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# 9-Phenylcarbazole-Based Hydrazone Twin Compounds as P-Type Organic Semiconductors

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# 9-Phenylcarbazole–Based Hydrazone Twin Compounds as P-Type Organic Semiconductors

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*Hole transporting glass-forming low-molar-mass hydrazones containing 9-phenylcarbazole moiety were synthesized and characterized by NMR-, infrared- and mass spectrometries. The thermal, optical and photoelectrical properties of the synthesized compounds are reported. Compounds containing 1,3-benzendithiol linking bridge were isolated as amorphous materials therefore differential scanning calorimetry experiments revealed glass transitions approximately at 60°C. The ionization potentials of the synthesized compounds were measured by electron photoemission technique in air range from 5.23 eV to 5.4 eV. Hole drift mobilities in the films of the solid solutions of some of the synthesized hydrazones in bisphenol Z polycarbonate measured by the time-of-flight technique exceed $10^{-5}$ $cm^2$ $V^{-1}$ $s^{-1}$ at high electric fields.*

**Keywords** Carbazole; glass transition; hole transport; hydrazone

## Introduction

Aromatic hydrazones which are usually prepared by condensation of formyl derivatives with aromatic hydrazines, are widely studied and used as organic hole transport materials for electrophotographic photoreceptors [1,3]. Among hole-transporting hydrazones carbazole-containing derivatives prevail [4,5]. Carbazole is a relatively cheap commercial compound widely used for the synthesis of electroactive compounds [6]. Most of the modern organic electrophotographic photoreceptors have a dual-layer configuration. A charge generation layer usually consists of a dye such as titanyl phthalocyanine dispersed in a polymer binder, *e.g.*, poly(vinylbutyral). A charge transport layer is usually prepared by inbeding an organic hole transport material into a host polymer, *e.g.*, polycarbonate. This layer has to contain a large amount (50% or even more) of the active material to ensure effective charge transport. Introduction of such a large amount of low-molar-mass charge transport compound into a polymer matrix can lead to crystallization. To prevent this problem

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charge transporting compounds which do not readily crystallize are required. Increasing of molecular size is one of the methods of preventing crystallization. In this article we report on the synthesis and properties of 9-phenylcarbazole-based twin hydrazones which are stable in a solid amorphous state and can be used for the preparation of electrophotographic photoreceptors with enhanced morphological stability.

## Experimental

### *Materials*

Carbazole was purchased from "Reakhim" (Russia). 1-Bromo-4-butylbenzene, iodobenzene, epichlorohydrin, N-phenylhydrazine, 4,4′-thiobisbenzenethiol, 1,3-benzenedithiol, phosphorous oxychloride were purchased from "Aldrich" and used as received.

*9-(4-Butylphenyl) carbazole-3-carbaldehyde (2a).* 7 g (0.023 mol) of 9-(4-butylphenyl)-carbazole (was prepared according the procedure described in [7]) (**1a**) were dissolved in DMF and cooled to 0°C. Then 11 ml (0.117 mol) of $POCl_3$ were added dropwise under stirring ($N_2$ atmosphere). The reaction mixture was stirred at 80–85°C for 72 h, and then poured into the beaker with crushed ice and neutralized with solution of sodium hydroxide. The obtained precipitate was washed using the surplus of water. The crude product after drying was purified by silica gel column chromatography (ethyl acetate/n-hexane = 1:3) to yield 5.85 g (78%) of brownish crystalline material (m.p.: 95°C, FW = 327 g/mol). A $^1$H NMR spectrum yielded the following chemical shifts (100 MHz, $CDCl_3$, $\delta$, ppm): 10.19 (s, 1H, CHO), 8.95 (d, 1H, 4-$H_{Ht}$), 8.08 (d, 1H, 5-$H_{Ht}$), 8.0 (d, 1H, 2-$H_{Ht}$), 7.37–7.61 (m, 8H, Ar, Ht), 2.8 (t, 2H, $J = 6.5$ Hz, $PhCH_2$), 1.23–1.9 (m, 4H, $CH_3\underline{CH_2}\underline{CH_2}$), 0.99 (t, 3H, $J = 6.75$ Hz, $CH_3CH_2$-). An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (aliphatic CH) 2940, 2830; $\nu$ (aldehydic CH) 2720; $\nu$ (C=O) 1650; $\nu$ (C=C in Ar) 1600, 1580; $\nu$ (C−N) 1250, 1160; $\gamma$ (arene C−H) 780. MS (APCI$^+$, 20 V), m/z: 328 ($[M + H]^+$).

*9-Phenylcarbazole-3-carbaldehyde (2b).* was synthesized by Vilsmeier reaction using $POCl_3$/DMF complex under nitrogen atmosphere. 7 g (0.029 mol) of 9-phenylcarbazole were dissolved in DMF and cooled to 0°C. Then 10.6 ml (0.116 mol) of $POCl_3$ were added dropwise under stirring ($N_2$ atmosphere). The reaction mixture was stirred at 85°C for 72 h, then poured into the ice water and neutralized with aqueous solution of sodium hydroxide (30%). The crude product was filtered and washed with the surplus of water. The crude product was purified by silicagel column chromatography (eluent: ethylacetate-n-hexane, 1:6). Yield of yellowish crystals 5.6 g (70%, m.p.: 108–109°C). A $^1$H NMR spectrum yielded the following chemical shifts (100 MHz, $CDCl_3$, $\delta$, ppm): 10.12 (s, 1H, CHO), 8.65 (s, 1H, 4-$H_{Ht}$), 8.20 (d, 1H, 5-$H_{Ht}$), 7.30–7.75 (m, 9H, Ar, Ht), 7.93 (d, 1H, 2-$H_{Ht}$). An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (arene C−H) 3052; $\nu$ (C=O) 1700; $\nu$ (C=C in Ar) 1600, 1500; $\nu$ (C−N) 1280, $\gamma$ (arene C−H) 744.

*9-(4-Butylphenyl) carbazole-3-carbaldehyde N-phenylhydrazone (3a).* 8.82 g (0.027 mol) of 9-(4-butylphenyl) carbazole-3-carbaldehyde was dissolved in 200 ml

of methanol under mild heating. The solution of 4.38 g (0.04 mol) N-phenylhydrazine in methanol was added to the cooled reaction mixture. 9-(4-Butyl phenyl) carbazole-3-carbaldehyde reacted completely after 4 hours at room temperature. The precipitated product was filtered and washed with a big amount of cold methanol. After the drying it was obtained 9.19 g (81%) of yellowish crystals (m.p.: 120–122°C, FW = 417 g/mol). An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (NH) 3331; $\nu$ (arene C−H) 3030; $\nu$ (aliphatic CH) 2927, 2860; $\nu$ (C=C in Ar) 1600, 1514; $\nu$ (C−N) 1257, 1228; $\gamma$ (arene C−H) 745. MS ($APCI^+$, 20 V), m/z: 418 ($[M+H]^+$), 326.

*9-Phenylcarbazole-3-carbaldehyde N-phenylhydrazone (3b).* 4 g (0.0147 mol) of 9-phenylcarbazole-3-carbaldehyde were dissolved in 300 ml of methanol under mild heating. The solution of 2.5 g (0.023 mol) *N*-phenylhydrazine in methanol was added to the cooled reaction mixture. Starting compound 9-phenylcarbazole-3-carbaldehyde was reacted completely after 3 hours at room temperature. The reaction mixture was concentrated and then the flask was placed to the freezer for crystallization. The product was filtered, washed with a large amount of cold methanol and dried. Yield of yellowish crystals 3.62 g (68%) (m.p.: 84–88°C, FW = 361 g/mol). An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (NH) 3308; $\nu$ (arene C−H) 3030; $\nu$ (C=C in Ar) 1600, 1514; $\nu$ (C−N) 1257, 1228; $\gamma$ (arene C−H) 745. MS ($APCI^+$, 20 V), m/z: 362 ($[M+H]^+$), 270.

*9-(4-Butylphenyl) carbazole-3-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone (4a).* 6 g (0.014 mol) of 9-phenylcarbazole-3-carbaldehyde N-phenylhydrazone was dissolved in 20 g of 3-chloro-1,2-epoxypropane. 1.8 g (0.032 mol) of KOH was added to the reaction mixture in four portions. Also 0.8 g of $Na_2SO_4$ was added during the first addition of KOH. The reaction mixture was stirred for 25 hours at room temperature. The crude product was extracted with diethylether. The solvent was removed by rotary evaporation and 3-chloro-1,2-epoxypropane was removed by vacuum distillation. The crude product was purified by silicagel column chromatography (eluent: ethylacetate-n-hexane, 1:10). Yield of yellowish amorphous material 66% (4.47 g) (m.p.: 132–132.5°C, FW = 473 g/mol). A $^1H$ NMR spectrum yielded the following chemical shifts (100 MHz, $CDCl_3$, $\delta$, ppm): 8.423 (d, $J = 1.3$ Hz, 1H, 4-$H_{Ht}$), 8.2 (d, $J = 7.6$ Hz, 1H, 5-$H_{Ht}$), 7.93 (s, 1H, CH=N), 7.87 (dd, $J_1 = 1.6$ Hz, $J_2 = 8.5$ Hz, 1H, 2-$H_{Ht}$), 7.5–7.25 (m, 11H, Ht, Ph), 6.98 (t, $J = 7.2$ Hz, 1H, 4-$H_{Ph}$), 4.41 (dd, $J_1 = 1.9$ Hz, $J_2 = 16.4$ Hz, 1H, one $NCH_2$ proton), 4.06 (dd, $J_1 = 3.8$ Hz, $J_2 = 16.4$ Hz, 1H, another $NCH_2$ proton), 3.3 (m, 1H, CHO), 2.91 (t, $J = 4.7$ Hz, 1H, $CH_2O$ one proton), 2.81–2.68 (m, 3H, $CH_2O$ another proton, $PhCH_2$), 1.74 (p, 2H, $\underline{CH_2}CH_2CH_2CH_3$); 1.56–1.39 (m, 2H, $\underline{CH_2}CH_3$); 1.02 (t, $J = 7.3$ Hz, 3H, $CH_2\underline{CH_3}$). An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (arene C−H) 3055; $\nu$ (aliphatic CH) 2927, 2856; $\nu$ (C=C in Ar) 1595, 1515; $\nu$ (C−N) 1230; $\gamma$ (arene C−H) 748. MS ($APCI^+$, 20 V), m/z: 474 ($[M+H]^+$).

*9-Phenylcarbazole-3-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone (4b).* 3.5 g (0.0097 mol) of compound 9-phenylcarbazole-3-carbaldehyde N-phenylhydrazone was dissolved in 10 g of 3-chloro-1,2-epoxypropane. 1.8 g (0.032 mol) of KOH was added to the reaction mixture in four portions. $Na_2SO_4$ (0.5 g) was added during the first addition of KOH. The reaction mixture was stirred for 20

hours at room temperature. The crude product was extracted with diethylether. The solvent was removed by rotary evaporation and 3-chloro-1,2-epoxypropane was removed by vacuum distillation. The crude product was purified by silicagel column chromatography (eluent: ethylacetate/n-hexane, 1:10). Yield of yellowish crystals 2.7 g (67%) (FW = 417 g/mol). A $^1$H NMR spectrum yielded the following chemical shifts (250 MHz, $CDCl_3$, $\delta$, ppm): 8.423 (d, $J = 1.3$ Hz, 1H, 4-$H_{Ht}$), 8.2 (d, 1H, $J = 6.9$ Hz, 5-$H_{Ht}$), 7.9 (s, 1H, CH=N), 7.87 (dd, 1H, $J_1 = 1.6$ Hz, $J_2 = 8.4$ Hz, 2-$H_{Ht}$), 7.68–7.24 (m, 12H, Ht, Ph), 6.98 (t, $J = 6.6$ Hz, 1H, 4-$H_{Ph}$), 4.42 (dd, 1H, $J_1 = 1.6$ Hz, $J_2 = 16.7$ Hz, one $NCH_2$ proton), 4.05 (dd, 1H, $J_1 = 4.4$ Hz, $J_2 = 15.8$ Hz, another $NCH_2$ proton), 3.3 (m, 1H, CHO), 2.91 (t, 1H, $J = 4.4$ Hz, $CH_2O$ one proton), 2.71 (dd, 1H, $J_1 = 5$ Hz, $J_2 = 2.5$ Hz, $CH_2O$ onother proton). An infrared absorption spectrum yielded the following peaks (KBr windows), (in cm$^{-1}$): $\nu$ (arene C−H) 3055; $\nu$ (C=C in Ar) 1596, 1499; $\nu$ (C−N) 1232; $\gamma$ (arene C−H) 747. MS (APCI$^+$, 20 V), m/z: 418 ($[M + H]^+$).

*Di(4-{[9-(4-butylphenyl) carbazole-3-methylene 1-phenylhydrazino]-2-hydroxypropyl}-thiophenyl)sulphur (5a).* 3 drops of TEA were slowly added to the solution of 1.5 g (3.17 mmol) of 9-(4-butylphenyl) carbazole-3-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone (**4a**) and 0.37 g (1.5 mmol) of 4,4′-thiobisbenzenethiol in 7 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30°C. The reaction mixture than was stored over night at room temperature. The product precipitated when reaction was complete. The crude product (0.77 g) was washed with acetone. The fine amorphous powder was purified by silica gel chromatography eluting with THF. It was obtained 0.43 g (24%) of yellowish powder (m.p.: 200–202°C, FW = 1196 g/mol). A $^1$H NMR spectrum yielded the following chemical shifts (250 MHz, DMSO-$d_6$, $\delta$, ppm): 8.34 (s, 2H, 4,4′-$H_{Ht}$); 8.26 (d, $J = 7.7$ Hz, 2H, 5,5′-$H_{Ht}$); 7.98 (s, 2H, 2CH=N); 7.74 (d, $J = 9.2$ Hz, 2H, 2,2′-$H_{Ht}$); 7.52–7.08 (m, 32H, Ht, Ar); 6.83 (t, $J = 7.3$ Hz, 2H, 4,4′-$H_{Ph}$); 5.54 (d, $J = 4.4$ Hz, 2H, OH); 4.25–3.98 (m, 6H, $NC\underline{H_2}C\underline{H}$); 3.20–3.12 (m, 4H, $CH_2S$); 2.69 (t, $J = 7.5$ Hz, 4H, $PhC\underline{H_2}CH_2$); 1.63 (p, 4H, $C\underline{H_2}CH_2CH_2CH_3$); 1.44–1.27 (m, 4H, $C\underline{H_2}CH_3$); 0.92 (t, $J = 7.3$ Hz, 6H, $CH_2C\underline{H_3}$). An infrared absorption spectrum yielded the following peaks (KBr windows), (in cm$^{-1}$): $\nu$ (br, OH) 3419; $\nu$ (arene C−H) 3035; $\nu$ (aliphatic CH) 2926, 2856; $\nu$ (C=C in Ar) 1594, 1515; $\nu$ (C−N) 1232; $\gamma$ (arene C−H) 746.

*Di{4-[(9-phenylcarbazole-3-methylene 1-phenylhydrazino)-2-hydroxypropyl]-thiophenyl}sulphur (5b).* 3 drops of TEA were slowly added to the solution of 1.2 g (2.87 mmol) of 9-phenylcarbazole-3-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone (**4b**) and 0.343 g (1.37 mmol) of 4,4′-thiobisbenzenethiol in 5 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30°C. The reaction mixture than was stored over night at room temperature. The product precipitated when reaction was complete. The crude product was washed with plenty of acetone. The fine amorphous powder was dried in the vacuum oven. It was obtained 0.9 g (60%) of yellowish powder (m.p.: 213–215°C, FW = 1084 g/mol). A $^1$H NMR spectrum yielded the following chemical shifts (250 MHz, DMSO-$d_6$, $\delta$, ppm): 8.35 (s, 2H, 4,4′-$H_{Ht}$); 8.27 (d, $J = 7.7$ Hz, 2H, 5,5′-$H_{Ht}$); 7.99 (s, 2H, 2CH=N); 7.77 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.4$ Hz, 2H, 2,2′-$H_{Ht}$); 7.73–7.08 (m, 34H, Ht, Ar); 6.83 (t, $J = 7.2$ Hz, 2H, 4,4′-$H_{Ph}$); 5.54 (d, $J = 4.6$ Hz, 2H, OH); 4.25–4.00 (m, 6H, $NCH_2CH$); 3.22–3.11 (m, 4H, $CH_2S$).

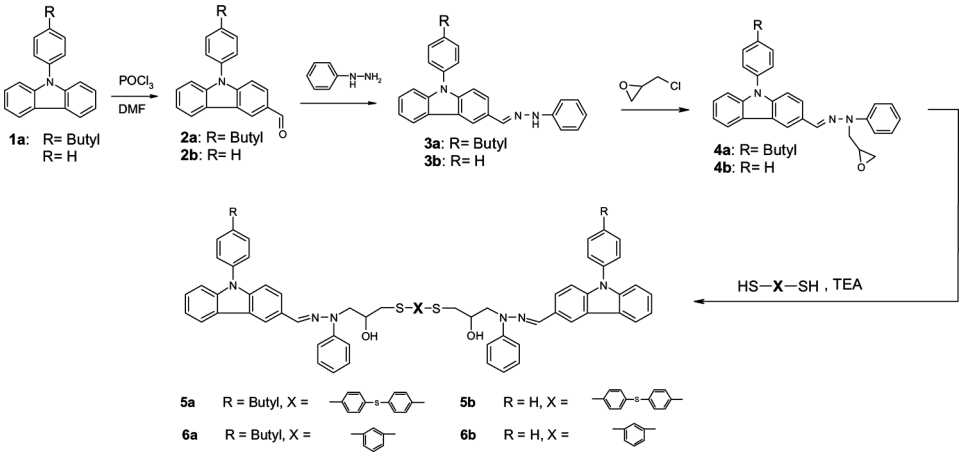
An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (br, OH) 3503; $\nu$ (arene C−H) 3055; $\nu$ (C=C in Ar) 1596, 1499; $\nu$ (C−N) 1232; $\gamma$ (arene C−H) 744.

*1,3-Bis{4-[9-(4-butylphenyl) carbazole-3-methylene 1-phenylhydrazino] (3-hydroxy)thiabutyl}benzene (6a).* 3 drops of TEA were slowly added to the solution of 1.5 g (3.17 mmol) of 9-(4-butylphenyl) carbazole-3-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone (**4a**) and 0.21 g (1.5 mmol) of 1,3-benzendithiol in 10 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30°C. The reaction mixture than was stored over night at room temperature. After evaporation of the solvent the residue was subjected by chromatography (silica gel, Aldrich) using 1:5 ethyl acetate:hexane and only ethyl acetate for the final eluting of the product. It was obtained 1.3 g (80%) of yellow amorphous material (FW = 1088 g/mol). A $^1$H NMR spectrum yielded the following chemical shifts (250 MHz, $CDCl_3$, $\delta$, ppm): 8.23 (dd, $J_1 = 4.2$ Hz, $J_2 = 1.2$ Hz, 2H, 4,4′-$H_{Ht}$); 8.13 (d, $J = 7.6$ Hz, 2H, 5,5′-$H_{Ht}$); 7.77 (d, $J = 4.7$ Hz, 2H, 2CH=N); 7.74–7.67 (m, 2H, 2,2′-$H_{Ht}$), 7.74–7.17 (m, 30H, Ht, Ph); 6.99 (t, $J = 6.6$ Hz, 2H, 4,4′-$H_{Ph}$), 4.26 (m, 2H, C<u>H</u>OH); 4.10–3.92 (m, 4H, NC<u>H</u>$_2$CH); 3.26–3.04 (m, 6H, OH, $CH_2$S); 2.72 (t, $J = 7.7$ Hz, 4H, PhC<u>H</u>$_2$$CH_2$); 1.69 (p, 4H, $CH_2$C<u>H</u>$_2$$CH_2CH_3$); 1.50–1,38 (m, 4H, C<u>H</u>$_2$$CH_3$); 0.99 (t, $J = 7.2$ Hz, 6H, $CH_2$C<u>H</u>$_3$). An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (br, OH) 3525; $\nu$ (arene C−H) 3032; $\nu$ (aliphatic CH) 2954, 2927, 2856; $\nu$ (C=C in Ar) 1595, 1515, 1497; $\nu$ (C−N) 1232; $\gamma$ (arene C−H) 745.

*1,3-Bis[4-(9-phenylcarbazole-3-methylene 1-phenylhydrazino)(3-hydroxy)-thiabutyl] benzene (6b).* 3 drops of TEA were slowly added to the solution of 1 g (2.39 mmol) of 9-phenylcarbazole-3-carbaldehyde N-(2,3-epoxypropyl)-N-phenylhydrazone (**4b**) and 0.16 g (1.14 mmol) of 1,3-benzendithiol in 5 ml of 2-butanone, while the temperature of the reaction mixture was maintained below 30°C. The reaction mixture than was stored over night at room temperature. After evaporation of the solvent the residue was subjected by chromatography (silica gel) using 1:5 ethyl acetate : hexane and only ethyl acetate for the final eluting of the product. It was obtained 1 g (90%) of yellow amorphous material (FW = 976 g/mol). A $^1$H NMR spectrum yielded the following chemical shifts (250 MHz, $CDCl_3$, $\delta$, ppm): 8.226 (dd, $J_1 = 4.6$ Hz, $J_2 = 1.2$ Hz, 2H, 4,4′-$H_{Ht}$); 8.13 (d, $J = 7.6$ Hz, 2H, 5,5′-$H_{Ht}$); 7.77 (d, $J = 4.7$ Hz, 2H, 2CH=N); 7.74–7.67 (m, 2H, 2,2′-$H_{Ht}$), 7.63–7.18 (m, 30H, Ht, Ph); 6.99 (t, $J = 6.7$ Hz, 2H, 4,4′-$H_{Ph}$), 4.25 (m, 2H, C<u>H</u>OH); 4.17–3.86 (m, 4H, NC<u>H</u>$_2$CH); 3.26–3.05 (m, 6H, OH, $CH_2$S). An infrared absorption spectrum yielded the following peaks (KBr windows), (in $cm^{-1}$): $\nu$ (OH, br) 3416; $\nu$ (arene C−H) 3055; $\nu$ (C=C in Ar) 1595, 1499; $\nu$ (C−N) 1231; $\gamma$ (arene C−H) 746.

### *Methods*

$^1$H NMR spectra were obtained on a Bruker AC 250 (250 MHz) instrument. Mass (MS) spectra were obtained on a Waters ZQ (Waters, Milford, USA). IR-spectroscopy was performed on Specord 75 IR and Perkin Elmer Spectrum GX spectrophotometers, using KBr pellets. Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC-7. Thermogravimetric analysis




**Scheme 1.** Synthetic route to 9-phenylcarbazole–based hydrazone twin compounds.

(TGA) was fulfilled using NETZSCH STA 409 thermogravimeter at a heating rate 10 K/min under $N_2$. Melting points were measured on a Buchi 510 melting point apparatus. The ionisation potentials ($I_p$) of the films of the synthesized compounds were measured by the electron photoemission in air method as described [8]. Standard error in the mean to 95% confidence for values of ionisation potential were up to 0.04 eV. Hole drift mobilities were measured by a xerographic time-of-flight method [9].

### *Synthesis and Characterization*

The charge transport materials **5a,b** and **6a,b** were prepared by multi-step synthetic route involving formylation of 9-phenylcarbazole or 9-(4-butylphenyl)carbazole (**1a**) (prepared by Ullmann coupling as described in [7]) followed by the synthesis of the corresponding phenylhydrazones (**3a,b**) and their reaction with 3-chloro-1,2-epoxypropane. The last step i.e., coupling of oxiranes **4a,b** with 4,4′-thiobisbenzenethiol and 1,3-benzenedithiol, respectively, at the room temperature in 2-butanone in the presence of triethylamine gave compounds **5a,b** and **6a,b**, respectively (Scheme 1). All final products **5a,b** and **6a,b** were purified by column chromatography. The structures of the synthesized compounds were confirmed by $^1$H NMR, IR spectroscopies and mass spectrometry.

### *Thermal Properties*

Thermal properties of the synthesized compounds were examined by DSC and TGA. The data obtained are presented in Table 1. TGA experiments in nitrogen atmosphere revealed that all of the synthesized molecules exhibit moderate thermal stability. The temperatures of the onset of their thermal degradation are up to 254°C.

Figure 1 shows TG and differential thermogravimetry (DTG) curves of compound **4b**.

Three peaks can be observed in the DTG curve, which means that three stages can be distinguished in the process of thermal degradation of **4b**. The first stage of thermal degradation of **4b** starts at around 218°C, reaches maximum weight loss rate

**Table 1.** Thermal characteristics of **4a,b–6a,b**

| Compound | $T_m$, [°C][1] | $T_g$, [°C][1] | $T_{ID}$, [°C][2] |
|---|---|---|---|
| **4a** | 134[a] | 32[a] | 220 |
| **4b** | — | 43[a] | 218 |
| **5a** | 198 | 72 | 242 |
| **5b** | 207 | 88 | 254 |
| **6a** | — | 62 | 225 |
| **6b** | — | 65 | 215 |

[1]Determined by DSC, scan rate 20°C/min, $N_2$ atmosphere.
[2]Onset of decomposition determined by TGA, heating rate 10°C/min, $N_2$ atmosphere.
[a]Heating rate 10°C/min.



at ca. 255°C and ends at 270°C. The weight loss of 17% observed at the end of the first stage of the thermal degradation of **4b** corresponds approximately to the mass fraction of epoxypropyl residue. The second stage ends at ca. 470°C. At this temperature, the compound apparently loses the hydrazone functionality and phenyl ring at the nitrogen atom of the carbazole moiety. The third stage ends at ca. 580°C with the degradation of the carbazolyl group. All the hydrazone compounds described in this article showed glass–transitions with $T_g$ ranging from 32°C to 88°C. Endothermic melting peaks were observed for **4a** and **5a,b** in the 1st heating of DSC scans (Figure 2). The other compounds have been isolated as amorphous materials and revealed no recognizable melting peaks in the temperature range used. Compound **4a** with butyl substituted phenylcarbazole moiety exhibits $T_g$ by ~11°C lower than compound **4b** having no substituent at the phenyl group of phenylcarbazole

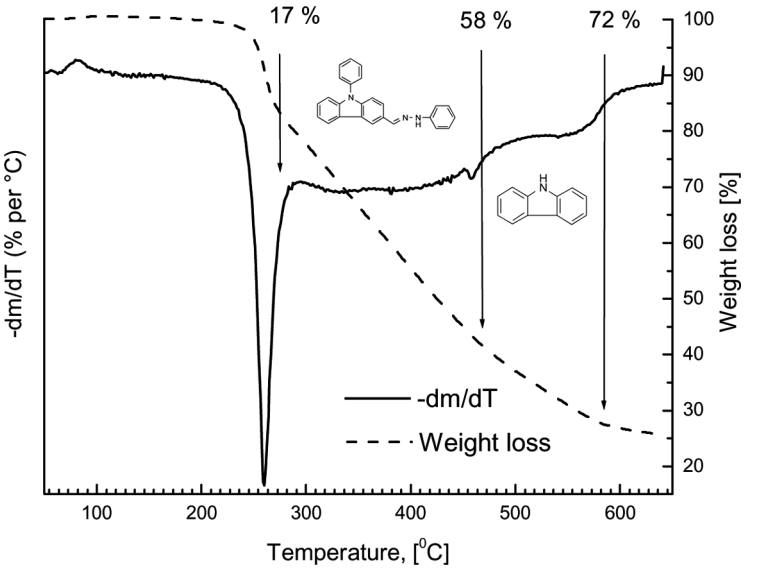



**Figure 1.** TG curve of **4b** obtained at a heating rate of 10°C/min, $N_2$ atmosphere (arrows show the end of thermal degradation stage).

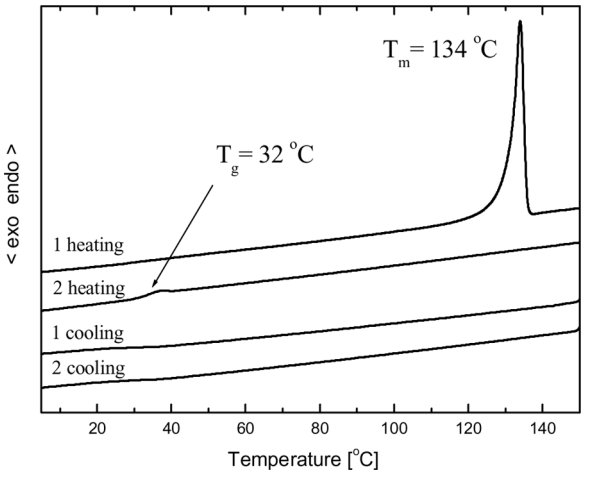



**Figure 2.** DSC thermogram of **4a** (scan rate 10°C/min, $N_2$ atmosphere).

moiety. The lower Tg's due to alkyl chain also were observed for the hydrazone twin compounds **5a** and **6a**. The twin compound bearing butyl chain in the phenyl ring (**5a**) have by ca. 16°C lower $T_g$ comparing with the twin compound **5b** having un-substituted phenyl group. The linkage **X** in the twin compounds **5b** and **6b** (Scheme 1) affects their $T_g$. If 4,4′-thiobisbenzenedithiol is used for the preparation of the twin compounds, the shape of the molecules obtained is expected to be linear therefore $T_g$'s are higher compared to banana-shaped molecules.

Nonlinearity of the molecules as well as the presence of alkyl chains lead to the increase of number of conformers and modes of packing of the molecules, therefore leading to lower glass transition temperatures [10].

### *Optical and Photoelectrical Properties*

Dilute solutions of all the compounds described in this article absorb electromagnetic radiation under 400 nm. Long–wavelength absorption band maxima of dilute solutions are between 341 and 347 nm. The data of UV absorption spectra of compounds **4a,b**–**6a,b** are summarized in Table 2.

UV spectra of the twin compounds show small bathochromic shift of 4–5 nm with respect of the spectra of the corresponding oxiranes.

**Table 2.** Optical characteristics of synthesized compounds

| Compound | $\lambda_{max}$, [nm] | $\Delta E_{opt}$, [eV] |
|---|---|---|
| **4a** | 342 | 3.18 |
| **5a** | 347 | 3.11 |
| **6a** | 347 | 3.11 |
| **4b** | 341 | 3.18 |
| **5b** | 345 | 3.12 |
| **6b** | 347 | 3.12 |

**Table 3.** Ionization potentials of phenylcarbazole–based hydrazones

| Compound | **4a** | **4b** | **5a** | **5b** | **6a** | **6b** |
|---|---|---|---|---|---|---|
| $I_p$, [eV] | 5.4 | 5.37 | 5.25 | 5.4 | 5.23 | 5.31 |

The values of $I_p$ of the amorphous films of compounds **4a,b**–**6a,b** are given in Table 3. 4-Butylphenyl-3-carbazol–based hydrazone dimers exhibit lower $I_p$ than the corresponding 9-phenyl-substituted twin molecules. The values of optical band gap and absorption maxima correlate with ionization potential data. From the point of the view of $I_p$ values the reported hydrazones are applicable as hole-transporting materials in electrophotographic photoreceptors.

Time flight technique was used to study charge transport properties of phenylcarbazole based hydrazone twin molecules doped in PC–Z (50 wt.%). The linear dependencies of $\mu$ on the square root of electric field were observed for all the systems (Figure 3). The zero field hole drift mobilities and the hole mobilities at the electric field of $6.4 \times 10^5$ V/cm are given in Table 4.

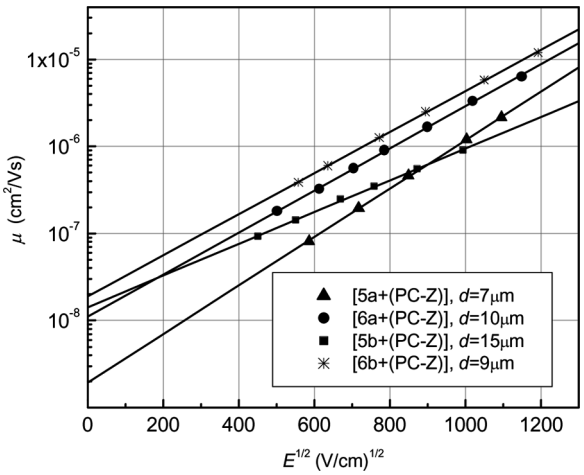



**Figure 3.** Electric field dependencies of hole drift mobilities for 50% solid solutions in PC–Z of compounds **5a,b** and **6a,b**.

**Table 4.** Mobility data

| Transport material, host polymer | $\mu_0$, [cm$^2$/Vs] | $\mu$, [cm$^2$/Vs] |
|---|---|---|
| **4a** + PC–Z, 1:1 | $1.0 \cdot 10^{-7}$ | $5.5 \cdot 10^{-6}$ |
| **4b** + PC–Z, 1:1 | $7.6 \cdot 10^{-8}$ | $5 \cdot 10^{-6}$ |
| **5a** + PC–Z, 1:1 | $2 \cdot 10^{-9}$ | $3.3 \cdot 10^{-7}$ |
| **5b** + PC–Z, 1:1 | $1.4 \cdot 10^{-8}$ | $4.1 \cdot 10^{-7}$ |
| **6a** + PC–Z, 1:1 | $1.1 \cdot 10^{-8}$ | $9.3 \cdot 10^{-7}$ |
| **6b** + PC–Z, 1:1 | $2 \cdot 10^{-8}$ | $1.5 \cdot 10^{-6}$ |

Hole mobility observed for hydrazones **5a,b** and **6a,b** doped in PC–Z ranged from $10^{-7}\,cm^2/Vs$ to $1.5 \times 10^{-5}\,cm^2/Vs$ at high electric fields.

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