Photoconductive, photoluminescent and glass-forming 6,6′-di(N-diphenylamino)-9,9′-dialkyl-3,3′-bicarbazoles

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Abstract

Novel branched molecules 6,6′-di(N-diphenylamino)-9,9′-dialkyl-3,3′-bicarbazoles have been synthesised and found to constitute glass-forming materials with glass-transition temperatures in the range of 72–128 °C, as characterised by differential scanning calorimetry. The electron photoemission spectra of the materials have been recorded and the ionisation potentials of 5.25–5.30 eV have been established. Room temperature hole-drift mobility in the amorphous film of 6,6′-di(N-dimethylphenylamino)-9,9′-butyl-3,3′-bicarbazole established by the time-of-flight technique approaches 10^{-6} cm^2/V s at an applied electric field of 6.4×10^5 V/cm.
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Keywords: Aromatic amine; Molecular glass; Hole-drift mobility; Ionisation potential

1. Introduction

Low molecular weight organic compounds that readily form stable glasses are called molecular glasses or amorphous molecular materials. They show excellent processability, transparency, isotropic and homogeneous properties and receive growing attention both in terms of academic interest and technological applications. Aromatic amine-based molecular glasses belong to the classes of light-emitting and charge-transporting materials and are known for various applications such as displays, photovoltaic cells, photorefractive materials and organic photoreceptors [1–3].

For the purpose of developing electronically active molecular glasses, we have been studying the synthesis, properties and applications of novel molecules based on aromatic amines. We have reported previously on hole-transporting compounds, 3,6-(N-diarylamino)carbazoles having different substituents at 9th position of the central carbazole ring [4,5]. 3,6-Di(diphenylamino)-9-alkylcarbazoles showed hole-drift mobilities of 10^{-5} to 10^{-4} cm^2/V s at an applied electric field of 3.6×10^5 V/cm [4]. Hole mobilities in the amorphous films of 3,6-di(4-methyldiphenylamino)-9-phenylcarbazole approached 10^{-3} cm^2/V s at the same electric field [5].

In the present study, we report on the synthesis and properties of glass-forming hole-transport molecules in which diphenylamine species are attached to 3,3′-bicarbazole core. For designing these molecules, we expected that enlargement of the molecules would increase the morphological stability of glasses and their glass-transition temperature (T_g). On the other hand, expansion of the conjugated π-electron systems has to influence spectroscopic characteristics of the compounds and their charge-transport properties.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using a Brucker AC 250 (250 MHz) apparatus. Mass spectra were obtained on a Varian MAT-312 spectrometer. UV spectra were measured with a Specord M-40 spectrometer. Fluorescence spectra were recorded with a Perkin-Elmer LS-5 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7 calorimeter. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermal analysis system 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10 °C/min.

The ionisation potentials of the layers of the compounds synthesised were measured by the electron photoemission method in air, which was described earlier [5]. The samples for the ionisation potential measurement were prepared as described previously [6]. The measurement method was, in principle, similar to that described by Miyamoto et al. [7].

The hole-drift mobility was measured by the time-of-flight technique in electrophotographic regime [8]. The samples for the charge carrier mobility measurements were prepared by casting the solutions of the compounds and their mixtures in weight proportion of 1:1 with polycarbonate Z (PC-Z) on glass plates with conductive SnO_2 layer or polyester films with Al layer. The thickness of the transporting layer varied in the range of 3–5 μm.

2.2. Materials

9-Butylcarbazole (**1**), 9-ethylcarbazole (**2**) and (3-methyl-phenyl)phenylamine (**8**) were purchased from Aldrich. Diphenylamine (**8**) was received from Reakhim (Russia).

9,9′-Dibutyl-3,3′-bicarbazole (**4**) and 9,9′-diethyl-3,3′-bicarbazole (**3**) were obtained by chemical oxidation of 9-butylcarbazole (**1**) and 9-ethylcarbazole (**2**), respectively, in the presence of $FeCl_3$ [9].

6,6′-Diiodo-9,9′-dibutyl-3,3′-bicarbazole (**5**) and 6,6′-diiodo-9,9′-diethyl-3,3′-bicarbazole (**6**) were obtained by a modified procedure of Tucker [10].

6,6′-Di(N-diphenylamino)-9,9′-dibutyl - 3,3′ - bicarbazole (**9**). 1.2 g (1.72 mmol) of 6,6′-diiodo-9,9′-dibutyl-3,3′-bicarbazole (**5**), 1.16 g (6.9 mmol) of diphenylamine (**8**), 1.9 g (13.8 mmol) of powdered anhydrous potassium carbonate, 0.43 g (6.9 mmol) of copper powder and 0.1 g (0.34 mmol) of 18-crown-6 were refluxed in o-dichlorobenzene (20 ml) under nitrogen for 48 h. Copper powder 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 silica gel column using hexane/ethylacetate (volumetric ratio 4:1) as an eluent to obtain 0.96 g of 9. Yield: 72%. Elemental analysis for $C_{56}H_{50}N_4$: % Calc. N 7.37, C 88.39, H 4.24; % Found N 7.34, C 88.27, H 4.39. IR (in KBr), ν (cm^{-1}): 2960, 1594, 1478, 1378, 870. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.0 (t, 6H, $J = 7.5$ Hz), 1.48–1.91 (m, 8H), 4.32 (t, 4H, $J = 7.2$ Hz), 6.92 (t, 4H, $J = 7.3$ Hz), 7.05–7.53 (m, 28H). MS (70 eV): $m/z = 778$ (M^+), 389, 735, 524, 346.

6,6′-Di[N-(3-methylphenyl)phenylamino] - 9,9′ - dibutyl - 3,3′-bicarbazole (**10**) was prepared from 1.17 g (1.69 mmol) of 6,6′-diiodo-9,9′-dibutyl-3,3′-bicarbazole (**5**), 1.86 g (13.52 mmol) of powdered anhydrous potassium carbonate, 0.43 g (6.8 mmol) of copper powder and 0.1 g (0.34 mmol) of 18-crown-6 in the same way as product **9**, using 1.24 g (6.76 mmol) of (3-methylphenyl)phenylamine (**8**) as secondary amine. Compound **10** was purified by column chromatography with silica gel using hexane/ethylacetate (volumetric ratio 4:1) as eluent. Yield: 0.75 g (55%). Elemental analysis for $C_{58}H_{54}N_4$: % Calc. N 7.11, C 88.29, H 4.6;

% Found N 6.98, C 88.53, H 4.48. IR (in KBr), ν (cm^{-1}): 2920, 1595, 1480, 1320, 1270, 715. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.03 (t, 6H, $J = 7.5$ Hz), 1.46–1.92 (m, 8H), 2.25 (s, 3H), 4.32 (t, 4H, $J = 6.7$ Hz), 6.82–8.16 (m, 26H). MS (70 eV): $m/z = 807$ (M^+), 546.

6,6′-Di(N-diphenylamino)-9,9′-diethyl - 3,3′ - bicarbazole (**11**). was prepared from 0.74 g (1.16 mmol) of 6,6′-diiodo-9,9′-diethyl-3,3′-bicarbazole (**6**), 1.28 g (9.24 mmol) of powdered anhydrous potassium carbonate, 0.29 g (4.63 mmol) of copper powder and 0.06 g (0.22 mmol) of 18-crown-6 in the same way as product **9**, using 0.54 g (3.18 mmol) of diphenylamine (**8**) as secondary amine, and purified by column chromatography with silica gel using hexane/acetone (volumetric ratio 4:1) as eluent. Yield: 0.43 g (52%). Elemental analysis for $C_{52}H_{42}N_4$: % Calc. C 86.39, H 5.86, N 7.75; % Found C 86.91, H 4.47, N 8.62. IR (in KBr), ν (cm^{-1}): 2960, 1594, 1478, 1378, 870. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.52 (t, 6H, $J = 7.5$ Hz), 4.32–4.47 (m, 4H), 6.96 (t, 4H, $J = 7.3$ Hz), 7.48–8.25 (m, 28H). MS (70 eV): $m/z = 722$ (M^+), 681, 555, 510, 361, 333, 255.

3. Results and discussion

6,6′-Di(N-diphenylamino)-9,9′-dialkyl-3,3′-bicarbazoles (**9–11**) were prepared as described in Scheme 1 via the Ullmann coupling reaction of 6,6′-diiodo-9,9′-dialkyl-3,3′-bicarbazoles (**5–6**) with an excess of secondary amine, i.e. diphenylamine (**7**) and (3-methylphenyl)phenylamine (**8**), respectively. The diiodocompounds (**5–6**) were prepared by the Tucker iodination of 9,9′-dialkyl-3,3′-bicarbazoles (**3–4**), which were synthesised by chemical oxidation of the corresponding 9-alkylcarbazoles (**1–2**) in the presence of $FeCl_3$. All the materials **9–11** were identified by mass spectrometry, IR and electronic absorption, as well as ^{1}H NMR spectroscopy.

The thermal properties of the materials **9–11** were examined using DSC and TGA analysis under a nitrogen atmosphere. TGA measurements revealed that the compounds are thermally stable. The onset of decomposition for **9–11** occurs above 370 °C, and temperature for 5 wt.% loss is near 400 °C.

All the compounds **9–11** were obtained as amorphous glasses as confirmed by DSC. When the samples of **9–11** were heated the glass transitions were observed at 104 °C for **9**, at 72 °C for **10** and at 128 °C for **11**, and no peaks due to crystallisation and melting appeared. Cooling down and the following repeated heating revealed only the glass transition again. As an example, the DSC thermograms of **11** are shown in Fig. 1.

All the attempts to crystallise the compounds **9–11** in different solvents failed. It is of interest to compare T_g of 6,6′-di(N-diphenylamino)-9,9′-dialkyl-3,3′-bicarbazoles with that of earlier reported 3,6-di(diphenylamino)-9-alkyl-carbazoles. T_g of 6,6′-Di(N-diphenylamino)-9,9′-diethyl-3,3′-bicarbazole (**11**) is by more than 40 °C higher than

9: R=C$_4$H$_9$, R$_1$=H; 10: R=C$_4$H$_9$, R$_1$=CH$_3$; 11: R=C$_2$H$_5$, R$_1$=H;
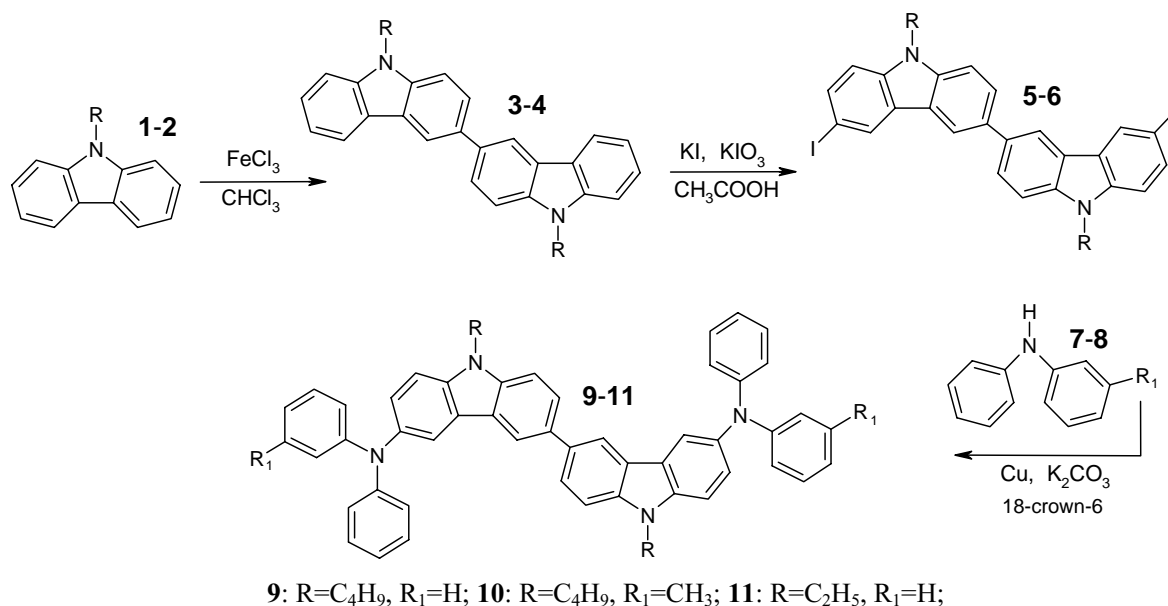
Scheme 1.

that of 3,6-di(diphenylamino)-9-ethylcarbazole [11]. It is evident that the replacement of carbazole core by a more bulky 3,3′-bicarbazole core enables considerably to increase T_g. The values of T_g of the 6,6′-di(N-diphenylamino)-9,9′-dialkyl-3,3′-bicarbazoles can be varied not only by changing the length of the alkyl chains at the 9th position of carbazole ring (cf. T_g of 10 with that of 11) but also by incorporation of an additional methyl groups into N-diphenylamino moieties (cf. T_g of 9 with that of 10).

UV absorption and photoluminescence (PL) emission spectra of dilute solutions of compounds 9–11 in tetrahydrofuran we recorded and the pertinent data are presented in Table 1. The electronic absorption energy of these compounds is very similar, and the λ_{max} values are in the range of 240–320 nm. Their PL emission maxima appear in the region of wavelengths from 430 to 435 nm. The absorption band of the lowest energy and the photoluminescence band of compound 10 are slightly red-shifted with respect to the corresponding bands of compounds 9 and 11 due to the conjugation of σ- and π-electrons.

The comparison of the UV absorption and fluorescence emission spectra (Fig. 2) of the 6,6′-di(N-diphenylamino)-9,9′-diethyl-3,3′-bicarbazole (11) with those of 9,9′-dialkyl-3,3′-bicarbazole and 9-ethylcarbazole indicates that the spectra of 11 exhibit strong bathochromic shift with respect of the spectra of 9-ethyl-9H-carbazole and 9,9′-dialkyl-3,3′-bicarbazole. In the UV spectra of 11, B and R bands are submerged by the bathochromically and hyperchromically shifted K bands attributed to π → π∗ transitions [12]. This observation shows that molecules of 6,6′-di(N-diphenylamino)-9,9′-dialkyl-3,3′-bicarbazoles are significantly π-conjugated through the 3,3′-bicarbazole unit and the lone electron pair at the nitrogen atom and that π-electrons are de-localised over these molecules. Fluores-
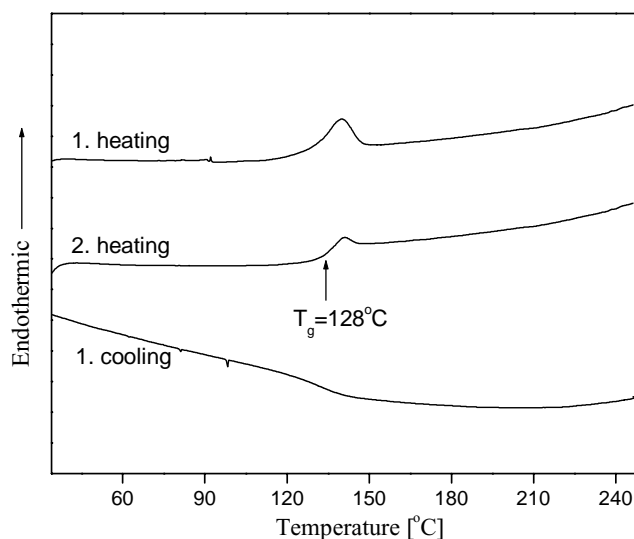
Fig. 1. DSC curves of 11. Heating rate: 10 °C/min.

Table 1
UV absorption and PL[a] emission maxima of the compounds 9–11[b]

Compound	UV: λ_{max} (nm)	PL: λ_{max} (nm)
9	251, 286, 304	430
10	250, 285, 308	435
11	249, 286, 304	431

[a] Excitation wavelength: 290 nm.
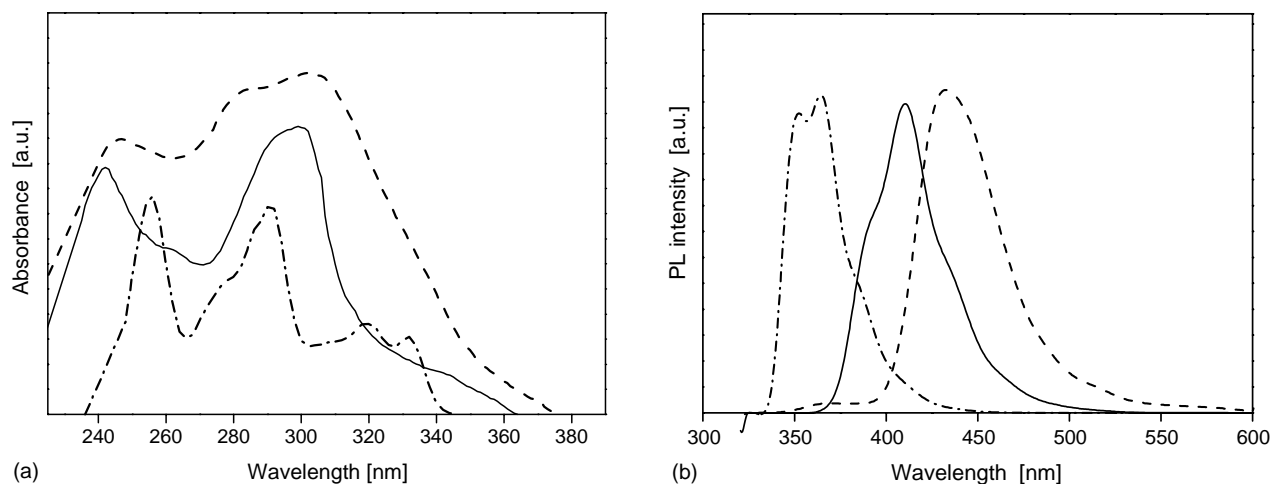[b] 10^{-5} mol l^{-1}.

Fig. 2. UV absorption (a) and PL emission (b; λ_{ex} = 290 nm) spectra of **11** (- - -), **3** (—) and 9-ethylcarbazole (- ·· - ·· -) dilute solutions.

cence spectrum of **11** is structureless, apparently because of the non-planar configuration of the chromophore.

The extended conjugation stabilises the oxidised state of molecules and compound **11** shows lower ionisation potential (I_p) than bicarbazole **3** (Fig. 3). The values of I_p for the films of compounds **9–11** determined by the electron photoemission method range from 5.25 to 5.3 eV. These values are very close to the ionisation potentials earlier observed for 3,6-di(diphenylamino)-9-phenylcarbazoles [5]. Holes would be easily injected into the layers of these materials from a charge generation layer or a conductive anode with I_p or work function close to these values. The I_p-values for charge generation materials, including those widely used in electrophotographic photoreceptors pigments, such as titanyl phthalocyanines [13,14], perylene pigments [15] and bisazo pigments [16] are in the range of 5.1–5.6 eV. I_p of compounds **9–11** are close to that of indium–tin oxide (4.8 eV), which is used as anode in electroluminescent devices [17].
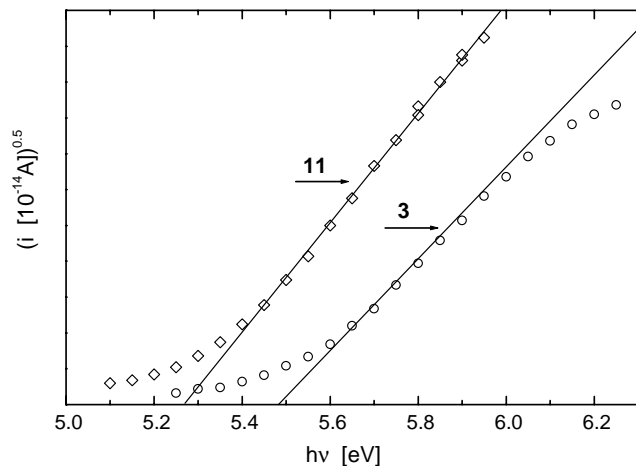
The injection barrier of holes from an electrode into the layers of **9–11** would be 0.45–0.5 eV.

The compound **10** with the best film-forming properties has been subjected to the charge carrier mobility studies. Time-of-flight technique was used to characterise hole-drift mobilities in amorphous films of the pure compound **10** and in molecularly doped PC-Z (50 wt.% of **10**).

The room temperature hole mobility (μ) in this compound shows a linear dependence on the square root of the electric field (Fig. 4). This observation is characteristic of the majority of non-crystalline organic semiconductors and is attributed to the effects of disorder on charge transport [18]. The glass of **10** exhibits hole-drift mobility value of 0.7×10^{-6} cm^2/V s at an electric field of 6.4×10^5 V/cm at room

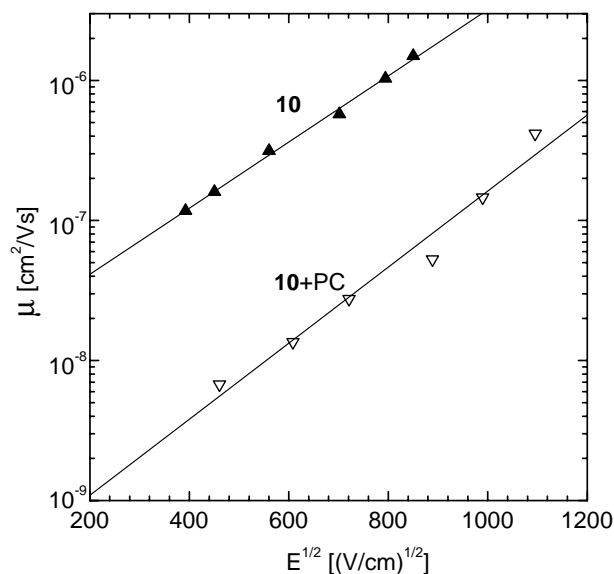Fig. 3. The electron photoemission spectra of the compounds **11** and **3**.

Fig. 4. The electric field dependencies of the hole-drift mobility (μ) in an amorphous charge-transport layer of **10** and of that doped in PC (50 wt.%).

temperature. The mobility in PC-Z doped with **10** at the same conditions is 2.2×10^{-8} cm^2/V s. These values are by more than two orders of magnitude lower than those observed earlier for 3,6-di(diphenylamino)-9-alkylcarbazoles [4] and 3,6-di(diphenylamino)-9-phenylcarbazoles [5] although, as it was mentioned above, ionisation potentials of these materials are very close. Unexpectedly, low hole mobilities in the films of **10** and of its solid solutions in PC-Z can apparently be explained by the presence of defects in the films and by unfavourable packing of big non-planar molecules for the electron transfer from the neutral molecules to the radical cations.

In conclusion, we have synthesised the photoluminescent compounds 6,6'-di(N-diphenylamino)-9,9'-dialkyl-3,3'-bicarbazoles exhibit high thermal stability and form amorphous films with glass-transition temperatures in the range of 72–128 °C. These films show low ionisation potentials (5.25–5.30 eV); however, hole mobilities observed in the layers of pure 6,6'-di[N-(3-methylphenyl)phenylamino]-9,9'-dibutyl-3,3'-bicarbazole and of its solid solutions solutions in polycarbonate Z were rather low.

Acknowledgements

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