

**KAUNAS UNIVERSITY OF TECHNOLOGY**

**Ingrida Vilionskienė**

**SYNTHESIS AND PROPERTIES OF CHARGE  
TRANSPORTING MOLECULAR GLASSES POSSESSING  
HYDRAZONE, AZINE AND ANTHRAQUINONE MOIETIES**

Summary of the Doctoral Dissertation

Physical Sciences, Chemistry (03P)

**KAUNAS, 2005**

The research was carried out at Kaunas University of Technology, Department of Organic Chemistry in the period of 2000-2004. It was supported by Lithuanian State Science and Studies Foundation.

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The official presentation of the Dissertation will be held at the open meeting of the Council of Chemistry sciences trend at 11 a. m. on May 24, 2005 in the Dissertation Defence Hall at the Central building of Kaunas University of Technology (K. Donelaičio g. 73 - 403, Kaunas).

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The send out date of the summary of the Dissertation is 20 March, 2005.

The Dissertation is available at the library of Kaunas University of Technology (K. Donelaičio g. 20, Kaunas).

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DARINIŲ SINTEZĖ IR SAVYBĖS**

Daktaro disertacijos santrauka

Fiziniai mokslai, chemija (03P)

**KAUNAS, 2005**

Disertacija parengta 2000-2004 metais Kauno technologijos universiteto Cheminės technologijos fakultete, Organinės chemijos katedroje. Mokslinius tyrimus rėmė Lietuvos mokslo ir studijų fondas.

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Disertacija bus ginama viešame Chemijos mokslo krypties tarybos posėdyje, kuris įvyks 2005 m. gegužės 24 d. 11 val. Kauno technologijos universitete, Centrinųjų rūmų Disertacijų gynimo salėje (K. Donelaičio g. 73 - 403, Kaunas).

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Su disertacija galima susipažinti Kauno technologijos universiteto bibliotekoje (K. Donelaičio g. 20, Kaunas).

## Introduction

Recently, the application of various organic compounds has been started in such areas, where inorganic compounds were predominating until now. Investigating of photoquantum, optical, electric properties of low-molecular mass organic compounds, especially those forming stable amorphous state, revealed earlier unknown features, which afforded the beginning of their usage in the production of diverse photonic and optoelectronic devices. This was just the beginning of the application of organic compounds in these areas, thus the improvement of the properties of the materials already known and the investigation of the synthesis of the new ones are very relevant.

Depending on their properties and, particularly, their electronic structure, electronically active low-molecular mass compounds, used in various photonic and optoelectronic devices are classified as follows:

- hole-transporting materials;
- electron-transporting materials;
- materials transporting carriers of both charges.

Organic charge-transporting materials are divided into polymers and low-molar mass film-forming materials, which are called molecular glasses. Both polymers and molecular glasses have their own advantages and shortcomings. Polymers exhibit good mechanical properties and can be used for the preparation of flexible devices. However synthesis and purification of polymers is fairly complicated. It is possible to synthesize a large variety of molecular glasses with different functional groups and different properties. Their purification can be carried out by the conventional techniques of preparative organic chemistry such as crystallization, adsorption chromatography, sublimation. Unfortunately many of molecular glasses exhibit low morphological stability, i.e. often they show inclination to crystallize.

At the Department of Organic Chemistry of Kaunas University of Technology branched hydrazone dimers with hydroxygroups were synthesized by interaction of N-2,3-epoxypropyl derivatives of photoconductive chromophores with various bifunctional nucleophiles. The hydroxygroups of the obtained dimers make good adhesion and compatibility with various polymeric binders, such as polycarbonate or polyvinylbutyral. These original molecules can be cross-linked together through hydroxygroups, for example, with the help of polyisocyanates, or they can be linked to the polymeric binder polyvinylbutyral, thus becoming the constituent of a polymer. This is very important in the case of using the liquid developer. Thus formed organic photoreceptor becomes resistant to organic solvents, bending and stretching.

The aims of the work were as follows:

- synthesis of branched dimers with stable amorphous state possessing thiophenylsulphide, sulphide and hydroxygroups in the linking fragment of chromophores from aromatic and heteroaromatic alde-

hyde phenylhydrazones. A thorough study of physical and optoelectrographic properties of these charge-transporting compounds;

- synthesis of new crosslinkable charge transporting molecular glasses exhibiting high charge carrier mobilities, high morphological stability;
- design and synthesis of new hole transporting molecular glasses and polymers (from 9-(2,3-epoxypropyl)carbazole);
- investigation of the interaction of 1(2)-aminoanthraquinone and 1-chloro-2,3-epoxypropane (CEP) with the aim to use the products for the creation of hydroxygroups possessing electron-transporting materials, having stable amorphous state.

The main results reflecting the novelty, originality and significance of the present investigation are the following:

- a thorough study of physical and optoelectrographic properties of the crosslinkable branched hydrazone dimers, which were synthesized by the reaction of 9-ethyl-3-carbazole-, julolidin-9-carbaldehydes, 4-diethylamino-, 4-benzylethylamino-, 4-(diphenylamino)- and 4-(4,4'-dimethyldiphenylamino)benzaldehydes phenylhydrazones N-2,3-epoxypropyl derivatives with 4,4'-thiobisbenzenethiol, dimer-captoalkanes, hydrogen sulfide was carried out;
- an effective method (using thioacetamide as a source of H<sub>2</sub>S) was proposed for the synthesis of the branched hydrazone dimers possessing OH- and -S- groups in the chromophores linking fragment.
- new molecular glasses possessing various chromophores connected via azine linkage were synthesized and investigated for electrophotography;
- an alternative method (without using 1-chloro-2,3-epoxypropane) was proposed for obtaining molecular glasses possessing hydroxy-group;
- new hole transporting molecular glasses and polymers were designed and synthesized from 2,3-(epoxypropyl)carbazole;
- a novel class of crosslinkable electron transporting molecular glass possessing anthraquinone moiety was synthesized.

## 1. Branched hydrazones - hole transporting materials

A novel class of well defined hole-transporting materials (TM), obtained by the reaction of oxiranes containing photoconductive groups with different bifunctional nucleophiles, was developed at the department of Organic Chemistry in Kaunas University of Technology. Such branched hydrazone compounds were synthesized by the reaction of N-2,3-epoxypropyl-N-phenylhydrazones, possessing N,N-diethylaniline, N,N-benzylethylaniline, N-ethylcarbazole and dimethyltriphenylamine chromophores, with different linking agents, for example, benzenediols or aromatic dimercapto compounds. The molecules of these

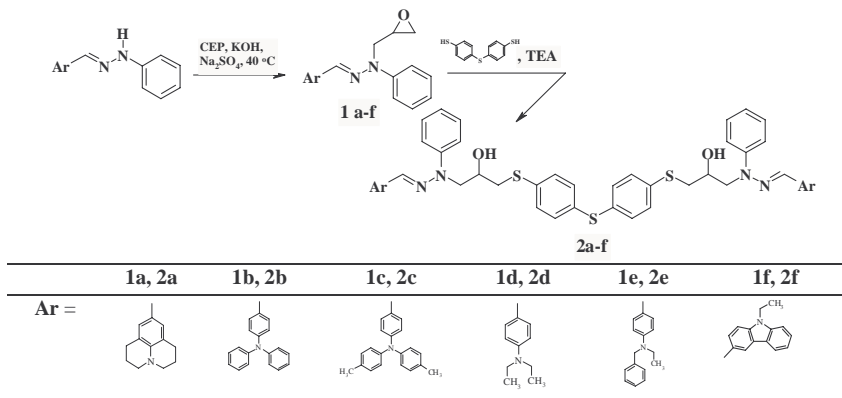
TM consist of two hydrazone branches linked by the central flexible bridge. The existence of several diastereoisomers, the possibility of intermolecular hydrogen bonding and flexibility of aliphatic linking chains make crystallization in solid state difficult, so these materials are molecular glasses. Another peculiarity of these TM is the presence of two hydroxygroups in the molecule. This improves adhesion and compatibility not only with traditional polycarbonate (PC) binder material (BM) but also with polyvinylbutyral (PVB). Meanwhile, such branched hydrazone dimers can be chemically crosslinked in the layer, for example, by reaction of the hydroxygroups with polyisocyanates. These branched hydrazone properties increase the layer stability to bending and stretching of electrophotography belts and the effects of liquid developer. The synthesized TM and compositions with binder exhibit good hole transporting properties and high mobility making them useful for preparation of high sensitivity electrophotographic photoconductors.

### 1.1. Branched hydrazones, possessing a thiophenylsulfide moiety

The goal of this work was to make a thorough study of the branched arom- and heteroaromaldehyde phenylhydrazones, obtained by the reaction of N-2,3-epoxypropyl derivatives with 4,4'-thiobisbenzenthiole, making an attempt to find out the dependence of the drift mobility of synthesized organic photoconductors as well as the stability of glassy state on the structure.

#### 1.1.1. Synthesis

A series of N-2,3-epoxypropylated N-phenylhydrazones **1a-f** was prepared by reaction of the corresponding N-phenylhydrazones of julolidin-9-carbaldehyde, 4-(diphenylamino)-, 4-(4',4'-dimethyldiphenylamino)-, 4-(diethylamino)-, 4-(benzylethylamino)benzaldehydes, 9-ethyl-3-carbazolecarboxaldehyde with 1-chloro-2,3-epoxypropane in the presence of KOH and anhydrous Na<sub>2</sub>SO<sub>4</sub>.



Scheme 1

The branched hydrazone compounds **2a-f**, with flexible central thiophenyl sulphide containing bridge, were prepared by the reaction of 4,4'-thiobisbenzenethiol with 2 equivalents of corresponding *N*-2,3-epoxypropyl derivative **1a-f** in the presence of catalyst triethylamine (TEA): bis{4,4'-[6-(julolidine-4-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]phenyl} sulphide (**2a**), bis{4,4'-[6-(4-(diphenylamino)benzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]phenyl} sulphide (**2b**), bis{4,4'-[6-(4-(4,4'-dimethyldiphenylamino)benzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]phenyl} sulphide (**2c**), bis{4,4'-[6-(4-(diethylamino)benzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]phenyl} sulphide (**2d**), bis{4,4'-[6-(4-(benzylethylamino)benzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]phenyl} sulphide (**2e**), bis{4,4'-[6-(9-ethyl-carbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-thiahexyl]phenyl} sulphide (**2f**).

### 1.1.2. Thermal analysis\*

The formation of the glassy state in **2a-f** was confirmed by differential scanning calorimeter (DSC) at the heating-cooling regime (10 K/min). Monocrystalline TMs were heated twice: during the first heating cycle was determined melting point ( $T_m$ ), and during the second heat – glass transition temperature ( $T_g$ ). Polycrystalline materials were heated three times: during the first heating cycle was determined  $T_{m1}$  crystal form with lower melting temperature; during the second heating -  $T_{g1}$  produced by melting of the lower melt transition and a  $T_{m2}$  of second crystal form; during the third heating cycle was determined  $T_{g2}$  of the metastable glass phase. Table 1 lists the melting and glass transition temperatures for **2a-f** in this study.

The **2d** sample produced endothermic melting transition at 155 °C during the first heating cycle, did not subsequently recrystallized when cooled, and exhibited a glass transition temperature of 54 °C during the heating leg of the second cycle. Thermal analysis indicates that this material formed a metastable glass phase for the time period of this thermal investigation. This is a common feature for all of investigated **2a-e**, with the exception of **2f**.

**Table 1.** The data of DSC analysis of **2 a-f**

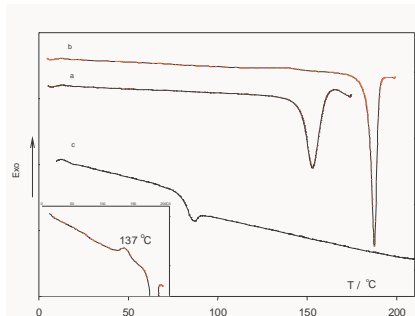
TM	$T_{m1}$ , °C	$T_{g1}$ , °C	$T_{m2}$ , °C	$T_{g2}$ , °C
<b>2a</b> <sup>a</sup>	94	71	120	75
<b>2b</b> <sup>a</sup>	134	82	188	83
<b>2c</b> <sup>a</sup>	83	85	126	83
<b>2d</b>	155	54	---	---
<b>2e</b>	118	51	---	---
<b>2f</b> <sup>a</sup>	147	78	184	84
	(recry. 149 °C; 23 %) <sup>b</sup>	very weak	(recry. 137 °C; 6 %) <sup>c</sup>	

<sup>a</sup> Exhibits polymorphism. <sup>b</sup>Recrystallization exothermic transition during cooling. <sup>c</sup>Recrystallization exothermic transition during heating.

\* Analysis were carried out at the Digital Printing Solutions Laboratory, USA, by Dr. Z. Tokarski.



The presence of rigid N-ethylcarbazolyl groups in **2f** increased the  $T_g$  by 30 °C over the  $T_g$  of **2d**. A very weak  $T_g$  was observed at 78 °C during the second heat leg that was not visible during the third heat leg (Fig. 1). Also, two small exothermic transitions were observed.



**Fig. 1.** DSC curves of **2f**. Curve (a) is for the first heat through the lower left transition; curve (b) is for the second heat through the second melt transition; curve (c) is for the third heat. The insert shows the recrystallization exotherm in curve (b).

The onset temperatures for the exothermic transitions occurred at 149 °C and 137 °C during the first cooling and the subsequent heating legs, respectively. If these exothermic transitions were the result of recrystallization of the material phase that melted at 147 °C during the first heat leg then these cooling and heating exotherms represents 23% and 6% recrystallization of the melted material at 147 °C, respectively. No subsequent exothermic transitions (recrystallizations) were observed following the melting of the second transition at 184 °C, i.e., no exothermic transitions were observed during

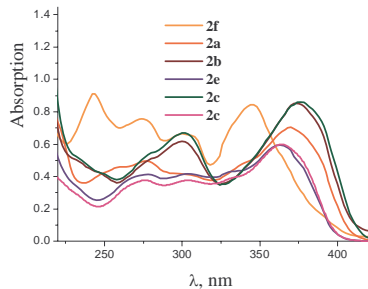
the second cooling or the third heat legs.

The DSC data demonstrated that the  $T_g$  increased as the molecular size and weight of the **2a-f** increased (compare **2d** with **2f** and **2b** with **2c**) and the branched hydrazones **2a-c** and **2f** displayed polymorphism.

The DSC analysis of investigated branched hydrazones **2a-f** demonstrated that the hydrazone dimer **2f** possessing ethylcarbazolyl chromophore indicates less stable glassy state as others exhibit stable glassy state.

### 1.1.3. Electrophotographic parameters

The light absorption spectra of the branched hydrazones **2a-f** are presented in the Figure 2. The largest shift of absorption to longer wavelengths was



observed for TM with triphenylamine moieties **2b,c**. On the other hand, julolidine containing hydrazone **2a** exhibits bathochromic shift compared with diethylaniline (**2d**), benzylethylaniline (**2e**) and ethylcarbazole (**2f**) chromophores containing TM.

**Fig. 2.** Light absorption spectra of **2a-f** in  $\text{CH}_3\text{CN}$ ,  $c = 10^{-4}$  mol/l,  $d = 1$  mm

The ionisation potentials ( $I_p$ ) of investigated **2a-f** were measured by the photoemission in air method and  $I_p$  values are presented in Table 2\*.

**Table 2.** Drift mobility and ionisation potential measurement data

Layer composition	$\mu_0$ , (cm <sup>2</sup> /Vs)	$\mu$ , (cm <sup>2</sup> /Vs)**	$I_p$ , eV	Layer composition	$\mu_0$ , (cm <sup>2</sup> /Vs)	$\mu$ , (cm <sup>2</sup> /Vs)**	$I_p$ , eV
<b>2a</b>	6.0·10 <sup>-8</sup>	4.7·10 <sup>-6</sup>	5.03	<b>2c</b> +PVB1, 1:1	1.8·10 <sup>-7</sup>	7.6·10 <sup>-6</sup>	-
<b>2a</b> +PVB1, 1:1	2.9·10 <sup>-9</sup>	2.4·10 <sup>-7</sup>	-	<b>2c</b> +PVB1 +DEL, 70:15:15	1.8·10 <sup>-7</sup>	4.0·10 <sup>-6</sup>	-
<b>2b</b>	5.10 <sup>-6</sup>	2.6·10 <sup>-4</sup>	5.34	<b>2d</b>	2.2·10 <sup>-7</sup>	2.3·10 <sup>-5</sup>	5.10
<b>2b</b> +PVB1, 1:1	4.6·10 <sup>-8</sup>	1.5·10 <sup>-6</sup>	-	<b>2d</b> +PVB1, 1:1	1.2·10 <sup>-8</sup>	1.6·10 <sup>-6</sup>	-
<b>2b</b> +PVB2, 1:1	5.5·10 <sup>-8</sup>	2.0·10 <sup>-6</sup>	-	<b>2d</b> +PVB1 +DEL, 70:15:15	5.0·10 <sup>-9</sup>	1.0·10 <sup>-6</sup>	-
<b>2b</b> +PVB3, 1:1	5.8·10 <sup>-8</sup>	1.8·10 <sup>-6</sup>	-	<b>2e</b>	3.8·10 <sup>-7</sup>	1.7·10 <sup>-5</sup>	5.24
<b>2b</b> +PVB4, 1:1	6.3·10 <sup>-8</sup>	2.5·10 <sup>-6</sup>	-	<b>2e</b> +PVB1, 1:1	1.3·10 <sup>-8</sup>	5.8·10 <sup>-7</sup>	-
<b>2b</b> +PC-Z, 1:1	1.7·10 <sup>-7</sup>	4.9·10 <sup>-6</sup>	-	<b>2f</b>	1.3·10 <sup>-7</sup>	1.3·10 <sup>-5</sup>	5.38
<b>2b</b> +PVB1 +DEL, 70:15:15	1.0·10 <sup>-7</sup>	1.9·10 <sup>-6</sup>	-	<b>2f</b> +PVB1, 1:1	2.8·10 <sup>-9</sup>	5.2·10 <sup>-7</sup>	-
<b>2c</b>	9.0·10 <sup>-6</sup>	4.7·10 <sup>-4</sup>	5.21	<b>2f</b> +PVB1 +DEL, 70:15:15	1.6·10 <sup>-9</sup>	6.0·10 <sup>-7</sup>	-

\*\* at 6.4·10<sup>5</sup> V/cm electric field.

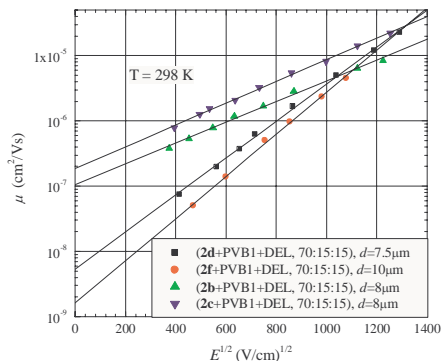
The lowest values of  $I_p$  are for the **2a** and **2d** with julolidine and diethylaniline groups. The largest values are for **2f** and **2d** with carbazole or triphenylamine groups. Ionisation potential shows tendency to decrease with increasing number of aliphatic substituents.

The drift mobility\* of branched hydrazones was measured by xerographic time of flight technique. Samples were prepared from neat TM and from 1:1 mass proportion compositions of them with various BM. The various types of polyvinylbutyral and polycarbonate include PVB1 from Aldrich PVB 41,843-9 with average  $M_w=70,000 - 100,000$  and 18-20 wt. % of hydroxygroups; PVB2 from Sekisui S-LEC B BX-1; PVB3 from Sekisui S-LEC B BX-5; PVB4 from Solutia PVB B-79 with average  $M_w=50,000 - 70,000$  and 10.5-13 wt. % of hydroxygroups; and PC-Z from Mitsubishi Gas Chemical Co. polycarbonate Iupilon Z-200. The crosslinked samples were prepared from composition of TM, PVB1 and polyisocyanate Desmodur L75 of Bayer AG (DEL) in wt.

\* Measurements were carried out in the research group of Prof. E. Montrimas at the Faculty of Physics, Vilnius University by Habil. Dr. V. Gaidelis and Dr. V. Jankauskas.

proportion 70:15:15. The dependence of the drift mobility on the electric field strength are given in Table 2 and Fig. 3.

As seen from the results presented the mobility value is influenced by the charge TM chromophore nature. The highest mobility values are with chromophores based on triphenylamine (**2b**) and dimethyltriphenylamine (**2c**) moieties. This is natural because conjugated  $\pi$ -electron systems are largest in these chromophores.



**Fig. 3.** Mobility field dependencies in cross-linked compositions

of **2a-f** with BM is considerably lower as compared with neat TM. The difference makes up to two orders of magnitude. The highest mobility among the **2b** composition, as one can see from Table 2, is in the case of polycarbonate BM. Mobility in this case is by more than by two order of magnitude higher than in compositions with various sorts of PVB. The hydroxygroups present in PVB, probably, cause this. However, special properties of PVB due to presence of hydroxygroups, such as good adhesion, stability to bending and stretching and effects of liquid developer may outweigh loss of mobility.

The drift mobility data of **2a-b** cross-linked compositions with polyisocyanate Desmodur L75 are presented in Table 2 and Figure 3. The mobility values at strong electric field, as rule, are close to the values in the compositions with PVB. However, concentration of TM in the uncrosslinked compositions is 50 wt. % while it is 70 wt. % in crosslinked compositions. This means that crosslinking is effecting mobility more than does simple admixture of BM.

So, the best before discussed feature exhibit the branched hydrazone dimers possessing dimethyltriphenylamine (**2c**) and triphenylamine (**2b**) chromophores. Cheap raw material of last-mentioned synthesis determined that **2b** was used in tests of organic photoreceptor. During creation of a new organic photoreceptor, in our laboratory was synthesised 300 g of **2b**.

## 1.2. Branched hydrazones, possessing an aliphatic chromophores linking fragment

In the previous chapter there have been discussed arom- and hetaromalde-

phores. Aliphatic groups attached directly to the chromophore lead to increased mobility. However, chromophore size seems not always to be the decisive factor determining mobility. So chromophore of **2f** with carbazole ring is large as chromophore of **2d** with diethylaniline, but mobility is higher in **2d**. It is necessary to note that mobility in the TM investigated as well as compositions of them with BM is large enough for practical application in many cases.

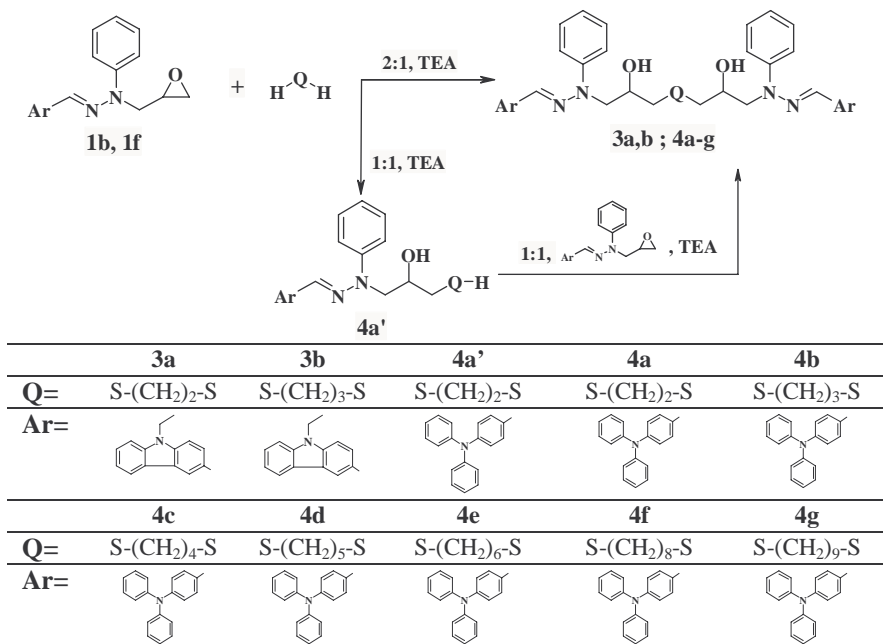
Mobility in the compositions

hyde phenylhydrazone dimers of stable glassy state, having aromatic rings in the chromophores linking fragment. The electrographic properties of these organic photoconductors are mostly determined by a  $\pi$ -conjugated electrons, while chromophores linking fragments make a greater influence upon the physicochemical properties of these TM.

The aim of the work in this part was to synthesize the branched hydrazones, in order to investigate how the aliphatic, chromophores linking fragment, of a various structure, influences the glassy state and charge carry of the TM.

### 1.2.1. Branched hydrazones, obtained by the use of dimercaptoalkanes

As the interest was based more on the influence of the chromophores linking fragment towards the properties of TM, for the synthesis of the branched hydrazones there were chosen only two epoxypropylated phenylhydrazones, i.e. **1b** and **1f**, having triphenylamine and ethylcarbazolyl chromophores. The nucleophilic opening of the oxirane ring in the hydrazones **1b** and **1f** with 1,2-ethan-, 1,3-propan-, 1,4-butan-, 1,5-pentan-, 1,6-hexan-, 1,8-octan-, 1,9-nonan-dithiol in the presence of the catalyst TEA at the reflux of butanone gave new TM **3a,b** and **4a-g**, where there is no aromatic rings in the chromophores linking fragment (scheme 2).



Scheme 2

The obtained structures of dimers was proved by the data of elemental and spectral analysis as well as the intermediate 1-[4-(diphenylamino)benzyliden]-2-(2-hydroxy-6-mercapto-4-tiahexyl)-2-phenylhydrazine (**4a'**) synthesis. By interaction of 4-(diphenylamino)benzaldehyde-N-2,3-epoxypropyl-N-phenylhydrazine with excess of 1,2-ethanedithiol in the presence of TEA at the reflux of butanone monosubstituted 1,2-ethanedithiol **4a'** was isolated. **4a'** under the same conditions was transformed into the appropriate TM **4a**.

The branched hydrazones **3a,b**, i.e. dimers, possessing carbazolyl chromophore, were obtained as crystallin materials. In the case of triphenylamine chromophore, the crystalline product was obtained only by linking chromophores with the shortest dimercapto compound 1,2-ethanedithiol. Thus, the present of rigid 9-ethylcarbazolyl groups increase the crystallization of the synthesized branched hydrazones. In all other cases, all our attempts to crystallize **4b-g** were unsuccessful. These hydrazone dimers were purified by column chromatography with the following pouring a 20% solution of **4b-g** into a tenfold excess of hexane.

The formation of the glassy state in the investigated TM **3a,b**, **4a-g** was confirmed by DSC analysis. During the DSC analysis the temperatures of melting and glass transition were determined (Table 3). The investigations have revealed that some dimers have both crystalline and amorphous state, while others are found only in amorphous state.

**Table 3.** The data of DSC analysis of **3a,b**, **4b-g**

TM	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$	TM	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$
<b>3a</b>	69	174 and 181	<b>4d</b>	47	-
<b>3b</b>	73	102 and 107	<b>4e</b>	51	-
<b>4a</b>	45	76	<b>4f</b>	46	61
<b>4b</b>	54	62	<b>4g</b>	40	61
<b>4c</b>	50	63			

From the given data in the Table 3, it is seen that hydrazone dimer chromophores have influence not only upon the crystallization of TM, but also upon the glass transition temperature. The data shows that dimers **3a,b** with 9-ethylcarbazole chromophores are displayed polymorphism, whereas TM **4a,b** possessing triphenylamine chromophore and the same linking fragments - just one crystalline form. The rigid 9-ethylcarbazolyl groups increase the glass transition temperatures of compounds about 19-24 °C in comparison to **3a** with **4a** and **3b** with **4b**. On the other hand, the linking fragment has a significant influence on the glass transition temperatures of the investigated TM: becoming the distance between chromophores bigger, i. e. a dimercapto chain longer, the glass transition temperature is obviously decreasing.

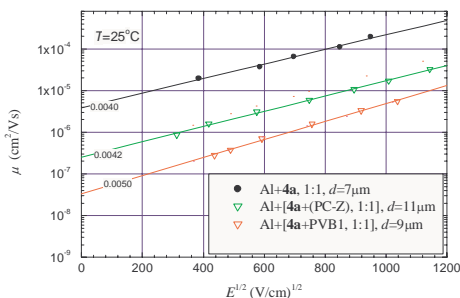
The presence of hydroxygroups in these TM, improves the compatibility not only with a traditional PC binder material but also with PVB. That is why the samples for measurements were prepared in compositions with PVB. The

results of the drift mobility dependences on the electric field strength of TM **3a,b**, **4a-g** are presented in Table 4.

**Table 4.** Drift mobility measurement data in electrographic compositions of **3a,b**, **4a-g**

Layer composition	$\mu_0$ , (cm <sup>2</sup> /Vs)	$\mu$ , (cm <sup>2</sup> /Vs)*	Layer composition	$\mu_0$ , (cm <sup>2</sup> /Vs)	$\mu$ , (cm <sup>2</sup> /Vs)*
<b>3a</b> +PVB1, 1:1	$7.0 \cdot 10^{-9}$	$1.3 \cdot 10^{-6}$	<b>4d</b> +PVB1, 1:1	$8 \cdot 10^{-8}$	$2.8 \cdot 10^{-6}$
<b>3b</b> +PVB1, 1:1	$2 \cdot 10^{-9}$	$4.2 \cdot 10^{-7}$	<b>4e</b> +PVB1, 1:1	$8 \cdot 10^{-8}$	$2.2 \cdot 10^{-6}$
<b>4a</b> +PVB1, 1:1	$3.6 \cdot 10^{-8}$	$1.8 \cdot 10^{-6}$	<b>4f</b> +PVB1, 1:1	$9 \cdot 10^{-9}$	$3 \cdot 10^{-7}$
<b>4b</b> +PVB1, 1:1	$1.2 \cdot 10^{-7}$	$5 \cdot 10^{-6}$	<b>4g</b> +PVB1, 1:1	$2.6 \cdot 10^{-8}$	$2 \cdot 10^{-6}$
<b>4c</b> +PVB1, 1:1	$4.5 \cdot 10^{-8}$	$1.5 \cdot 10^{-6}$	* at $6.4 \cdot 10^5$ V/cm electric field		

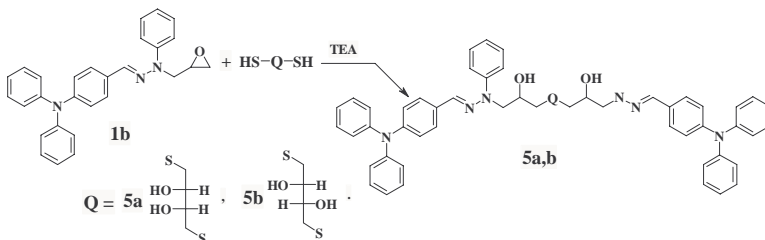
From the data it is clear that the chromophore makes the greatest influence upon the drift mobility charge (compare **3a** with **4a** and **3b** with **4b**). As it was expected, the chromophores linking fragment does not have much influence on the drift mobility (except the case of **4f**). In all hydrazone dimer compositions with PVB, the drift mobility is quite high and it reaches  $10^{-6}$  cm<sup>2</sup>/Vs at  $10^5$  V/cm electric field. As it can be observed from Fig. 4, the mobility in the compositions of **4a** with BM, is considerably lower as compared with neat TM. Also the mobility value in the compositions of **4a** with PC is by one order of magnitude higher compared with PVB.



**Fig. 4.** Hole mobility dependencies in neat **4a** and its 1:1 compositions with PC-Z and PVB1

### 1.2.2. Synthesis and properties of charge-transporting hydrazone dimers with the increased number of hydroxygroups

Based on the developed method, by interaction of epoxypropylated hydrazone **1b**, with *erythro*-1,4-dimercapto-2,3-butanediol 1,4-bis{6-[4-(diphenyl-



**Scheme 3**

mino)benzylidene]-3-hydroxy-5-phenyl-5,6-diaza-1-tiahexyl} *eritro*-2,3-butenediol (**5a**) was synthesized (scheme 3). **5a** was purified by crystallization followed by column chromatography to obtained pure and well defined branched dimer possessing the increased number of hydroxygroups.

The other hydrazone dimer **5b**, having hydroxygroups in *trans*-position in the chromophores linking fragment, was obtained in the case of *threo*-1,4-dimercapto-2,3-butanediol. All our attempts to crystallize **5b** was unsuccessful.

**Table 5.** The data of DSC analysis of **5a,b**

TM	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$	TM	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$
<b>5a</b>	72	165	<b>5b</b>	49	-

The DSC analysis data from the Table 5 exhibits that the position of the hydroxygroups in the chromophores linking fragment considerably influences the state and the glass transition of investigated TM.

**Table 6.** The drift mobility measurement data

Layer composition	$\mu_0, (\text{cm}^2/\text{V}\cdot\text{s})$	$\mu, (\text{cm}^2/\text{V}\cdot\text{s})^*$
<b>4c</b> +PVB1, 1:1	$1.2 \cdot 10^{-7}$	$5 \cdot 10^{-6}$
<b>5a</b> +PVB1, 1:1	$1.6 \cdot 10^{-8}$	$1.4 \cdot 10^{-6}$
<b>5b</b> +PVB1, 1:1	$1.3 \cdot 10^{-8}$	$1.4 \cdot 10^{-6}$
* at $6.4 \cdot 10^5$ V/s electric field		

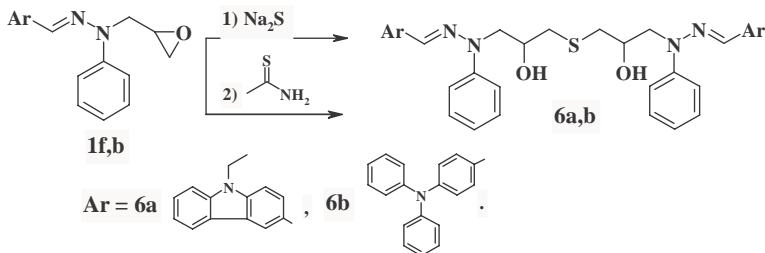
The mobility investigation results of TM **5a,b** and TM **4c** for comparison are given in Table 6. The drift mobility of the dimers possessing the increased number of hydroxygroups reaches  $10^{-6}$   $\text{cm}^2/\text{Vs}$  at  $10^5$  V/cm electric fields. Unlike the crystallization or the glass transition temperature, the position of hydroxygroups towards each other does not influence the value of mobility. Comparing the data of mobility of dimer **4c**, which has the aliphatic linking fragment of the same length, only without hydroxygroups, it is seen that the mobility is about one order of magnitude higher than in the compositions with TM **5a,b**.

### 1.2.3. Synthesis and the testing of the branched hydrazone dimers, linked by -S-group

The disadvantage of the synthesis route to the branched hydrazones described above (1.2.1., 1.2.2.) was an unpleasant smell of used aliphatic dimercaptoalkanes. We proposed synthesis of new class of hole TM comprising two hydrazone groups and -S- linking group instead of the dimercaptoalkanes.

The branched dimers bis[5-(9-ethylcarbazol-3-ylmethylene)-2-hydroxy-4-phenyl-4,5-diaza]sulfide (**6a**) and bis[5-(4-(diphenylamino)benzylidene)-2-hydroxy-4-phenyl-4,5-diaza]sulfide (**6b**) were synthesized during the reaction of **1f** and **1b** with  $\text{Na}_2\text{S}$  in the presence of TEA at the reflux of butanone (scheme 4). Sodium sulphide is several times cheaper than used above aliphatic dimercapto compounds and it is more convenient to use it in contrast to dimercaptoalkanes.

However, the yield reaches only 40 % in this case. That is explained by oxidation of sodium sulphide to sodium sulphite.



Scheme 4

The alternative synthesis route to **6a** and **6b** was realized by the addition of thioacetamide to the solution refluxed butanone of epoxypropylated hydrazones **1b,f** and TEA. In this case the yield of **6a,b** reaches 75 %.

Table 7. The data of DSC analysis of **6a,b** and **3a**, **4a**.

TM	$T_g$ , °C	$T_m$ , °C	TM	$T_g$ , °C	$T_m$ , °C
<b>3a</b>	69	174, 181	<b>4a</b>	45	76
<b>6a</b>	74	188	<b>6b</b>	76	154

The data of DSC analysis (Table 7) demonstrate that glass transition temperatures of the TM **6a,b** are quite similar. Comparing  $T_g$  of **6a,b** with TM obtained by the use of the shortest dimercapto alkanes (**6a** with **3a** and **6b** with **4a**), it is seen that in the case of 9-ethylcarbazolyl chromophore, the difference of glass transition temperatures is 5 °C, while the difference of  $T_g$  in the case of triphenylamine chromophore is more significant (31 °C).

Table 8. The drift mobility measurement data of **6a,b**

Layer composition	$\mu_0$ , (cm <sup>2</sup> /V·s)	$\mu$ , (cm <sup>2</sup> /V·s)*
<b>6a</b> +PVB1, 1:1	$1.7 \cdot 10^{-9}$	$4.2 \cdot 10^{-7}$
<b>6b</b> +PVB1, 1:1	$2.8 \cdot 10^{-8}$	$1.8 \cdot 10^{-6}$
* at $6.4 \cdot 10^5$ V/s electric field		

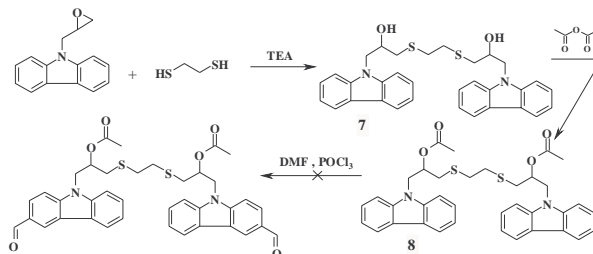
The data of drift mobility of TM **6a,b** in the 1:1 composition with PVB are presented in Table 8. As seen from the results presented, mobility is higher in the branched hydrazone possessing triphenylamine moieties as compared to TM with carbazolyl chromophores. Both **6a** and **6b** can be used for preparation of organic photoconductors.

### 1.3. Synthesis of organic photoconductors with the increased conjugated $\pi$ -electron system

The advantage of presented scheme below compared with the synthesis

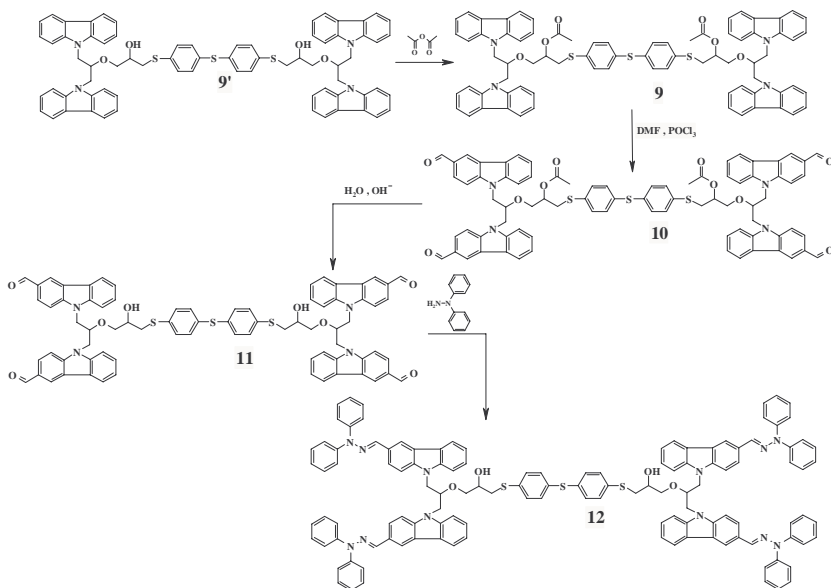


route to the branched hydrazone dimmers described above is that linking group connected the photoconductive chromophores is attached in 9 position of carbazole ring and to preserve the possibility to synthesize the hydrazone dimer with two aromatic rings at N atom in the hydrazine moieties. Unfortunately all our attempts to introduce formyl groups in to the precursor **8** with protected hydroxygroups were unsuccessful (scheme 5).



Scheme 5

With the aim to realise our previous idea from 9-(2,3-epoxypropyl)-carbazole we resynthesized bis{4-[6-(carbazol-9-methyl)-7-(carbazol-9-yl)-3-hydroxy-5-oxa-1-thiaheptyl]phenyl}sulphide (**9'**) by stepwise reaction<sup>[1]</sup>.

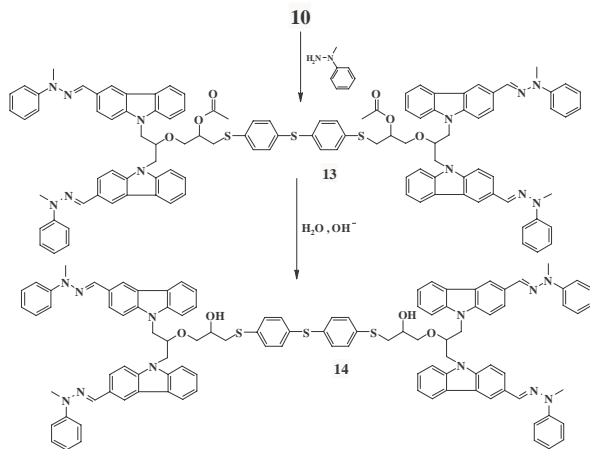


Scheme 6

[1] Kutkevicius S., Stanisauskaitė A., Getautis V., Railaitė A.. *J. Prakt. Chemie*, **337**, p 315, 1995.

the hydroxygroups of this carbazolytetramer were protected with acylation to form compound **9**. The branched tetramer **11** containing four 9-ethylcarbazolecarbaldehyde-*N,N*-diphenylhydrazone groups and protected hydroxygroups was prepared by a procedure of Vilsmeier reaction followed by the reaction with *N,N*-diphenylhydrazine in the next stage. The goal TM **12** with enlarged conjugated  $\pi$ -electron system and comprising two hydroxygroups was synthesized following the hydrolysis of acetyl groups in **11** (scheme 6).

1-methyl-1-phenylhydrazone bis{4-[6-(3-formylcarbazole-9-methyl)-7-(3-formylcarbazol-9-yl)-3-hydroxy-5-oxa-1-thiaheptyl]phenyl} sulfide (**14**), i.e. TM with the decreased conjugated  $\pi$ -electrons system in the chromophores, was synthesized (scheme 7) in order to evaluate the influence of the conjugated  $\pi$ -electrons on the photoconductive properties. Here there was chosen a little bit different strategy for the synthesis of TM:

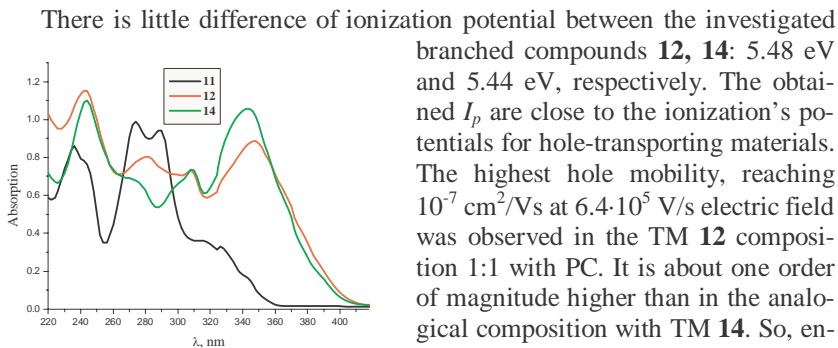


**Scheme 7**

In this way the total yield of **14** was higher to compare with the synthesis route to **12** presented above. It can be explained by the sensitivity of the aldehyde groups to alkaline hydrolysis, during the preparation of the intermediate **11**.

The goal compounds **12** and **14** were isolated by column chromatography followed by precipitation with a large excess of hexane. Isolated by such a procedure branched TM **12**, **14** are amorphous compounds. All our attempts to crystallize them were unsuccessful. X-ray diffraction patterns of these compounds show only broad halos. The comparison of the light absorption spectra of TM **12**, **14** (Fig. 5) and the precursor **11** indicates that branched molecules **12**, **14** are significantly  $\pi$ -conjugated through the nitrogen atoms and that  $\pi$ -electrons are delocalized over these molecules. As it was expected, the absorption band of diphenylhydrazone tetramer **12** is bathochromically shifted by 5 nm,

in comparison with TM **14** possessing N-phenyl-N-methylhydrazone chromophores.



**Fig.5** UV spectra of **11**, **12** and **14** in 1,4-dioxane,  $c=6.8 \cdot 10^{-5}$  mol/l,  $d=1$ mm.

There is little difference of ionization potential between the investigated branched compounds **12**, **14**: 5.48 eV and 5.44 eV, respectively. The obtained  $I_p$  are close to the ionization's potentials for hole-transporting materials. The highest hole mobility, reaching  $10^{-7}$   $\text{cm}^2/\text{Vs}$  at  $6.4 \cdot 10^5$  V/s electric field was observed in the TM **12** composition 1:1 with PC. It is about one order of magnitude higher than in the analogical composition with TM **14**. So, enlarged conjugated  $\pi$ -electron system is one of preconditions for effective charge transport in these derivatives.

#### 1.4. New hole transporting polymers containing carbazole moiety

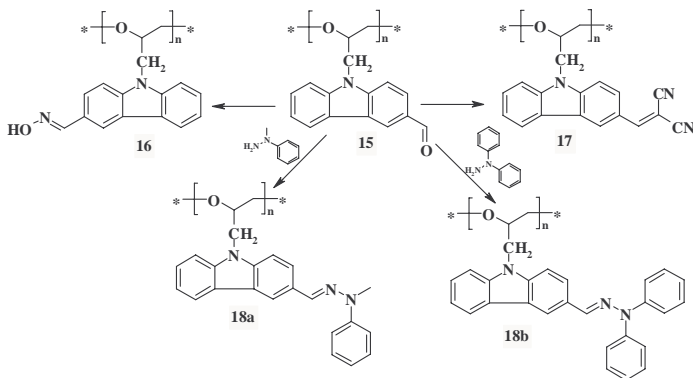
Nowadays, oligomers containing carbazole fragment are widely investigated. One of the reasons why PVK was phased out of the market are its poor mechanical properties. Bad adhesion to different substrates and poor film-forming properties hindered its wider application as an organic photoconductor in electrophotography. Nevertheless the search for organic photoconductors having high photosensitivity and good mechanical properties has been carried on among carbazole-containing compounds. The optimum combination of photoconductive and mechanical properties for certain applications like electrophotographic microfilming or photothermoplastic recording of information was discovered in carbazole containing oligomers. They have relatively low glass transition temperatures, good film forming properties and with respect to photoconductivity some of them are not inferior to PVK. One of the most widely studied materials among carbazole-containing oligomers is poly(N-(2,3-epoxypropyl)carbazole) (PEPK), synthesized and characterized at Kaunas University of Technology. The scientists from the former Vilnius Institute of Electrography used it for the production of electrophotographic microfishes on a flexible basis. However, due to the high ionization potential, which reaches 5.86 eV, this oligomer is not suitable for use in optoelectronic devices with quicker electrographic processes.

Several polymeranalogue reactions were performed to synthesize poly(N-2,3-epoxypropylcarbazole) possessing a hydrazone fragments. It was done in order to increase the conjugation of the  $\pi$ -electrons and to obtain new hole transporting oligomers.

Poly[3-formyl-9-(2,3-epoxypropyl)carbazole] (**15**) was synthesized according to the well known Vilsmeier reaction. The  $^1\text{H}$  NMR analysis of the **15**

shows that all PEPK chromophores have been formylated. Obtained oligomer **15** reacted with hydroxylamine and malononitrile, to yield poly[9-(2,3-epoxypropyl)-3-carbazolecarbaldehydeoxime] (**16**) and poly[3-(2,2-dicyanoethenyl)-9-(2,3-epoxypropyl)carbazole] (**17**) (scheme 8), possessing easily identifiable (with the help of IR spectra) functional groups.

In order to obtain PEPK polymeranalogue with hydrazone fragments and increased  $\pi$ -conjugated system, the reactions between poly[3-formyl-9-(2,3-epoxypropyl)carbazole] and methylphenylhydrazine or diphenylhydrazine were carried out. New hole transporting oligomers **18a** and **18b** containing both carbazole and hydrazone moieties were isolated.



**Scheme 8**

Stability of PEPK under rather strict conditions of Vilsmeier reaction and forming of the oligomers with a higher molecular mass is confirmed by the gel-chromatographic analysis (GPC) (Table 9) and UV spectroscopy data (Fig. 6).

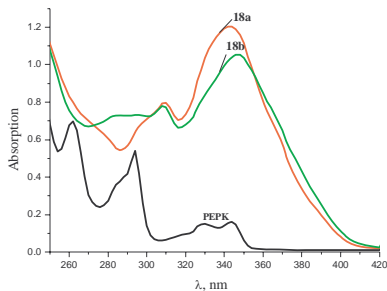
**Table 9.** The GPC\* analysis and ionization potentials ( $I_p$ ) of the oligomers **PEPK**, **15**, **18a**, **18b**

Oligomers	$\overline{M}_n$ , g/mol	$\overline{M}_w$ , g/mol	$\overline{M}_n/\overline{M}_w$	$I_p$ , eV
<b>PEPK</b>	639	748	1,17	5,86
<b>15</b>	647	815	1,28	-
<b>18a</b>	966	1286	1,33	5,43
<b>18b</b>	1238	1793	1,45	5,49

The absorption spectra of the oligomers **18a**, **18b** are bathochromically shifted with respect to the spectrum of the PEPK, this is the consequence of the increased conjugated  $\pi$ -electron system. On the other hand difference in  $\pi$ -electron conjugation between corresponding oligomers is not significant (4 nm).

\* GPC analysis were carried out at Cergy-Pontoise University, France. Author: Dr. Francois Tran-Van.

Being aware of the fact that  $\pi$ -electrons are very important in the structures of organic photoconductors for the carrying process of the quantum charge,



**Fig. 6.** PEPK, **18a**, **18b** UV spectra in 1,4-dioxane,  $c=5.1 \cdot 10^{-6}$  mol/l,  $d=1$ mm.

from the given absorption spectrum, it can be stated that the excitation energy of the obtained oligomers, possessing Hydrazone fragments, is lower than that of well analyzed PEPK. This assumption is also confirmed by the values of the ionization potentials. The ionization potential of **18a** is 5.43 eV and of **18b** is 5.49 eV, and it is lower than that of PEPK (5.86 eV). Judging from these facts we can state that charge carriers are easier to excite in the new oligomeric compounds.

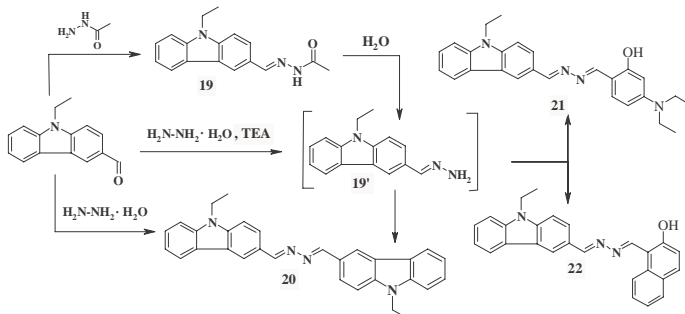
## 1.5. Synthesis and properties of new molecular glasses possessing aromatic, heteroaromatic aldehyde and ketone azine moieties

Nowadays hydrazine derivatives are of considerable technical and commercial importance. Hydrazine is used in simple qualitative tests for carbonyl functions and for identification of carbonyl compounds. Carbonyl compound easily react with the hydrazine to form hydrazone, which can react with second molecule of the carbonyl compound to yield azine. Generally, these are crystalline materials, easily synthesized and purified by recrystallization. Namely, the good crystallization is the limiting factor for applying various chromophores connected via azine linkage for preparation of electrophotographic layers. Unsymmetrical azines are more perspective from this point of view.

### 1.5.1. Synthesis of new molecular glasses possessing aromatic and heteroaromatic aldehyde azine moieties

The reaction between 9-ethyl-3-carbazolecarboxaldehyde and hydrazine hydrate was carried out in order to achieve these goals. During this reaction, in any proportion of the aldehyde and hydrazine hydrate, only one product was isolated. Results of spectral analysis show that obtained product is not the expected 9-ethylcarbazolecarboxaldehyde hydrazone (**19'**), which could be used in the reaction of condensation with the other aromatic aldehyde, but 1,2-bis(9-ethylcarbazole-3-ylmethylene)hydrazine (**20**) (scheme 9). All our attempts to obtain mono substituted hydrazone **19'** by hydrolyzing its acyclic derivative **19** in different conditions were also unsuccessful. In the condensation of 9-ethylcarbazolecarbaldehyde with hydrazinhydrat in the presence of TEA, the searching out of the conditions under which only the derivative of monosubstituted hydrazone **19'** is formed, was successful. As it was mentioned before, **19'** is not

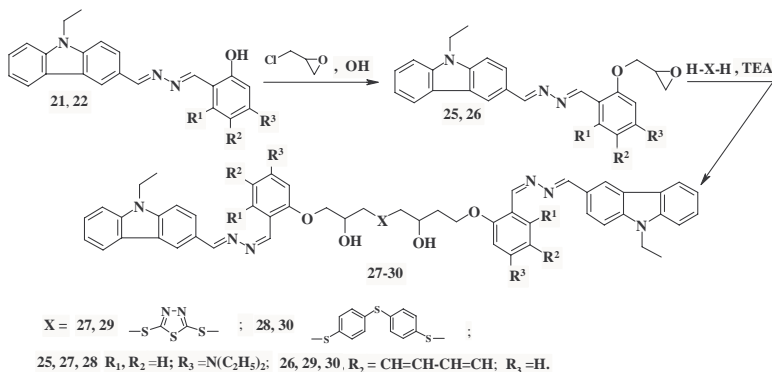
a stable compound, so its condensation with aldehyde, having another chromophoric system, immediately occurs. By interaction of **19'** with 2-hydroxy-4-(diethylamino)benzaldehyde and 2-hydroxynaphthaldehyde unsymmetrical azines 1-(4-diethylamino-2-hydroxyphenylmethylene)-2-(9-ethylcarbazol-3-ylmethylene)hydrazine (**21**) and 1-(9-ethylcarbazol-3-ylmethylene)-2-(2-hydroxy-1-naphthylmethylene)hydrazine (**22**) were isolated.



Scheme 9

1,2-Bis[4-(diphenylamino)phenylmethylene]hydrazine (**23**) and 1-(4-diethylamino-2-hydroxyphenylmethylene)-2-[4-(diphenylamino)phenylmethylene]hydrazine (**24**) were obtained and identified in the case of using 4-(diphenylamino)benzaldehyde.

The presence of phenol groups in the synthesized unsymmetrical azines **21**, **22**, allows to transform them easily into 1-(4-diethylamino-2-hydroxyphenylmethylene)-2-(9-ethylcarbazol-3-ylmethylene)hydrazine glycidyl ether (**25**) and 1-(9-ethylcarbazol-3-ylmethylene)-2-(2-hydroxy-1-naphthylmethylene)hyd-



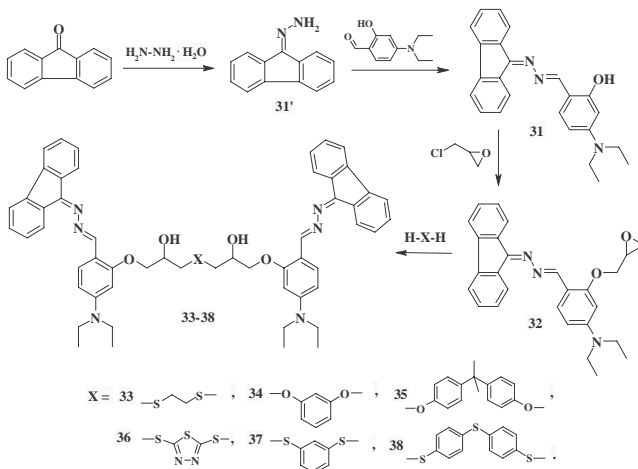
Scheme 10

razine glycidyl ether (**26**). Based on the developed method, by interaction of ac-

tive azines **25**, **26** with 2,5-dimercapto-1,3,4-tiadiazole and 4,4'-tiobisbenzenethiol new molecular glasses **27-30**, possessing aromatic and heteroaromatic aldehyde azine moieties, were synthesized (scheme 10).

### 1.5.2. Synthesis of new molecular glasses possessing aromatic ketone and aromatic aldehyde azine moieties

The synthesis of a novel class of the molecular glasses possessing both aromatic ketone and aromatic aldehyde chromophores connected via azine linkage was done in a 4-step reaction sequence. The first step was synthesis of fluorenone hydrazone (**31'**). The second step was the synthesis of unsymmetrical azine 1-(4-diethylamino-2-hydroxyphenylmethylene)-2-(9-fluorenylmethylene)hydrazine (**31**) followed by alkylation with 1-chloro-2,3-epoxypropane to give glycidyl ether **32**. Finally, the intermediate **32** was reacted with various difunctional nucleophiles (1,2-dimercaptoethane, 1,3-benzenediol, 2,2-bis(4-hydroxyphenyl)propane, 2,5-dimercapto-1,3,4-thiadiazole, 1,3-benzenethiol, 4,4'-tiobisbenzenethiol) to form new branched molecular glasses **33-38** for electrophotography (scheme 11).

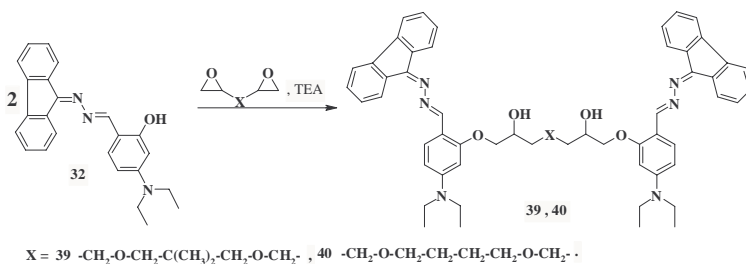


Scheme 11

The goal compounds **33-38** were isolated by column chromatography followed by precipitation with a large excess of hexane. Isolated by such a procedure branched TM **33-38** are amorphous compounds. All our attempts to crystallize them were unsuccessful. X-ray diffraction patterns of these compounds show only broad halos.

An alternative synthesis route to the molecular glasses was used in the synthesis of the branched unsymmetrical azines **39**, **40**. By interaction of the intermediate **31** with 1,4-butanediol diglycidyl ether or neopentyl glycol diglycidyl ether in the presence of TEA at reflux of butanone the molecular glasses **39**, **40**

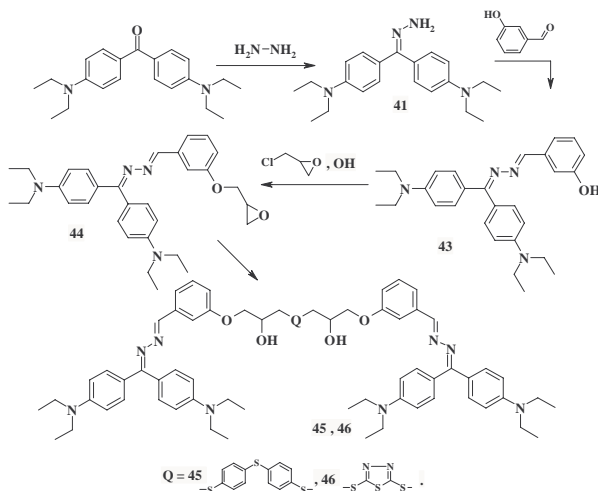
were isolated (scheme 12). The advantage of this method against the method described above is that 1-chloro-2,3-epoxypropane, which causes environmental problems, was eliminated.



Scheme 12

Further on, there was used 4,4'-bis(diethylamino)benzophenone as the starting material for the synthesis of the molecular glasses possessing aromatic ketone and aldehyde azine moieties. This chromophoric system has the potential to be applied in electrophotography as two strong donor groups presence in this aromatic system.

The synthesis of new molecular glasses possessing aromatic ketone and aromatic aldehyde chromophores connected via azine linkage was done in a 4-step reaction sequence. The first step was synthesis of bis(4,4'-diethylamino)benzophenone hydrazone (**41**). The second step was the synthesis of unsymmet-



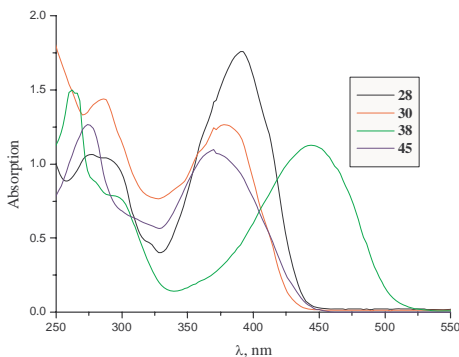
Scheme 13



rical azine **42** by interaction of hydrazone **41** with 3-hydroxybenzaldehyde at refluxed dioxane. The next step was alkylation of azine **42** possessing aromatic hydroxygroup with 1-chloro-2,3-epoxypropane to give the glycidyl ether **44**. Finally, the intermediate **32** was reacted with 4,4'-tiobisbenzenethiol and 2,5-dimercapto-1,3,4-thiadiazole to form new branched molecular glasses **45** and **46** (scheme 13).

### 1.5.3. Light absorption spectra and drift mobility of branched azine dimers

The investigated branched azine dimers **28**, **30**, **33-38**, **45** contain several isolated  $\pi$ -electron systems. Since those  $\pi$ -electron systems do not interact with each other, total light absorption spectrum is a sum of spectra of the separate molecule fragments. In quantum processes, quantum jumps of azine moiety



**Fig. 7.** UV spectra of dimers **28**, **30**, **38** and **45** in 1,4-dioxane,  $c=10^{-5}$  mol/l,  $d=1$  mm.

electrons are most important, because extinction of the linking fragment is lower and is located hypsochromically further away.

The comparison of molecules with various chromophoric systems and the same chromophore linking fragment (Fig. 7) leads to the conclusion, that branched dimer **38**, containing fluorenone and 2-hydroxy-4-diethylaminobenzaldehyde chromophores connected via azine linkage, possess the lowest energy

of  $\pi$ -electrons. Changing the fluorenone chromophore to 9-ethylcarbazolyl, there occurs strong (54 nm) hypsochromical shift (compare **38** with **28**). The obtained results enable us to conclude that  $\pi$ -electron conjugation in the azine of 9-ethyl-3-carbazolcarbaldehyde and 2-hydroxynaphthaldehyde (**30**) is weaker than that in **28**. Thus, the presence of a strong, donor diethylaminogroup is more determinant than the additional ring of benzene: the bathochromic shift by 12 nm and a noticeable hyperchromic effect are observed in a case of dimer **28**, as compared with **30**. Unexpectedly, the highest energy of  $\pi$ -electrons was observed for azine dimers possessing bis(4-diethylamino)benzophenone moieties. Due to what was said before, it can be concluded that azine dimers, possessing fluorenone and 2-hydroxy-4-diethylaminobenzaldehyde chromophores connected via azine linkage, are most suitable for charge transport. Our assumption was proved by the drift mobility measurement data of synthesized unsymmetrical azine dimers (Table 10).

**Table 10.** The drift mobility measurement data of TM **28, 30, 33-40**

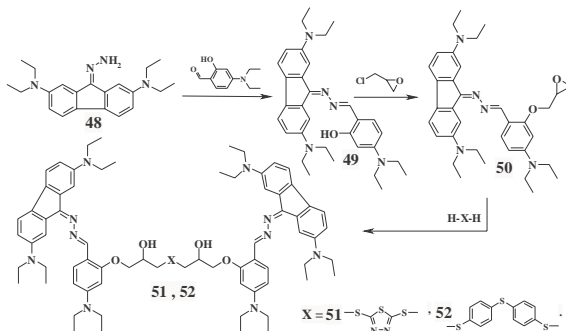
Layer composition	Layer thickness, nm	$\mu_0, (\text{cm}^2/\text{V}\cdot\text{s})$	$\mu, (\text{cm}^2/\text{V}\cdot\text{s})^*$
Al+ <b>28</b>	~8	$\sim 3 \cdot 10^{-13}$	$2.5 \cdot 10^{-8}$
Al+[ <b>28</b> +(PC-Z), 1:1]	7	$1 \cdot 10^{-12}$	$4 \cdot 10^{-9}$
Al+[ <b>28</b> +PVB1, 1:1]	6,5	$5 \cdot 10^{-13}$	$2.8 \cdot 10^{-10}$
Al+[ <b>30</b> +PVB1, 1:1]	9	$1.3 \cdot 10^{-12}$	$5 \cdot 10^{-9}$
Al+[ <b>33</b> +PVB1, 1:1]	~10	$1.3 \cdot 10^{-11}$	$6 \cdot 10^{-9}$
Al+[ <b>34</b> +PVB1, 1:1]	~10	$3 \cdot 10^{-13}$	$8 \cdot 10^{-10}$
Al+[ <b>35</b> +PVB1, 1:1]	~10	$1 \cdot 10^{-13}$	$4 \cdot 10^{-11}$
Al+[ <b>36</b> +PVB1, 1:1]	~10	$4 \cdot 10^{-13}$	$7 \cdot 10^{-10}$
Al+ <b>38</b>	~15	$\sim 1.5 \cdot 10^{-10}$	$\sim 6 \cdot 10^{-8}$
Al+[ <b>38</b> +PVB1, 1:1]	7	$3.3 \cdot 10^{-11}$	$1.1 \cdot 10^{-8}$
Al+[ <b>40</b> +PVB1, 1:1]	~10	$2 \cdot 10^{-2}$	$1.3 \cdot 10^{-9}$
Al+[ <b>45</b> +(PC-Z), 1:1]	6	$1.2 \cdot 10^{-9}$	$2.8 \cdot 10^{-7}$

\* at  $6.4 \cdot 10^5$  V/s electric field

### 1.2.4. Synthesis and the properties of branched azine dimers with the improved drift mobility

From the data applied in chapter 1.2.3., it is obvious that the drift mobility of synthesized, branched azine dimers is only satisfactory. Relying on the conclusions made in the previous chapter we designed synthesis rout to the branched azine dimers with the improved hole drift mobility.

For this purpose, reduction of 2,7-dinitro-9-fluorenone was proceeded followed by alkylation with iodethane to give 2,7-bis(diethylamino)-9-fluorenone (**48**). **48** was reacted with 2-hydroxy-4-diethylaminobenzaldehyde to yield un-

**Scheme 14**

symmetrical azine **49**. The azine glycidyl ether **50** was synthesized by alkylation of **49** with epychlorohydrin. Finally, based on the developed method, by interaction of epoxypropylated azine **50** with 2,5-dimercapto-1,3,4-thiadiazole and 4,4'-tiobisbenzenethiol new branched molecular glasses **51** and **52** were isolated (scheme 14).

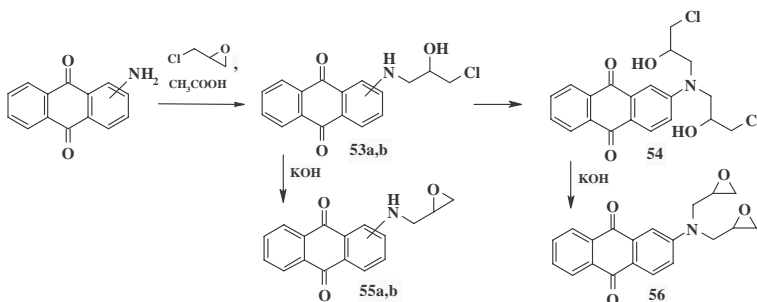
The drift mobility in the compositions (1:1) of molecular glasses **51**, **52** with PC reaches  $10^{-6}$  cm<sup>2</sup>/Vs at  $10^5$  V/cm electric fields. The mobility values are by two-three order of magnitude higher compared with results presented in Table 10.

## 2. Branched anthraquinone derivatives - electron-transporting materials

### 2.1. Interaction between 1(2)-aminoanthraquinone and 1-chloro-2,3-epoxypropane

In order to develop a new class of electron transporting molecular glasses the interaction of 1(2)-aminoanthraquinones with 1-chloro-2,3-epoxypropane (CEP) was studied.

After treating of 1-aminoanthraquinone with the excess of CEP in the presence of 85% acetic acid as a catalyst, 1-(3-chloro-2-hydroxypropylamino)anthraquinone (**53a**) was isolated from the reaction mixture (scheme 15). In this case, formation of bis-3-chloro-2-hydroxypropyl derivative was not observed. It may happen because of the appearance of hydrogen bonding between the carbonyl group at *peri*-position and the hydrogen of  $\alpha$ -amino group: the cyclization into a six-membered cycle decreases the mobility of the mentioned hydrogen. According to D.N.Shygorin and N.S.Dokunychin, the interaction between  $\alpha$ -amino group and *peri*-carbonyl group of 1-aminoanthraquinone, 1,4- and 1,8-diaminoanthraquinones is relatively weak, since these groups are not situated on one plane. According to these authors, the spatial effects are the most likely to prevent the formation of bis(3-chloro-2-hydroxypropyl)derivative.

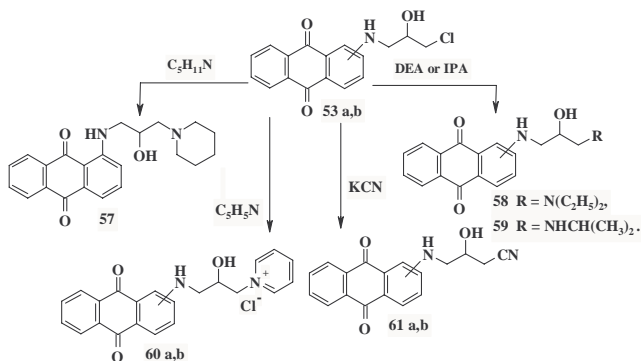


Scheme 15

Under the analogous conditions, when 2-aminoanthraquinone is treated with CEP, formation of two products is being noticed by means of chromato-

graphy. After 26 h heating, 2-(3-chloro-2-hydroxypropylamino)anthraquinone (**53b**) was successfully isolated from this mixture (yield 53,5%). Further heating of the mother filtrate with the excess of CEP till the disappearance of the trace of **53b** on the chromatogram (additionally 28h), gave 2-[*N,N*-bis(3-chloro-2-hydroxypropylamino)]anthraquinone (**54**), which was isolated as a mixture of diastereomers. This is illustrated best by two doublets, being observed in  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 250 MHz) spectrum of **54**, which can be assigned to the secondary hydroxygroup. From the integral curves the ratio of the formed diastereomers was estimated to be 1:2.

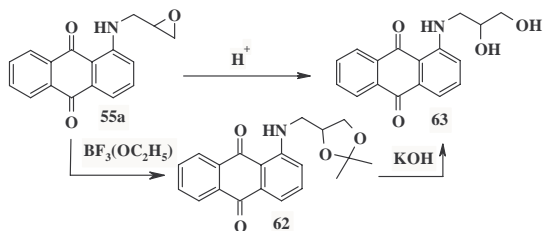
The work-up of the solutions of **53a,b**, **54** in 1,4-dioxane with 85% powdered KOH gave appropriate epoxy compounds: 1(2)-(2,3-epoxypropylamino)anthraquinones (**55a,b**) and 2-[*N,N*-bis(2,3-epoxypropylamino)]anthraquinone (**56**). Besides this reaction, some other characteristic transformations of 3-chloro-2-hydroxypropyl derivatives were performed in order to confirm the structure of **53a,b**, i.e., the reactions of **53a** with piperidine, diethylamine (DEA), isopropylamine (IPA), as well as the reactions of **53a,b** with pyridine and KCN. In this way the following 1(2)-aminoanthraquinone derivatives were synthesized: 1-(2-hydroxy-3-piperidinopropylamino)anthraquinone (**57**), 1-(3-diethylamino-2-hydroxypropylamino)anthraquinone (**58**), 1-(3-isopropylamino-2-hydroxypropylamino)anthraquinone (**59**), 1-(2-hydroxy-3-piridiniopropylamino)antraquinone (**60a**), 2-(2-hydroxy-3-piridiniopropylamino)antraquinone (**60b**), 4-(antraquinone-1-amino)-3-hydroxybutannitrile (**61a**), 4-(antraquinone-2-amino)-3-hydroxybutannitrile (**61b**) (scheme 16).



Scheme 16

The structure of epoxycompound **55a** can be confirmed as well by the formation of dioxolanes and propanediols, what is quite typical for epoxypropyl compounds. Treatment of **55a** with acetone, in the presence of catalyst  $\text{BF}_3(\text{OC}_2\text{H}_5)$ , or diluted sulphuric acid gave correspondingly: 1-[(2,2-dimethyl)-1,3-dioxolan-4-methylenamino]antraquinone (**62**) and 1-(2,3-dihydroxypropylamino)antraquinone (**63**) (sheme 17). In addition, the **62** was transformed

into **63** in the presence of KOH.



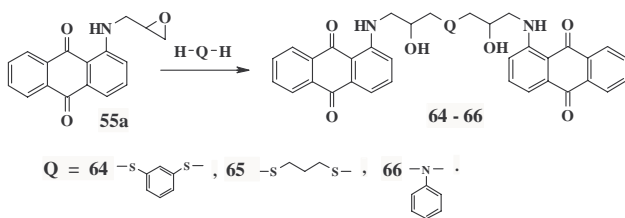
Scheme 17

## 2.2. Synthesis of electron-transporting molecular glasses

In the previous chapters of this work we have described the synthesis of organic photoconductors, which was carried out by the interaction of appropriate 2,3-epoxypropyl derivatives, containing photoconductive chromophores, with various nucleophiles, such as dimercaptive compounds, at ratio 2:1. By this way aliphatic chains are introduced into the molecule of organic photoconductor, which improve markedly the film-forming properties of TM.

According to the data of physicists of the Faculty of Physics at Vilnius University, 1-aminoanthraquinone derivatives are the only ones able to carry electrons. Hence, the only 1-aminoanthraquinone 2,3-epoxypropyl derivative was used for the further synthesis of electron-transporting molecular glasses.

New molecular glasses **64-66**, possessing anthraquinone moieties, were synthesized by treating **53a** with aromatic and aliphatic dimercaptive compounds, i.e. 1,3-benzenedithiol and 1,3-propanedithiol, also with aromatic amine (aniline) (scheme 18).



Scheme 18

According to the method, described in chapter 1.1., i.e. by treating of 1-(2,3-epoxypropylamino)anthraquinone with 1,3-benzenedithiol (2,1:1) in 2-butanone at room temperature, in the presence of catalyst TEA, dimer **64** was obtained. Meanwhile the analogous reaction with 1,3-propanedithiol was carried out at the boiling temperature of THF, and gave **65**. The ring opening reaction of nucleophilic oxirane **53a** by aromatic amine (aniline) took place under more severe conditions, i.e. at 135-140 °C. In this way dimer **66** was synthesized.

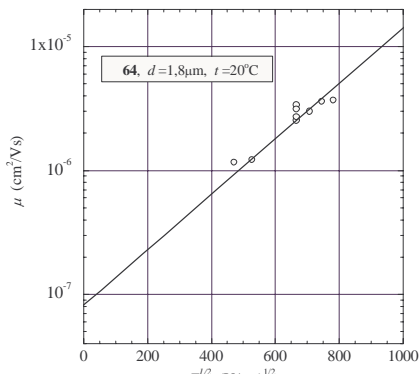
Dimers **65** and **66** were isolated as crystalline substances while the dimer **64** as an amorphous one. These materials do not melt at a narrow interval (1.5–2.0 °C), what is characteristic of crystalline organic compounds. Thus, the newly synthesized compounds possessing anthraquinone moieties are molecular glasses. This was proved by DSC analysis. From the data presented in Table 11, it can be concluded that molecular glass **66** is characterized by most stable amorphous state, as  $T_g$  reaches 90 °C, but this compound does not dissolve in common organic solvents. Meanwhile, the  $T_g$  of dimer **65**, the chromophores of which are linked by aliphatic chain, is hardly over the room temperature.

**Table 11.** The DSC and TG analysis of compounds **64-66**

Compound	$T_m$ , °C	$T_g$ , °C	$T_{dec-5\%}$ , °C
<b>64</b>	118	63	330
<b>65</b>	137	49	320
<b>66</b>	221	90	337

The thermal stability of these compounds was obviously confirmed by the results of thermogravimetical (TG) analysis. The stability of compounds **64-66** is similar. Their decomposition begins at 320–340 °C (Table 11).

One of the most important parameters of organic electrophotographic layers is a good surface quality.



**Fig. 8.** The dependence of electrons drift mobility of **64** on the electric field strength.

This demonstrates the possible application of bis[4-(anthraquinone-1-amino)-3-hydroxy-1-thiabutyl]benzene (**64**) in preparation of organic photoreceptors.

From the above given DSC analysis results of dimers with anthraquinone fragments, it is evident that compounds **64** and **66** are characterized by stable glassy state. Meanwhile, only the latter is quite soluble. Therefore, at the Faculty of Physics at Vilnius University the electrographic properties of the molecular glass **64** were investigated. The dependence of electrons drift mobility of **64** on the electric field strength is presented in Fig.8.

## Conclusions and results

- Photoconductive branched hydrazone dimers possessing hydroxygroups were investigated, which were synthesized by the reaction of 9-ethyl-3-carbazole-, julolidin-9-carbaldehydes, 4-diethylamino-, 4-benzylethylamino-, 4-(diphenylamino)- and 4-(4,4'-dimethyldiphenylamino)benzaldehydes phenylhydrazones N-2,3-epoxypropyl derivatives with 4,4'-thiobisbenzenethiol, dimercaptoalkanes, hydrogen sulfide. It was determined, that:

  - dimers possessing 9-ethylcarbazolyl group have less stable glassy state, whereas the rest of the TM are characterized by stable glassy state. Changing the photoconductive chromophores in the investigated TM, varies their  $T_g$  from 40 °C till 84 °C. The probability of amorphous state increases when the distance between chromophores is becoming bigger and the  $T_g$  lower;
  - dimers exhibit polymorphism, except those with 4-diethylamino-, 4-benzylethylaminobenzene chromophores;
  - ionization potential of the branched hydrazones varies from 5.03 eV till 5.38 eV. The potential decreases when the number of the aliphatic substituents in a molecule increases;
  - the branched hydrazones possessing triphenylamine and 4,4'-dimethyltriphenylamine chromophores distinguish themselves by the most intensive  $\pi$ -electrons conjugation. This influences higher drift mobility of charge carriers up to  $10^{-4}$  cm<sup>2</sup>/Vs ( $E = 6.4 \cdot 10^5$  V/cm), in comparison with TM containing other chromophores;
  - the increase of the synthesized TM quantity, even up to 70% of the whole electrophotographic composition mass, demonstrates the advantage of these materials, compared to those used in practice.
- An effective method (using thioacetamide as a source of H<sub>2</sub>S) was proposed for the synthesis of photosensitive branched dimers of aromatic, heteroaromatic aldehyde phenylhydrazones, with OH- and -S- groups in the chromophores linking fragment.
- Branched, stable in their glassy state hydroxygroups possessing asymmetric azine dimers of aromatic, heteroaromatic aldehydes (9-ethyl-3-carbazolcarbaldehyde, 2-hydroxy-1-naphthaldehyde, 4-(diphenylamino)benzaldehyde), and ketones (9-fluorenone, bis(4,4'-diethylamino)benzophenone, 2,7-bis(diethylamino)-9-fluorenone) were synthesized:

  - their ionization potentials (5.25-5.4 eV) are favourable for the hole transporting. The exceptions are 9-ethyl-3-carbazolcarbaldehyde and 2-hydroxy-1-naphthaldehyde azine dimers ( $I_p \sim 5.7$  eV);
  - TM having 9-fluorenone and 2-hydroxy-4-diethylaminobenzaldehyde azine chromophores, are characterized by the lowest energy of  $\pi$ -electrons (their drift mobility is up to  $10^{-8}$  cm<sup>2</sup>/V, when  $E = 6.4 \cdot 10^5$  V/cm);

- synthesis of asymmetric azines with the improved drift mobility ( $10^{-6}$  cm<sup>2</sup>/Vs,  $E = 6.4 \cdot 10^5$  V/cm) was planned and realised.
4. The presence of the hydroxygroups of the synthesized branched dimers and their position in the chromophores linking fragment influences markedly the properties of the organic photoconductor:
    - them, being in *eritro*-position towards each other, the crystallization and  $T_g$  increase more than in *treo*-position;
    - the presence of hydroxygroups in the synthesized TM, gives them good compatibility not only with a traditional polymeric binder (polycarbonate) but also with polyvinylbutyral, however, decreases the hole-transporting mobility;
    - with the help of these functional groups, hydrazone dimers can be cross-linked with polyisocyanates.
  5. An alternative method (without using 1-chloro-2,3-epoxypropane) was proposed for obtaining branched organic photoconductor with hydroxygroups, stable in its amorphous state.
  6. New perspective hole TM's were designed and synthesized from 9-(2,3-epoxypropyl)carbazole and polymeranalogue:
    - due to a step-by-step synthesis there were obtained and investigated branched, well defined compounds of stable glassy state, possessing four carbazole-3-carbaldehyde N,N-diphenylhydrazone moieties as well as carbazole-3-carbaldehyde N-phenyl-N-methylhydrazone chromophores.
    - new hole-transporting polymers, containing hydrazone moiety were synthesized and investigated.
  7. The interaction of 1(2)-aminoanthraquinones with 1-chloro-2,3-epoxypropane was investigated, with the aim to use its products for the creation of electron TM: the electrons drift mobility of bis[(4-anthraquinon-1-amino)-3-hydroxy-1-thiabutyl]benzene, having stable glassy state, is up to  $10^{-7}$  cm<sup>2</sup>/Vs at the electric field strength of  $8 \cdot 10^5$  V/cm.

## Publications

### Publications in Editions Approved by Information Sciences Institute (ISI)

1. Tokarski Z., Jubran N., Getautis V., Paliulis O., Daskeviciene M., **Paulauskaite I.**, Jankauskas V., Gaidelis V., Sidaravicius J.. Crosslinkable branched hydrazones as potential hole transporting materials // *IS&T'S NIP 19: International Conference on Digital Technologies*. ISBN: 0-89208-247-X, Society Imaging Science Technology, **2003**, p. 702-707.
2. Getautis V., Paliulis O., **Paulauskaite I.**, Gaidelis V., Jankauskas V., Sidaravicius J., Tokarski Z., Law K., Jubran N.. Crosslinkable branched hydrazones as hole transporting materials // *Journal of Imaging Science and Technology*. ISSN: 1062-3701. CODEN: JIMTE6, **2004**, 48(3), p.265-272.
3. В. Гягаугис, **И. Паулаускайте**, А. Станишаускайте "Некоторые превращения



1(2)-аминоантрахинонов" // *Khimiya Geterotsiklicheskikh Soedinenii*. ISSN 0132-6244. "Khimiya Geterotsiklicheskikh Soedinenii", Riga, **2005** (accepted; in Russian).

### Publications in the Proceedings of Conferences

1. Getautis V., **Paulauskaitė I.**, Sidaravičius J., Jankauskas V.. Synthesis and investigation of bipolar charge-transporting material // *Organic chemistry: conference proceedings*. - Kaunas, **2001**, p. 59-61 (in Lithuanian).
2. Daškevičienė M., Getautis V., **Paulauskaitė I.**, Stanišauskaitė A.. Synthesis of new molecular glasses // *Chemistry 2001: 5<sup>th</sup> National Lithuanian Conference*. – Vilnius: Institute of Chemistry, **2001**, 123.
3. **Paulauskaitė I.**, Getautis V., Stanišauskaitė A., Daškevičienė M.. Synthesis of branched compounds with methanoyl groups // *Organic chemistry: conference proceedings*. - Kaunas, **2002**, p. 14-15 (in Lithuanian).
4. Getautis V., Paliulis O., Daskeviciene M., Stanisauskaite A., **Paulauskaitė I.**, Jankauskas V., Maldzius R.. Synthesis and properties of the branched hydrazone dimers // *International Conference on Organic Synthesis (BOS)*. Vilnius, **2002**, PO22.
5. Getautis V., Daškevičienė M., Paliulis O., **Paulauskaite I.** et al. Molecular glasses containing the hydrazone moieties // *Baltic Polymer Symposium (Nida): Proceedings*, Vilnius, **2002**, 213-218.
6. **Paulauskaitė I.**, Getautis V., Daškevičienė M.. Investigation of hydrazine interaction with aromatic aldehydes and ketones// *Organic chemistry: conference proceedings*. - Kaunas, **2003**, p. 55-56.
7. **Paulauskaitė I.**, Getautis V., Daškevičienė M., Stanišauskaitė A.. Synthesis of stable amorphous state hydrazones // *Organic chemistry: conference proceedings*. – Kaunas, **2004**, p. 26-29.

### ACKNOWLEDGEMENTS

*I wish to thank my supervisor Assoc. Prof. Dr. Vytautas Getautis and research group leader Prof. Dr. Habil. Albina Stanišauskaite for the provided possibility to perform a research work, thorough help in synthesis, understanding and patience.*

*All staff of the Department of Organic chemistry for cosy atmosphere during the period of my master's and doctoral studies.*

*Prof. Habil. Dr. V. Gaidelis and Dr. V. Jankauskas for preparation of photoconductive layers and measurements of ionisation potential, drift mobility and photosensitivity.*

*Prof. Dr. V. Cadiz Deleito and Prof. Dr. J. A. Reina Lozano for the provided permission to use laboratories and equipment of the Department of Analytical and Organic Chemistry during my research internship in Rovira & Virgili University, Tarragona, Spain.*

*Dr. Z. Tokarski for termal analysis of new charge TMs at Samsung Information Systems America, Digital Printing Solutions Laboratory, Minnesota, USA.*

*Dr. Francois Tran-Van for GPC analysis, Cergy-Pontoise University, France.*

*Organizers of Erasmus-Socrates program and Lithuanian State Science and Studies Foundation for research internship and support.*

*My Parents for the opportunity to study, their support and sincere love, and all fellow-people for their help during the period of my studies.*

## Reziūme

Pastaruju metu organiniai junginiai pradėti taikyti tokiose srityse, kuriose lig šiol vyravo tik neorganinės medžiagos. Pradėjus tirti mažamolekulių organinių junginių, ypač sudarančių stabilią amorfinę būseną, optines, fotokvantine ir elektrines savybes, buvo nustatytos iki šiol nežinomos jų savybės, dėl kurių šiuos junginius imta naudoti fotoninių ir optoelektroninių prietaisų gamybai. Įvairiose pasaulio laboratorijose atliekami intensyvūs tyrimai, siekiant padidinti šių medžiagų dreifinį jautrumą, fotojautrumą, atsparumą tempimui bei lenkimui, tačiau žinoma nedaug konkrečių rekomendacijų, kaip modeliuoti optimalių savybių organinio fotopulsleidininkio struktūrą.

## Darbo tikslai

- Susintetinti aromatinių bei heteromatinių aldehidų fenilhidrazonų šakotos struktūros, stabilios amorfinės būsenos dimerus, turinčius tiofenilsulfido, sulfido bei hidroksigrupių chromoforus jungiančiame fragmente. Išstudijuoti šių krūvius transportuojančių junginių fizikines bei optoelektrografines savybes.
- Susintetinti bei ištirti šakotos struktūros fotojautrius dimerus, turinčius hidroksigrupių bei aromatinių, heteroaromatinių aldehidų ir ketonų nesimetrinių azinų chromoforų. Pasiūlyti konkrečias rekomendacijas šių organinių fotopulsleidininkių savybių modeliavimui.
- Iš 9-(2,3-epoksipropil)karbazolo susintetinti naujas stabilios amorfinės būsenos krūvius transportuojančias medžiagas.
- Ištirti 1(2)-aminoantrachinono ir 1-chlor-2,3-epoksipropano tarpusavio sąveiką, o jos produktus panaudoti kuriant stabilios amorfinės būsenos bei hidroksigrupių turinčias elektronus transportuojančias medžiagas.

Pagrindiniai rezultatai atspindi pateiktų tyrimų naujumą, originalumą bei svarbą.

9-Etil-3-karbazolkarbaldehido, 4-dietilaminobenzaldehido, 4-benziletilaminobenzaldehido, julolidin-9-karbaldehido, 4-(difenilamino)benzaldehido ir 4-(4,4'-dimetildifenilamino)benzaldehido fenilhidrazonų N-2,3-epoksipropilinius darinius veikiant 4,4'-tiobisbenzentioliu, dimerkaptoalkanais ir sieros vandeniliu, susintetinti šakotos struktūros, hidroksigrupių turintys ir fotolaidūs hidrazonų dimerai. Nustatyta, kad šie hidrazonų dimerai su 9-etilkarbazolilo grupe turi mažiau stabilią amorfinę būseną, kai tuo tarpu likusieji pasižymi stabilia amorfine būsena. Keičiant fotolaidžius chromoforus dimerų  $T_g$  kinta nuo 40 °C iki 84 °C. Didėjant atstumui tarp chromoforų, amorfinės būsenos tikimybė didėja mažėjant  $T_g$ . Dimerai, išskyrus tuos, kurie turi 4-dietilamino, 4-benziletilaminobenzeno chromoforų, yra polimorfiški. Šakotos struktūros hidrazonų dimerų jonizacijos potencialas kinta nuo 5,03 eV iki 5,38 eV. Jis mažėja didėjant alifatinių pakaitų kiekiui molekulėje. Intensyviausia  $\pi$  elektronų konjugacija būdinga trifenilamino ir 4,4'-dimetiltrifenilamino chromoforų turintiems hidra-

zonų dimerams. Tai lemia didesnę nei kitų chromoforų turinčių dimerų krūvininkų dreifinį judrį, siekiantį  $10^{-4}$  cm<sup>2</sup>/Vs, esant elektrinio laiko stipriui  $6,4 \cdot 10^5$  V/cm. Susintetintų hidrazono kiekio padidininimui net iki 70 % nuo visos fotoreceptoriaus kompozicijos masės, demonstruoja šių medžiagų privalumą, palyginti su praktikoje naudojamais hidrazonais.

Pasiūlytas efektyvus aromatinių bei heteroaromatinių aldehidų fenilhidrazonų šakotos struktūros fotojautrių dimerų, turinčių OH- bei -S- grupių chromoforus jungiančiame fragmente, sintezės, kaip H<sub>2</sub>S šaltinį naudojant tioacetamidą, būdas.

Susintetinti aromatinių bei heteroaromatinių aldehidų (9-etil-3-karbazol-karbaldehido, 2-hidroksi-1-naftaldehido, 4-(difenilamino)bezaldehido) ir ketonų (9-fluorenono, bis(4,4'-dietilamino)benzofenono, 2,7-bis(dietilamino)-9-fluorenono) nesimetrinių azinų stabilios amorfinės būsenos, šakotos struktūros dimerai, turintys hidroksigrupių. Jų jonizacijos potencialai (5,25-5,4 eV) yra palankūs skylių transportui. Išimtis – 9-etil-3-karbazolkarbaldehido ir 2-hidroksi-1-naftaldehido azinų dimerai ( $I_p \sim 5,7$  eV). Mažiausia  $\pi$  elektronų energija būdinga dimerams, turintiems 9-fluorenono ir 2-hidroksi-4-dietilaminobenzaldehido azino chromoforų. Jų dreifinis judris siekia  $10^{-8}$  cm<sup>2</sup>/V, esant elektrinio lauko stipriui  $6,4 \cdot 10^5$  V/cm. Sumanyta ir įgyvendinta nesimetrinių pagerinto dreifinio judrio ( $10^{-6}$  cm<sup>2</sup>/Vs, esant elektrinio lauko stipriui  $6,4 \cdot 10^5$  V/cm) azinų sintezė.

Susintetintų šakotos struktūros dimerų hidroksigrupės bei jų padėtyš chromoforus jungiančiame fragmente daro didelę įtaką organinio fotopūsleidininkio savybėms. Joms esant *eritro*-padėtyje viena kitos atžvilgiu, kristališkumas bei  $T_s$  didėja labiau nei *treo*-padėtyje. Hidroksigrupės užtikrina gerą susintetintų dimerų suderinamumą ne tik su tradiciniu polimeriniu rišikliu (polikarbonatu), bet ir su polivinilbutiraliu, tačiau mažina skylių dreifinį judrį. Šios funkcinės grupės leidžia hidrazonų dimerus chemiškai susiūti, pvz. naudojant poliizocianatus.

Pasiūlytas alternatyvus stabilios amorfinės būsenos šakotos struktūros organinio fotopūsleidininkio, turinčio hidroksigrupių, gavimo, nenaudojant 1-chlor-2,3-epoksiopropano, būdas.

Iš 9-(2,3-epoksipropil)karbazolo bei polimeranologo gauta naujų perspektyvių skyles transportuojančių medžiagų. Pakopine sinteze gauti ir ištirti keturis karbazol-3-karbaldehido N,N-difenilhidrazono bei karbazol-3-karbaldehido N-fenil-N-metilhidrazono chromoforus bei stabilią amorfinę būseną turintys šakotos struktūros individualūs junginiai. Polimeranaloginių kitimų metu susintetinti ir ištirti nauji skyles transportuojantys hidrazonų polimerai.

Ištirta 1(2)-aminoantrachinonų sąveika su 1-chlor-2,3-epoksiopropanu, kad jos produktus būtų galima naudoti, kuriant elektronus transportuojančias medžiagas: stabilios amorfinės būsenos bis[4-(antrachinon-1-amino)-3-hidroksi-1-tiabutil]benzeno elektronų dreifinis judris siekia  $10^{-7}$  cm<sup>2</sup>/Vs, esant elektrinio lauko stipriui  $8 \cdot 10^5$  V/cm.

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SL 344. 2005-04-20. 1 leidyb. apsk. 1. Užsakymas 178. Tiražas 70 egz..  
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