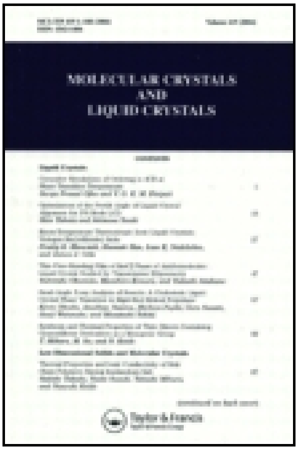


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

3,3′-Bicarbazolyl-Containing Oxirane and its Reaction Products as New Glass-Forming Electroactive Materials

V. Vaitkeviciene [a] , J. V. Grazulevicius [b] & V. Jankauskas [c]

[a] Nuclear Engineering Laboratory, Lithuanian Energy Institute, Breslaujos, Kaunas, Lithuania

[b] Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania

[c] Department of Solid State Electronics, Vilnius University, Vilnius, Lithuania

Version of record first published: 10 Jun 2010

To cite this article: V. Vaitkeviciene, J. V. Grazulevicius & V. Jankauskas (2008): 3,3′-Bicarbazolyl-Containing Oxirane and its Reaction Products as New Glass-Forming Electroactive Materials, Molecular Crystals and Liquid Crystals, 497:1, 241/[573]-253/[585]

To link to this article: http://dx.doi.org/10.1080/15421400802462938

Mol. Cryst. Liq. Cryst., Vol. 497, pp. 241/[573]–253/[585], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802462938

3,3′-Bicarbazolyl-Containing Oxirane and its Reaction Products as New Glass-Forming Electroactive Materials

V. Vaitkeviciene[1], **J. V. Grazulevicius**[2], **and V. Jankauskas**[3]
[1]Nuclear Engineering Laboratory, Lithuanian Energy Institute, Breslaujos, Kaunas, Lithuania
[2]Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania
[3]Department of Solid State Electronics, Vilnius University, Vilnius, Lithuania

Low-molar-mass oxiranyl-substituted 3,3′-bicarbazolyl derivatives were synthesized by the reaction of 3,3′-bicarbazolyl-containing oxirane with dimercapto compounds as linking agents. The cationic ring opening polymerization of oxirane monomers was performed using ytterbium (III) trifluoromethanesulfonate [Yb(OTf)$_3$] as a cationic initiator to obtain polyether. The full characterization of the compounds by mass spectrometry, IR, ^{1}H NMR, and ^{13}C NMR is presented. All the compounds represent amorphous materials with glass transition temperatures ranging from 28°C to 112°C and with 5%-weight-loss temperatures exceeding 308°C. The electron photoemission spectra of the materials were recorded, and the ionization potentials of ca. 5.5 eV were established. Time-of-flight hole drift mobilities of the amorphous films of some synthesized compounds exceed 10^{-5} cm^2/Vs at high electric fields.

Keywords: bicarbazolyl; glass transition; hole drift mobility; ionization potential; oxiranyl

1. INTRODUCTION

Poly[9-(2,3-epoxypropyl)carbazole] (**PEPK**) is apparently one of the most thoroughly studied and most widely used compounds among

Financial support of this research by the Lithuanian State Science and Studies Foundation is gratefully acknowledged. Habil. Dr. V. Gaidelis from the Department of Solid State Electronics, Vilnius University is thanked for the data of ionization potential measurements.

Address correspondence to J. V. Grazulevicius, Department of Organic Technology, Kaunas University of Technology, 19, Radvilenu Pl., Kaunas LT-50254, Lithuania. E-mail: juozas.grazulevicius@ktu.lt

carbazolyl-containing photoconductors [1,2]. High-molar-mass PEPK exhibits one of the highest hole mobilities among the photoconductive polymers with pendant photoactive groups [3,4]. Synthesis of low-molar-mass organic glass-forming photoconductors by the reactions of carbazolyl-containing glycidyl ethers with different bifunctional compounds such as aromatic diols, dimercaptanes, and the derivatives of aniline has been reported in the literature [5,6]. Till recently, no such work has been done with 3,3′-bicarbazolyl-containing oxiranes. The aim of this work was the synthesis and investigation of properties of the oxiranyl-substituted 3,3′-bicarbazolyl derivative and of the compounds prepared by the reaction of oxirane with dimercapto compounds as linking agents. The cationic ring opening polymerization of 9-(2-ethylhexyl)-3-[9-(oxiran-2-ylmethyl)carbazol-3-yl]carbazole using ytterbium (III) trifluoromethanesulfonate [$Yb(OTf)_3$] as a cationic initiator is reported as well. Lanthanide triflates are commercially available cationic initiators and have many advantages over BF_3 derivatives and other Lewis acids, since they do not require expensive anhydrous solvents [7,8].

2. EXPERIMENTAL

2.1. Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded, by using Varian Unity Inova and JOEL JNM- FX 250 apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FTIR spectra were recorded using a Perkin Elmer FT-IR System. UV spectra were measured with a Spectronic Genesys^{TM} 8 spectrometer. Fluorescence (FL) spectra were recorded with an MPF-4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer Pyris Diamond calorimeter. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 20°C/min and 10°C/min, respectively.

The ionization potentials of layers of the compounds synthesized were measured by the electron photoemission method in air, as was described earlier [9,10]. The samples for the ionization potential measurement were prepared as described previously [11].

The charge drift mobilities were measured by the xerographic time-of-flight technique [12]. The samples for the charge carrier mobility measurements were prepared by casting the pure material or mixtures in the weight proportion 1:1 with polycarbonate-Z (PC-Z) on polyester films with an Al layer. The thickness of the charge transport layer varied in an interval of 5–9 μm.

2.2. Materials

Carbazole, 3-chloro-1,2-epoxypropane, 1-bromo-2-ethylhexane, 1,3-benzenedithiol, 4,4′-thiobisbenzenethiol and [Yb(OTf)$_3$] were purchased from Aldrich and used as-received.

9-(2-Ethylhexyl)-3,3′-bicarbazolyl (**2**) and 9-(2-ethylhexyl)-3-[9-(2-ethylhexyl)-9H-carbazol-3-yl]-9H-carbazole (**Di(EtHexCz)**) were prepared by alkylation of 3,3′-bicarbazolyl (**1**) in the presence of a phase transfer catalyst [13]. The key starting material **1** was obtained by chemical oxidation of carbazole in the presence of FeCl$_3$ [14].

9-(2-Ethylhexyl)-3-[9-(oxiran-2-ylmethyl)carbazol-3-yl]carbazole (**3**) (FW = 500 g/mole) was prepared by the procedure similar to that earlier described in the literature [5]. Compound **2** (2.0 g, 4.51 mmole) was dissolved in 15.31 g of 3-chloro-1,2-epoxypropane under mild heating. Potassium hydroxide (1.0 g, 17.82 mmole) was added to the reaction mixture in three portions. Sodium sulfate (1.2 g, 8.45 mmole) was added additionally before every addition of potassium hydroxide into the flask. The reaction mixture was stirred for 3 h at 30°C. It was filtrated and then 3-chloro-1,2-epoxypropane was removed by vacuum distillation. After the distillation, the product was subjected to chromatography using the mixture of ethyl acetate and hexane in a volume ratio of 15:1 as an eluent. The yield of 1.52 g (68%) of brownish material was obtained. MS (APCI$^+$, 20 V), m/z: 501 ([M + H]$^+$, 100%). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 8.46 (split s, $J = 1.5$ Hz, 2H, H-4, H-4′), 8.26 (d, $J = 2.4$ Hz, 1H, H-5′), 8.23 (d, $J = 2.4$ Hz, 1H, H-5), 7.92–7.85 (m, 2H, H-2, H-2′), 7.62–7.45 (m, 6H, H-1, H-1′, H-7, H-7′, H-8, H-8′), 7.37–7.28 (m, 2H, H-6, H-6′), 4.72 (dd, $^3J_{cis} = 3.3$ Hz, $^2J_{AB} = 15.3$ Hz, 1H, one of >N−CH$_2$-protons, >CH$_B$), 4.48 (dd, $^3J_{trans} = 4.8$ Hz, $^2J_{AB} = 16.2$ Hz, 1H, another >N−CH$_2$-proton, >CH$_A$), 4.26 (dd, $^3J_{HH} = 7.5$ Hz, $^2J_{HH} = 2.1$ Hz, 2H, >N−CH$_2$−), 3.48–3.40 (m, 1H, >N−CH$_2$−CH−O−), 2.88 (dd, $^3J_{cis} = 3.9$ Hz, $^2J_{A'M} = 4.8$ Hz, 1H, one of −O−CH$_2$-protons, >CH$_M$), 2.65 (dd, $^3J_{trans} = 2.4$ Hz, $J_{A'M} = 4.8$ Hz, 1H, −O−CH$_2$-another proton, >CH$_{A'}$), 2.24–2.12 (m, 1H, >N−CH$_2$−CH<), 1.56–1.28 (m, 8H, –(CH$_2$−CH$_3$) −CH$_2$−CH$_2$−CH$_2$−CH$_3$), 1.04–0.9 (m, 6H, −CH$_3$). ^{13}C NMR (75.4 MHz, CDCl$_3$, δ, ppm): 141.65, 141.42, 140.06, 140.35, 134.29, 133.36, 126.26, 126.10, 125.93, 125.74, 123.87, 123.61, 123.51, 123.25, 120.75, 120.66, 119.68, 119.52, 119.13, 119.01, 109.45, 109.35, 109.29, 109.16, 50.95, 47.78, 45.64, 44.95, 39.75, 31.29, 29.15, 24.69 (>CH–(CH$_2$−CH$_3$)), 23.39, 14.38, 11.24. IR (KBr window), (in cm^{-1}): 3052, 2958, 2922, 2856, 1601, 1489, 1379, 1290, 1256, 970, 851, 799, 746, 727. Elemental analysis for C$_{35}$H$_{36}$N$_2$O: % Calc.: C 83.96, H 7.25, N 5.59, O 3.20; % Found: C 84.02, H 7.26, N 5.60.

Poly{oxy[2-({[9-(2-ethylhexyl)carbazol-3-yl]carbazol-9-yl}methyl) ethylene]} (**4**). Compound **3** (0.5 g, 0.999 mmole) was polymerized in 3 ml of CH_2Cl_2 in the presence of the catalyst ytterbium(III) trifluoromethane sulfonate ($Yt(TfO)_3$) (0.06 g, 0.1 mmole) at reflux temperature under nitrogen atmosphere during 72 h. Polymer **4** was purified by several reprecipitations into methyl alcohol, recovered by filtration, and dried. We obtained 0.13 g (26%) of white powder. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.5–7.7 (m, 4H, H-4, H-5), 7.6–7.0 (m, 10H, Ht), 4.6–3.95 (m, 4H, $>N-CH_2-$), 3.85–3.4 (m, 2H, $-O-CH_2-$), 2.2–1.9 (m, 2H, $>N-CH_2-CH-$), 1.56–1.10 (m, 8H, $-(CH_2-CH_3)-CH_2-CH_2-CH_2-CH_3$), 1.04–0.8 (m, 6H, $-CH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ, ppm): 141.49, 140.36, 134.26, 133.35, 126.21, 126.14, 125.93, 125.78, 123.90, 123.56, 123.50, 123.28, 120.69, 119.66, 119.15, 109.50, 109.37, 75.02, 69.24, 47.80, 39.76, 31.32, 29.16, 24.71, 23.41, 14.41, 11.25. IR (KBr window), (in cm^{-1}): 3551, 3049, 2956, 2927, 2870, 1600, 1459, 1379, 1330, 1216, 1204, 799, 746, 727.

Bis[4-({3-[9-(2-ethylhexyl)carbazol-3-yl]carbazol-9-yl}-2-hidroxyprop-1-yl-thio)phenyl]sulfide (**5**) (FW = 1250 g/mole). Three drops of triethylamine were added to the solution of **3** (0.9 g, 1.798 mmole) and 4,4′-thiobisbenzenethiol (0.21 g, 0.84 mmole) in 10 ml of dry THF under the nitrogen atmosphere. The reaction mixture was kept below 60°C over night. After evaporation of the solvent, the residue was subjected to chromatography using the mixture of ethyl acetate and hexane in a volume ratio of 1:7 as an eluent. The yield of yellowish powder was 0.52 g (50%). MS ($APCI^+$, 20 V), m/z: 1251 ($[M+H]^+$, 98%). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.43 (s, 4H, H-4, H-4′), 8.21 (d, $J = 7.8$ Hz, 4H, H-5, H-5′), 7.83 (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1.5$ Hz, 4H, H-2, H-2′), 7.55 – 7.4 (m, 12H, H-1, H-1′, H-7, H-7′, H-8, H-8′), 7.34 – 7.25 (m, 4H, H-6, H-6′), 7.21 (d, $J = 3$ Hz, 8H, Ph), 4.58–4.4 (m, 4H, $>N-CH_2$ $-CHOH-$), 4.36–4.26 (m, 2H, $>CH-OH$), 4.22 (dd, $^3J_{HH} = 6$ Hz, $^2J_{HH} = 2.1$ Hz, 4H, $>N-CH_2$ $-CH<$), 3.2–2.98 (m, 4H, $-S-CH_2-$), 2.44 (d, 2H, $J = 3.6$ Hz, $>CH-OH$), 2.2–2.08 (m, 2H, $>N-CH_2-CH<$), 1.52–1.24 (m, 16H, $-(CH_2-CH_3)-CH_2-CH_2-CH_2-CH_3$), 1.02–0.88 (m, 12H, $-CH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ, ppm): 141.62, 141.40, 140.34, 140.00, 139.94, 134.34, 134.21, 133.23, 131.87, 130.54, 126.26, 126.07, 125.94, 125.71, 123.90, 123.61, 123.54, 123.22, 120.79, 120.66, 119.72, 119.24, 119.14, 119.01, 109.49, 109.36, 69.38, 48.14, 47.74, 39.72, 39.10, 31.29, 29.12, 24.68, 23.36, 14.39, 11.21. IR (KBr window), (in cm^{-1}): 3535, 3049, 2956, 2925, 2870, 2855, 1628, 1600, 1575, 1472, 1459, 1330, 1256, 1214, 798, 745, 727. Elemental analysis for $C_{82}H_{82}N_4O_2S_3$: % Calc.: C 78.68, H 6.60, N 4.48, O 2.56, S 7.68; % Found: C 78.57, H 6.57, N 4.53.

1,3-Bis(4-{3-[9-(2-ethylhexyl)carbazol-3-yl]carbazol-9-yl}-2-hydroxy-prop-1-yl-thio)benzene (**6**) (FW = 1142 g/mole) was synthesized by the same procedure as compound **5**, only 1,3-benzenethiol (0.06 g, 0.42 mmole) was used instead of 4,4′-thiobisbenzenethiol. After evaporation of the solvent, the residue was subjected to chromatography using the eluent mixture of ethyl acetate and hexane in a volume ratio of 1:5. The yield of yellowish powder was 0.29 g (60%). MS ($APCI^+$, 20 V), m/z: 1143 ($[M+H]^+$, 97%). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.43 (s, 4H, H-4, H-4′), 8.20 (d, $J = 7.2$ Hz, 4H, H-5, H-5′), 7.76 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.5$ Hz, 4H, H-2, H-2′), 7.60 – 7.35 (m, 12H, H-1, H-1′, H-7, H-7′, H-8, H-8′), 7.30 – 7.25 (m, 4H, H-6, H-6′), 7.24–7.10 (m, 4H, Ph), 4.48–4.25 (m, 4H, $>N-CH_2-CHOH-$), 4.25–4.15 (m, 2H, $>CH-OH$), 4.16 (d, $J = 6.2$ Hz, 4H, $>N-CH_2-CH<$), 2.90–2.40 (m, 4H, $-S-CH_2-$), 2.52 (d, $J = 3.6$ Hz, 2H, $-OH$), 2.16–2.04 (m, 2H, $>N-CH_2-CH<$), 1.56–1.24 (m, 16H, $-(CH_2-CH_3)-CH_2-CH_2-CH_2-CH_3$), 1.04–0.80 (m, 12H, $-CH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ, ppm): 141.35, 140.07, 139.72, 133.94, 132.87, 129.60, 125.95, 125.77, 125.37, 123.56, 123.34, 122.96, 120.36, 119.41 118.75, 109.19, 109.06, 69.19, 48.00, 47.49, 39.43, 36.62, 31.02, 29.68, 28.83, 24.40, 23.06, 14.04, 10.90. IR (KBr window), (in cm^{-1}): 3370?, 3050, 2957, 2927, 2871, 2858, 1628, 1575, 1560, 1488, 1472, 1459, 1342, 1323, 1297, 798, 745, 727. Elemental analysis for $C_{76}H_{78}N_4O_2S_2$: % Calc.: C 79.82, H 6.87, N 4.9, O 2.8, S 5.61; % Found: C 79.77, H 6.93, N 4.68.

2. RESULTS AND DISCUSSION

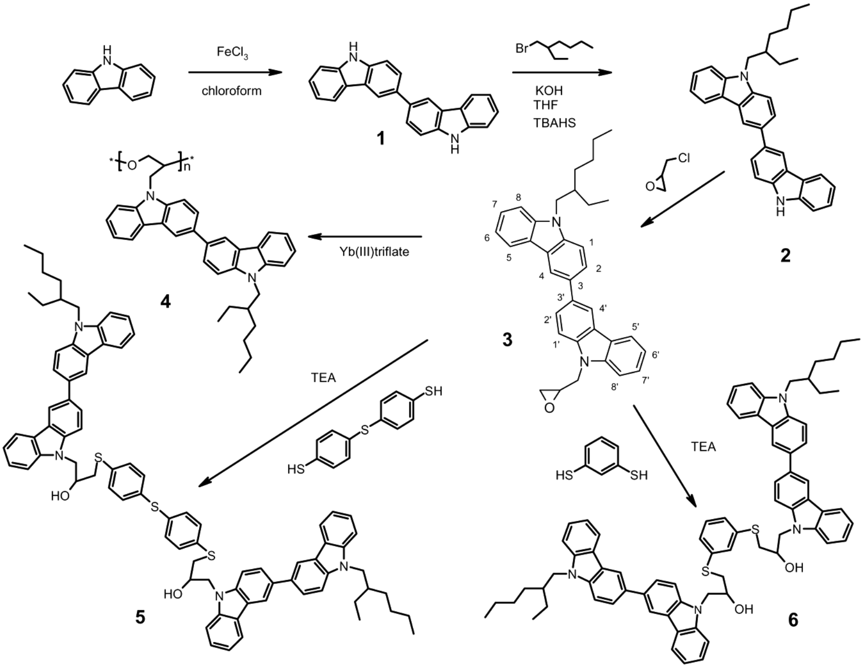
The synthetic routes to monomer (**3**), polymer (**4**), and twin compounds (**5** and **6**) are shown in Scheme 1. Compound **3** was synthesized by the reaction of **2** with 3-chloro-1,2-epoxypropane in the presence of KOH.

The cationic polymerization of **3** initiated with ytterbium (III) trifluoromethanesulfonate ($[Yt(OTf)_3] = 0.1$ M) was carried out in a 1,2-dichloroethane solution ($[\mathbf{3}] = 1.0$ M) at the reflux temperature under nitrogen during 72 h.

The average molecular weights of **4** were estimated by GPC. The obtained values were $M_n = 1220$, $M_w = 2090$, with the polydispersity index 2.

Compound **2** was prepared by alkylation of 3,3′-bicarbazolyl (**1**). The key starting material 3,3′-bicarbazolyl (**1**) was obtained by chemical oxidation of carbazole in the presence of $FeCl_3$ [14].

The reactions of **3** in THF solutions with 1,3-benzenedithiol and 4,4′-thiobisbenzenethiol at 60–65°C in the presence of a catalytic amounts of TEA yielded twin molecules **5** and **6**. In search for the



SCHEME 1 Synthetic route to compounds **3**, **4**, **5**, and **6**.

optimal solvent for these reactions, they were carried out in the solvents with different dipole moments, i.e. in 2-butanone and THF (Table 1). It was found that the rate of the reaction in THF was higher, and the higher yields of product **6** were obtained during the shorter periods of time. In addition, the solubility of **3** in 2-butanone was very poor.

TABLE 1 Influence of Solvents and Temperature on the Yield of Twin Compound **6**

Solvent	Dipole moment (25°C), [D]	Reaction time, [h]	Reaction temperature, [°C]	Product yield, [%]
2-Butanone	2.80	36	40	38
		48	40	40
THF	1.74	26	40	58
		8	65	76

Compounds **5** and **6** were purified by column chromatography. Their structures were confirmed by ^{1}H NMR-, IR-, and mass spectrometries. Since a 1,2-epoxypropan-3-yl group was attached, the characteristic NH stretches were not observed in the IR spectrum of **3**. In the synthesis of compounds **4**, **5**, and **6**, the strong IR absorption at 968 cm^{-1} due to the 1,2-epoxypropan-3-yl group which is observed in the IR spectrum of compound **3** disappears completely. The broad IR absorption at 3370–3535 cm^{-1} due to the hydroxyl group stretching appears in the spectra of twin compounds **5** and **6**. Compounds **3**, **4**, **5**, and **6** show the characteristic absorption of aromatic groups at 3050 cm^{-1} (C–H stretches), at 1575–1600 cm^{-1} and 1459–1488 cm^{-1} (C–C stretches), and absorption at 1290–1350 cm^{-1} due to C–N stretching.

The structures of the synthesized compounds were confirmed by ^{1}H NMR spectrometry. The split singlet at 8.46 ppm, ascribed to H-4 of 3,3′-bicarbazolyl fragment [14] is observed in the ^{1}H NMR spectrum of all the newly synthesized compounds (Fig. 1). The doublets of H-5 and H-5′ are at 8.26 ppm and 8.23 ppm. It is possible to distinguish the 4th, 5th, and 5′th proton signals not only in the spectrum of the monomer, but also in the spectrum of polymer **4**, where the peaks

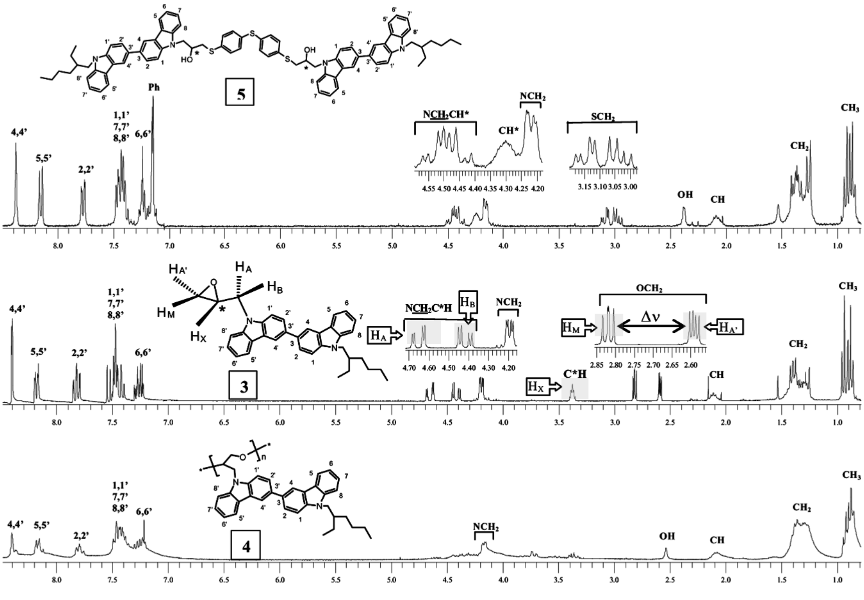


FIGURE 1 Proton signals in the ^{1}H NMR spectra (300 MHz, CDCl$_3$, δ, ppm) of **5**, **3**, and **4**.

are broadened due to the side-to-side interaction of 3,3′-bicarbazolyl monomeric units in macromolecules.

The signals of characteristic A′MX and ABX systems due to different CH_2 groups in the 1,2-epoxypropane ring and out of it, respectively, appear in the ^{1}H NMR spectrum of **3**. The signals in the 2.85–2.58-ppm region in the spectra of compound **3** confirm the existence of the characteristic A′MX ($\Delta\nu/J_{A'M} > 12$) system in the oxirane ring. The proton signals of A′MX and ABX systems of a 1,2- epoxypropan-3-yl group observed in the spectrum of 3-[9-(2-ethylhexyl)carbazol-3-yl]-9-(oxiran-2-ylmethyl)carbazole (**3**) disappear in the spectrum of oligomer **4** completely.

The signals of protons of a flexible aliphatic bridge connecting photoconductive fragments are well recognizable in the spectra of **5** and **6**. As an example, the ^{1}H NMR spectrum of **5** is given in Figure 1. Consequently, the above-mentioned protons appear after the reaction of oxirane with dithiol, forming the different environment for every proton in the alkyl spacer. The signals of the protons which are near the more electronegative nitrogen atom are shifted towards the lower fields to the 4.58–4.25-ppm region. The signals of the protons situated near the sulphur atom appear in the higher fields in the 3.2–2.98-ppm region of the ^{1}H NMR spectrum of compound **5** and in the 2.90–2.40-ppm region of the ^{1}H NMR spectrum of compound **6**. The doublet of O-H groups at 2.37 ppm in the spectrum of **5** shows that the desirable product was isolated. The signals confirming the existence of the characteristic A′MX system in the oxirane ring in the spectrum of compound **3** disappear in the spectra of compounds **5** and **6** completely, confirming the nucleophilic opening of the oxirane ring.

The thermal properties of the low-molar-mass compounds and the oligomer were examined using the DSC and TGA techniques. The glass transition (T_g, °C) and 5% weight loss (T_{ID}, °C) temperatures of the materials are summarized in Table 2.

TABLE 2 Thermal Characteristics of **3**, **4**, **5**, and **6**

Compound	T_g, [°C][a]	T_{ID}, [°C][b]
3	28	308
4	112	387
5	70	348
6	62	351

[a] Determined by DSC during the 1st and the 2nd heating, scan rate 20°C/min, N_2 atmosphere.

[b] The 5% weight loss temperature determined by TGA, heating rate 20°C/min, N_2 atmosphere.

All the synthesized 3,3′-bicarbazolyl-based compounds and even monomer (**3**) are capable of the glass formation. Neither melting nor crystallization peaks were observed in the DSC curves of these compounds. The presence of a relatively bulky bicarbazolyl fragment in these compounds apparently enhances their inclination to the glass formation. The influence of the rigidity of a linking spacer in twin compounds **5** and **6** on the value of their T_g is evident. The metasubstituted benzene spacer apparently allows the twisting of the molecules, and the numbers of conformers and modes of packing increase by leading to a lower T_g of **6** as compared to that of **5**. The increase in the molecular size due to the ring-opening polymerization leads to an increase of T_g. Oligoether **4** shows T_g higher by 85°C than that of the corresponding monomer (**3**). TGA experiments in nitrogen atmosphere revealed that all the synthesized compounds exhibit a high thermal stability. Their 5 % weight loss temperatures range from 308 to 387°C.

Optical, photophysical and photoelectrical properties of dilute solutions and films of compounds were investigated. The graphical representation of the absorption and emission spectra of dilute solutions of monomer **3**, polyether **4**, and the derivatives **5** and **6** are given in

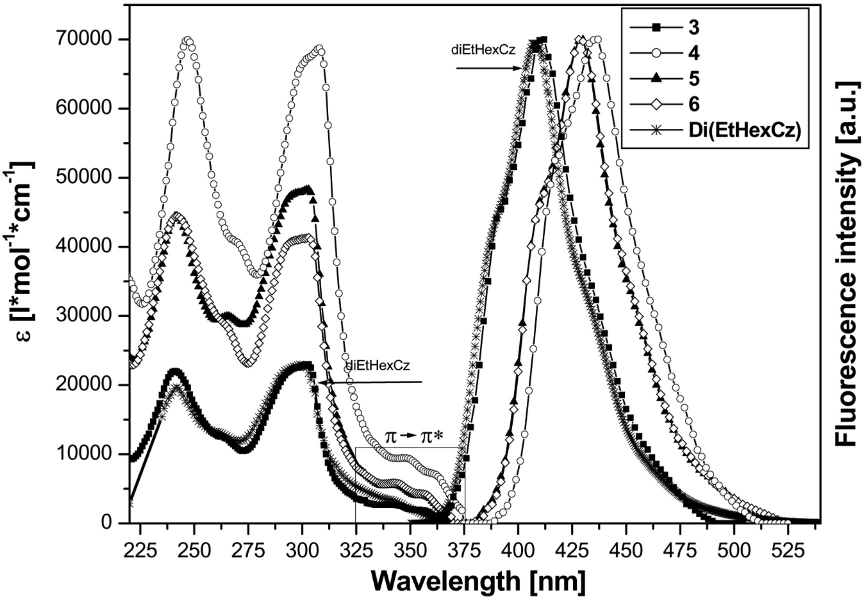


FIGURE 2 UV absorption and fluorescence spectra of the dilute THF solutions (10^{-5} mole/l) of **3**, **4**, **5**, and **6** ($\lambda_{ex} = 310$ nm).

TABLE 3 Optical Characteristics of Dilute Solutions in THF (10^{-5} mole/l) of **Di(EtHexCz)**, **3**, **4**, **5** and **6**

Compound	λ_{abs}, [nm]	λ_{em}, [nm][a]
3	241, 302, 345, 356	412
4	247, 308, 348, 360	437
5	242, 265, 303, 345, 356	430
6	242, 303, 345, 356	428
Di(EtHexCz)	242, 299, 344, 355	408

[a] $\lambda = 310$ nm.

Figure 2. The wavelengths of the absorption (λ_{abs}) and emission (λ_{em}) maxima of dilute solutions in THF are summarized in Table 3.

The absorption spectra of monomer **3**, oligomer **4**, and twin compounds **5**, **6** are similar to that of **Di(EtHexCz)**. They shows characteristic bands in the regions of 241–247, 299–308, and 325–375 nm. The last low-energy absorption bands are attributed to $\pi \rightarrow \pi^*$ transitions.

The absorption bands of oligomer (**4**) exhibit small bathochromic shifts ranging from 4 to 9 nm with respect of the absorption bands of **Di(EtHexCz)**. Such shifts of absorption bands could occur due to the interaction between monomer units in the macromolecule.

The UV spectra of compound **5** revealed a additional small absorption band with the maximum at 265 nm due to 4,4′-dimercaptobisbenzenethiol functionality present in the molecule.

The emission spectra of the dilute solution of twin compounds (**5**, **6**) and oligoether (**4**) exhibit considerable bathochromic shifts of 16–25 nm with respect of the spectrum of monomer (**3**). This is apparently due to the presence of intermolecular excimer-forming sites in oligomer **4** and twin compounds (**5**, **6**). The excited polymeric species occupy lower energy levels due to the formation of excimers. Therefore, the emission bands of dilute solutions of monomer **3**, on the one hand, and of oligomer **4**, as well as of twin compounds (**5**, **6**) on the other hand, are in different regions. These facts show that the behavior of the 3,3′-bicarbazolyl-containing oligoether is different from that of the earlier reported carbazolyl-containing oligoethers [15]. Carbazolyl-containing derivatives showed only the monomer emission, which means that excimer formation centers do not exist in such macromolecules. In the case of 3,3′-bicarbazolyl-containing twins **5** and **6**, the formed excimers are higher in energy as compared with the excimers of oligoether **4** (cf. the data in Table 3). One of the possible explanations of the different photophysical behavior of 3,3′-bicarbazolyl-containing oligoether and the twin molecules can be the possibility

TABLE 4 Ionization Potentials of the Films of Compounds **3**, **4**, **5**, **6** and **PEPK**

Compound	**Di(EtHexCz)**	**3**	**4**	**5**	**6**	**PEPK**
$\boldsymbol{I}_{\mathbf{p}}$, [**eV**]	5.5	5.5	5.5	5.5	5.5	5.9

for relatively bulky 3,3′-bicarbazolyl species linked by relatively flexible spacers to overlap.

The values of I_p of the materials described in this section are given in Table 4. For the comparison, the values of I_p of **Di(EtHexCz)** and **PEPK** [16] are given as well.

Compounds **3–6** demonstrate the same values of I_p as **Di(EtHexCz)** and lower than that of **PEPK**. From the viewpoint of I_p values, the reported compounds are applicable as hole transport materials in electrophotographic photoreceptors.

The time-of-flight technique was used to study the charge transport properties of compounds **3**, **5**, and **6**. The linear dependences of hole

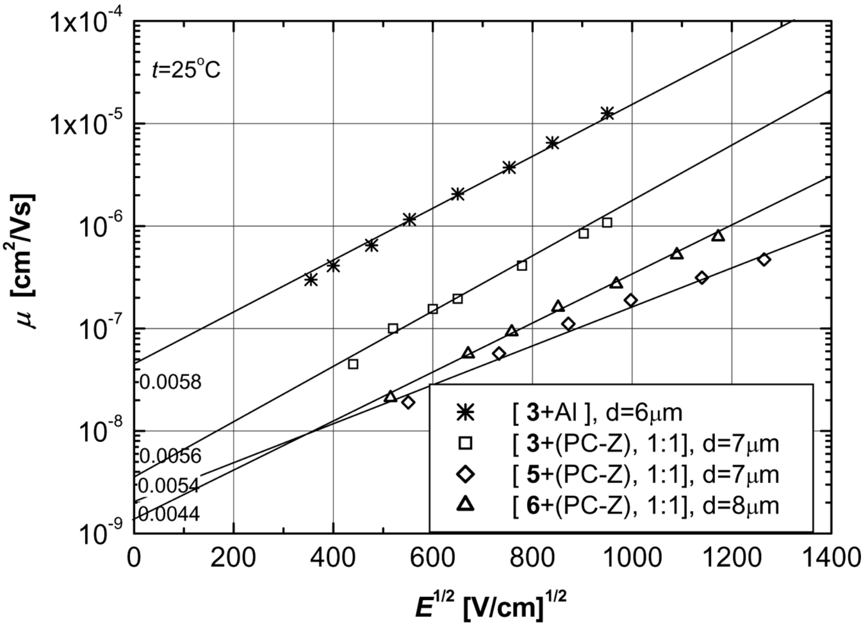


FIGURE 3 Electric field dependences of the drift mobility of holes for 50% solid solutions in PCZ of compounds **3**, **5**, and **6** and for the amorphous film of pure **3**.

TABLE 5 Hole Drift Mobility Data for an Amorphous Film of **3** and the Solid Solutions of **3**, **5**, **6** in PC-Z

Transport material: host polymer	μ_0, [cm^2/Vs]	μ, [cm^2/Vs]
3 + Al	4.6×10^{-8}	5.0×10^{-6}
3 + PC-Z, 1:1	3.6×10^{-8}	4.7×10^{-7}
5 + PC-Z, 1:1	2×10^{-9}	7×10^{-8}
6 + PC-Z, 1:1	1.5×10^{-9}	1.1×10^{-7}

drift mobilities on the square root of the electric field strength were observed for all the systems under study (Fig. 3).

The zero field mobilities (μ_0) and the mobilities at a field of 6.48×10^5 V/cm ($\boldsymbol{\mu}$) are given in Table 5. The hole mobility values for compounds **3**, **5**, and **6** molecularly doped in the PC-Z range from 10^{-7} to 1.16×10^{-6} cm^2/Vs at high electric fields and are a little lower than those for the systems based on carbazole-containing compounds [6]. Rather low charge mobilities in molecularly doped polymers containing **3**, **5**, and **6** can apparently be explained by the unfavourable (non-planar) configuration of the relatively big molecules which causes an increase of the molecular or energy disorder in the molecular mixture of these materials with the polymer host.

The charge mobility of the amorphous film of pure **3** was 1.26×10^{-5} cm^2/Vs at 9.0×10^5 V/cm electric fields, i.e. by one order of magnitude higher than that of the molecular mixture with PC-Z (cf. the data presented in Fig. 3).

In conclusion, we have synthesized new oxiranyl-substituted 3,3′-bicarbazolyl derivatives which exhibit a good thermal stability with 5% weight loss temperatures exceeding 308°C and form amorphous films with glass transition temperatures ranging from 28 to 112°C. The electron photoemission spectra of the materials revealed the ionization potentials of ca. 5.5 eV for the synthesized compounds. Time-of-flight hole drift mobilities of the amorphous films of 9-(2-ethylhexyl)-3-[9-(oxiran-2-ylmethyl)carbazol-3-yl]carbazole exceed 10^{-5} cm^2/Vs at high electric fields.

REFERENCES

[1] Akhmedov, K. M., Karimov, K. S., Scherbakova, I. M., Porshnev, Yu. N., & Cherkashin, M. I. (1990). *Russ. Chem. Rev.*, *59*, 425.

[2] Pisarski, W. A., Swinarew, A. S., Czaja, M., Piekarnik, B., Grobelny, Z., Getautis, V., Grazulevicius, J. V., Niedziela, T., Trzebicka, B., & Stolarzewicz, A. (2008). *J. Mol. Struct.*, 887, 205.

[3] Gaidelis, V., Krisciunas, V., & Montrimas, E. (1976). *Thin Solid Films*, *38*, 9.

[4] Sasabe, H. & Wada, T. (1989). In: *Comprehensive Polymer Science*, Allen, G. & Bevington, J. (Eds.), Pergamon Press: Oxford.

[5] Kutkevičius, S., Stanišauskaitė, A., Getautis, V., Railaité, A., & Uss, S. (1995). *J. Prakt. Chem.*, *337*, 315.

[6] Daškevičiené, M., Getautis, V., Gražulevičius, J. V., Stanišauskaitė, A., Antulis, J., Gaidelis, V., Jankauskas, V., & Sidaravičius, J. (2002). *J. Imag. Sci. Techn.*, *46*, 467.

[7] Mas, C., Serra, A., Montecon, A., Salla, J. M., & Ramis, X. (2001). *Macromol. Chem. Phys.*, *202*, 2554.

[8] Aspinall, H. C., Dwyer, J. L. M., Greeves, N., McIver, E. G., Woole, J. C. (1998). *Organometalics*, *17*, 1884.

[9] Miyamoto, E., Yamaguchi, Y., & Yokoyama, M. (1989). *Electrophotography*, *28*, 364.

[10] Kirkus, M., Lygaitis, R., Tsai, M.-H., Grazulevicius, J. V., Wu, C.-C. (2008). *Synth. Met.*, *158*, 226.

[11] Ostrauskaite, J., Voska, V., Buika, G., Gaidelis, V., Jankauskas, V., Janeczek, H., Sidaravicius, J. D., & Grazulevicius, J. V. (2003). *Synth. Met.*, *138*, 457.

[12] Visciakas, J., Gaidelis, V., Montrimas, E., & Pocius, Z. (1966). *Lietuvos fizikos rinkinys*, *6*, 77.

[13] Beginn, C., Grazulevicius, J. V., Strohriegl, P., Simmerer, J., Haarer, D. (1994). *Macromol. Chem. Phys.*, *195*, 2353.

[14] Vaitkeviciene, V., Grigalevicius, S., Grazulevicius, J. V., Jankauskas, V., & Syromyatnikov, V. G. (2006). *Eur. Polym. J.*, *42*, 2254.

[15] Gražulevičius, J. V., Soutar, I., & Swanson, L. (1998). *Macromolecules*, *31*, 4820.

[16] Grigalevicius, S., Blazys, G., Ostrauskaite, J., Grazulevicius, J. V., Gaidelis, V., & Jankauskas, V. (2003). *J. Photochem. Photobiol., A*, *154*, 161.