Electron photoemission spectra in air of the films of hydrazones **4–9**.

obtained from time-of-flight transients in a linear plot from straight signal decay moment. It was impossible to obtain transit time of PC-Z doped with **4** because of the higher dark conductivity; however, the observed signals suggested the fast hole transfer.

The room-temperature electric field dependencies of hole-drift mobility (μ) values for the solid solutions of the synthesized hydrazones in PC-Z are given in Fig. 6. The linear dependencies of the hole-drift mobilities on the square root of the electric field E are observed. In all the cases, drift mobility may be well approximated by the formula $\mu = \mu_0 \exp(\alpha\sqrt{E})$; here α; is Pool–Frenkel parameter [1].

Such dependencies of charge mobility on electrical fields are characteristic of many organic photoconductors and are predicted

TABLE 2 Ionization Potentials of the Films of the Triphenylamine-Based Dihydrazones

Compound	I_p (eV)
4	5.26
5	5.16
6	5.32
7	5.30
8	5.25
9	5.30

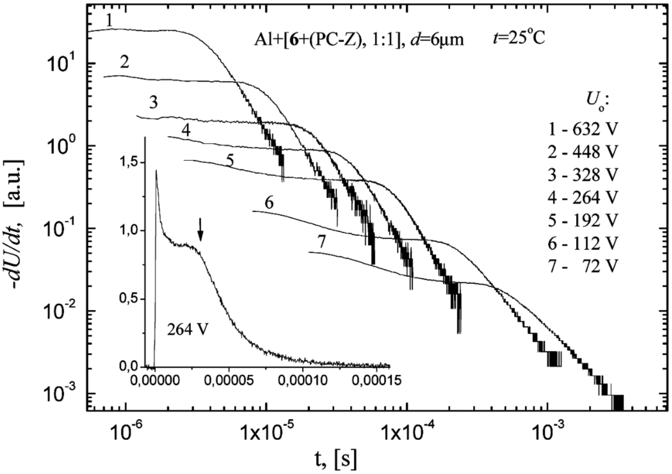


FIGURE 5 Typical time-of-flight transients for $\mathbf{6} + \text{PC-Z}$ at various surface potentials U_0. The arrow marks transit time t_t.

by the Bässler–Borsenberger model [1]. The solid solutions of triphenylamine-based hydrazones **5–9** in PC-Z (mass proportion 1:1.6 or 1:1) demonstrated hole-drift mobility values in a range from $1.8{\cdot}10^{-5}$ to $1.1{\cdot}10^{-4}\,\text{cm}^2/\text{Vs}$ at electric field $E = 6.4 \times 10^4\,\text{V/cm}$, at

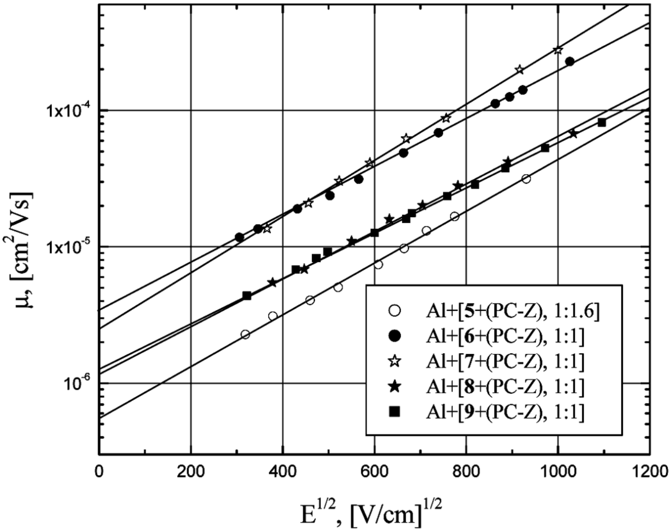


FIGURE 6 Electric field dependencies of the hole-drift mobilities (μ) for charge transport layers of compounds **5–9** doped in PC-Z (mass proportion 1:1.6 or 1:1).

TABLE 3 Hole-Mobility Data for Charge Transport Layers of Compounds **5–9** Doped in PC-Z

Composition	d (μm)	$\mu_0{}^*$ (cm^2/Vs)	μ^{**} (cm^2/Vs)	α (cm/V)$^{1/2}$
Al + [**5** + (PC-Z), 1:1.6]	12	$6 \cdot 10^{-7}$	$1.8 \cdot 10^{-5}$	0.0043
Al + [**6** + (PC-Z), 1:1]	6	$3.2 \cdot 10^{-6}$	$8.6 \cdot 10^{-5}$	0.0041
Al + [**7** + (PC-Z), 1:1]	10	$2.4 \cdot 10^{-6}$	$1.1 \cdot 10^{-4}$	0.0048
Al + [**8** + (PC-Z), 1:1]	7	$1.3 \cdot 10^{-6}$	$2.9 \cdot 10^{-5}$	0.0039
Al + [**9** + (PC-Z), 1:1]	5	$1.4 \cdot 10^{-6}$	$2.7 \cdot 10^{-5}$	0.0038

$\mu_0{}^*$: zero field mobility.
μ^{**}: hole-drift mobility values at electric field $E = 6.4 \cdot 10^4$ V/cm.

room temperature (Table 3). These are high charge mobilities, as for molecularly doped polymers.

In conclusion, new glass-forming triphenylamine-based hydrazones with reactive functional groups were synthesized and investigated as potential charge-transport materials for optoelectronics. The thermal, optical, and photoelectrical properties of the synthesized compounds were studied. The synthesized triphenylamine-based hydrazones form glasses with the glass-transition temperatures in the range of 64–109°C as characterized by DSC. The electron photoemission spectra of the synthesized compounds have been recorded, and the ionization potentials of 5.16–5.32 eV have been determined. Room-temperature hole-drift mobilities of some synthesized hydrazones molecularly dispersed in bisphenol Z polycarbonate exceed 10^{-4} cm^2 V^{-1} s^{-1} at high electric fields (10^6 V/cm). The synthesis and properties of polymeric materials based on the newly synthesized monomers will be included in a future publication.

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