

## Photoconductive glass-forming phenothiazine-based hydrazones

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### Abstract

The synthesis and optical, thermal as well as photoelectrical properties of a series of glass-forming phenothiazine-based mono- and dihydrazones are reported. The ionization potentials of the phenothiazine-based hydrazones measured by electron photoemission technique range from 5.2 to 5.41 eV. The hole drift mobilities in the amorphous films and the solid solutions in bisphenol-Z polycarbonate (PC-Z) of the synthesized hydrazones were studied by the time of flight technique. The highest room temperature charge mobilities were observed in the amorphous film of 10-(2-ethylhexyl)-10H-3,7-phenothiazine dicarbaldehyde bis(*N,N*-diphenylhydrazone) which exceeded  $10^{-4}$  cm<sup>2</sup>/(V s) at high electric fields.

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### 1. Introduction

The well known chemical modifications of phenothiazine had led to a great number of derivatives with different neuroleptic, antihistaminic, antiallergic, antiinflammatory, antibacterial, anticancer, etc. activities, which are used in the modern pharmacotherapy [1]. Investigations of phenothiazine derivatives as dyes, semiconductors and photoconductors, charge transfer complexes for electrochromic devices are also reported [2]. In the last few years a lot of studies on the synthesis and properties of phenothiazine based polymers [3], low molecular weight compounds [4] and their potential application in optoelectronic devices, especially in electroluminescent devices, have been published.

Molecularly doped polymers consisting of aromatic hydrazones, which are known as very effective charge-transporting compounds, and polymer hosts are widely used in electrographic photoreceptors [5]. The use of amorphous hydrazone compounds allows to increase their concentration in a polymer host and thus to increase the charge

carrier mobility in charge transport layers of electrographic materials [6].

In this paper, we report on the synthesis of amorphous phenothiazine based mono- and dihydrazones and their optical, thermal and photoelectrical properties.

### 2. Experimental

#### 2.1. Materials

10-Ethyl-10H-phenothiazine (**1a**) was synthesized by the known procedure [7]. Twenty grams (0.1 mol) of phenothiazine were dissolved in 300 ml of dry toluene. Then 9 g (0.15 mol) of potassium hydroxide, 0.41 g (2%, m/m) of tetrabutylammonium hydrosulfate and 24.6 g (0.15 mol) of iodoethane were added. Reaction mixture was refluxed for 12 h. After the reaction was finished (TLC monitoring), reaction mixture was cooled down to room temperature and filtered. Solvent was evaporated in vacuum. Compound **1a** was recrystallized from methanol, mp 103–104 °C. Yield of **1a** 18.7 g (83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 1.40 (t, 3H, CH<sub>3</sub>), 3.80–4.10 (m, 2H, CH<sub>2</sub>), 6.80–7.30 (m, 8H, ar).

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*10-(2-Ethylhexyl)-10H-phenotiazine (1b)* was synthesized by the same procedure as compound **1a**. Yield of **1b** 24.3 g (78%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.70–1.05 (m, 6H,  $\text{CH}_3$ ), 1.20–1.60 (m, 8H,  $\text{CH}_2$ ), 1.90 (m, 1H,  $\text{NCH}_2\text{CH}$ ), 3.70 (d, 2H,  $\text{NCH}_2\text{CH}$ ), 6.70–7.20 (m, 8H, ar).

*10-Ethyl-10H-3-phenotiazine carbaldehyde (2a)* was synthesized by Vilsmeier reaction [8]. 14.8 g (0.097 mol) of  $\text{POCl}_3$  were added dropwise to 8.6 g (0.116 mol) of freshly distilled *N,N*-dimethylformamide (molar ratio 1:1.2) at  $0^\circ\text{C}$  in nitrogen atmosphere. A solution of 6.8 g (0.03 mol) of **1a** in *N,N*-dimethylformamide was added dropwise to  $\text{POCl}_3/\text{DMF}$  complex at  $30^\circ\text{C}$ . The reaction mixture was stirred at  $80^\circ\text{C}$  for 4 h. When the reaction was finished (TLC monitoring), the reaction mixture was cooled down to the room temperature and poured into the ice water. The mixture obtained was neutralized with  $\text{NaOH}$  till  $\text{pH} = 7\text{--}8$ . The precipitates were separated by filtration and washed with methanol. The crude product was purified by column chromatography (eluent: ethylacetate–hexane, 1:8). Yield of **2a** 5.3 g (70%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.50 (t, 3H,  $\text{CH}_3$ ), 4.02 (m, 2H,  $\text{CH}_2$ ), 6.89–7.73 (m, 7H, ar), 9.83 (s, 1H, CHO).

*10-Ethyl-10H-3,7-phenotiazine dicarbaldehyde (2a')* was synthesized by the same procedure as compound **2a**. 6.8 g (0.03 mol) of compound **1a** and the eight-fold excess of  $\text{POCl}_3/\text{DMF}$  complex were taken for the reaction. The reaction mixture was stirred at  $85^\circ\text{C}$  for 72 h. Yield of **2a'** 3.8 g (45%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.60 (t, 3H,  $\text{CH}_3$ ), 4.10 (m, 2H,  $\text{CH}_2$ ), 7.00 (d, 2H, ar), 7.60–7.80 (m, 4H, ar), 9.90 (s, 2H, CHO).

*10-(2-Ethylhexyl)-10H-3-phenotiazine carbaldehyde (2b)* was synthesized by the same procedure as compound **2a**. Yield of **2b** 6.9 g (68%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.70–1.05 (m, 6H,  $\text{CH}_3$ ), 1.20–1.60 (m, 8H,  $\text{CH}_2$ ), 1.90 (m, 1H,  $\text{NCH}_2\text{CH}$ ), 3.70 (d, 2H,  $\text{NCH}_2\text{CH}$ ), 6.80–7.70 (m, 7H, ar), 9.80 (m, 1H, CHO).

*10-(2-Ethylhexyl)-10H-3,7-phenotiazine dicarbaldehyde (2b')* was synthesized by the same procedure as compound **2a**. Yield of **2b'** 4.9 g (45%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.70–1.00 (m, 6H,  $\text{CH}_3$ ), 1.20–1.50 (m, 8H,  $\text{CH}_2$ ), 1.90–2.10 (m, 1H,  $\text{NCH}_2\text{CH}$ ), 3.90 (d, 2H,  $\text{NCH}_2\text{CH}$ ), 7.00 (d, 2H, ar), 7.60–7.80 (m, 4H, ar), 9.80 (s, 2H, CHO).

*10-Ethyl-10H-3-phenotiazine carbaldehyde N,N-diphenylhydrazone (3a)*. A solution of 2.8 g (0.0156 mol) of *N,N*-diphenylhydrazine hydrochloride in methanol was added dropwise to a solution of 2 g (0.0078 mol) of compound **2a** in methanol. The reaction mixture was refluxed for 12 h and then cooled down to the room temperature. The crude product was filtered off and purified by column chromatography (eluent: ethylacetate–hexane, 1:6). Yield of **3a** ( $\text{C}_{27}\text{H}_{23}\text{N}_3\text{S} = 421,559\text{ g/mol}$ ) 2.6 g (80%). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3050 (ar.C–H), 2970, 2925 (alk.CH), 1590 (C=N), 1500, 1480 (ar.C=C), 1240 (C–N).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.40 (t, 3H,  $\text{CH}_3$ ), 3.90 (m, 2H,  $\text{CH}_2$ ), 6.73–7.48 (m, 17H, ar, 1H, methine). Mass spectra (MS):  $m/z = 421$  ( $M^+$ ), 253, 196.

*10-Ethyl-10H-3-phenotiazine carbaldehyde N-methyl-N-phenylhydrazone (3a')* was synthesized by the same procedure as compound **3a**. A solution of 1.9 g (0.0156 mol) of *N*-methyl-*N*-phenylhydrazone in methanol was added dropwise to a solution of 2 g (0.0078 mol) of compound **2a** in methanol. Yield of **3a'** ( $\text{C}_{22}\text{H}_{21}\text{N}_3\text{S} = 359,488\text{ g/mol}$ ) 2.3 g (85%). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3050 (ar.C–H), 2970, 2925 (alk.C–H), 1590 (C=N), 1500, 1480 (ar.C=C), 1240 (C–N).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.41 (t, 3H,  $\text{CH}_3$ ), 3.36 (s, 3H,  $\text{CH}_3$ ), 3.92 (m, 2H,  $\text{CH}_2$ ), 6.77–7.46 (m, 12H, ar, 1H, methine). MS:  $m/z = 359$  ( $M^+$ ), 344, 265, 253, 225, 196.

*10-(2-Ethylhexyl)-10H-3-phenotiazine carbaldehyde N,N-diphenylhydrazone (3b)* was synthesized by the same procedure as compound **3a**. Yield of **3b** ( $\text{C}_{33}\text{H}_{35}\text{N}_3\text{S} = 505,72\text{ g/mol}$ ) 2.8 g (71%). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3050 (ar.C–H), 2950, 2870 (alk.C–H), 1600 (C=N), 1500, 1470 (ar.C=C), 1290 (C–N).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.70–1.05 (m, 6H,  $\text{CH}_3$ ), 1.20–1.60 (m, 8H,  $\text{CH}_2$ ), 1.90 (m, 1H,  $\text{NCH}_2\text{CH}$ ), 3.70 (d, 2H,  $\text{NCH}_2\text{CH}$ ), 6.80–7.50 (m, 17H, ar, 1H, methine). MS:  $m/z = 506$  ( $M^+$ ), 337, 196.

*10-Ethyl-10H-3,7-phenotiazine dicarbaldehyde bis(N,N-diphenylhydrazone (4a)* was synthesized by the same procedure as compound **3a**. Yield of **4a** ( $\text{C}_{40}\text{H}_{33}\text{N}_5\text{S} = 615,794\text{ g/mol}$ ) 3.5 g (72%). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3050 (ar.C–H), 2940, 2850 (alk.C–H), 1590 (C=N), 1500, 1480 (ar.C=C), 1250 (C–N).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.50 (t, 3H,  $\text{CH}_3$ ), 3.95 (m, 2H,  $\text{CH}_2$ ), 6.60–7.75 (m, 26H, ar, 2H, methine). MS:  $m/z = 616$  ( $M^+$ ), 265, 224, 196.

*10-Ethyl-10H-3,7-phenotiazine dicarbaldehyde bis(N-methyl-N-phenylhydrazone (4a')* was synthesized by the same procedure as compound **3a'**. Yield of **4a'** ( $\text{C}_{30}\text{H}_{29}\text{N}_5\text{S} = 491,653\text{ g/mol}$ ) 3.2 g (82%). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3050 (ar.C–H), 2940, 2850 (alk.C–H), 1590 (C=N), 1480 (ar.C=C), 1250 (C–N).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 1.50 (t, 3H,  $\text{CH}_3$ ), 3.40 (s, 6H,  $\text{CH}_3$ ), 3.95 (m, 2H,  $\text{CH}_2$ ), 6.80–7.50 (m, 16H, ar, 2H, methine). MS:  $m/z = 492$  ( $M^+$ ), 385, 264, 244, 196.

*10-(2-Ethylhexyl)-10H-3,7-phenotiazine dicarbaldehyde bis(N,N-diphenylhydrazone (4b)* was synthesized by the same procedure as compound **3a**. Yield of **4b** ( $\text{C}_{46}\text{H}_{45}\text{N}_5\text{S} = 699,955\text{ g/mol}$ ) 3.5 g (65%). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3050 (ar.C–H), 2940, 2870 (alk.C–H), 1590 (C=N), 1500, 1480 (ar.C=C), 1290 (C–N).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.70–1.05 (m, 6H,  $\text{CH}_3$ ), 1.20–1.60 (m, 8H,  $\text{CH}_2$ ), 1.90 (m, 1H,  $\text{NCH}_2\text{CH}$ ), 3.70 (d, 2H,  $\text{NCH}_2\text{CH}$ ), 6.80 (d, 2H, ar), 7.00–7.50 (m, 24H, ar, 2H, methine). MS:  $m/z = 700$  ( $M^+$ ), 531, 196.

## 2.2. Instrumentation

$^1\text{H NMR}$  spectra were recorded using a JOEL JNM-FX 100 (100 MHz) apparatus. All data are given as chemical shifts  $\delta$  (ppm) downfield from  $(\text{CH}_3)_4\text{Si}$ . IR and UV-Vis spectra were recorded using a Perkin-Elmer 1330 and Varian Cary 219 spectrophotometers, respectively. Emission spectra were recorded using a Hitachi MPF-4

spectrofluorophotometer. Mass spectra were obtained on a Waters Micromass ZQ mass spectrometer. The samples for the ionisation potential ( $I_p$ ) and hole drift mobility measurements were prepared as described previously [9]. The ionisation potentials were measured by the electron photoemission in air method, described in earlier [10]. The hole drift mobilities in the amorphous films of the synthesized compounds and in their 50% solid solutions in bisphenol-Z polycarbonate (PC-Z) were measured by the xerographic time-of-flight technique (XTOF) [11].

### 3. Results and discussion

We have synthesized a series of 10-alkylphenothiazinylhydrazones by three step synthetic route, as schematically shown in Fig. 1. The first step was the alkylation of phenothiazine according to the known method [7] followed by the formylation of 10-alkylphenothiazines **1a** and **1b** using the Vilsmeier method [8] to get mono- and diformyl compounds **2a–b'**. The last step was the condensation of aldehydes **2a–b'** with differently substituted hydrazines to get mono- and dihydrazones **3a–b** and **4a–b**.

All the final hydrazones **3a–b** and **4a–b** were purified by column chromatography and characterized by IR,  $^1\text{H}$  NMR spectroscopy and mass spectrometry (see Section 2). They are soluble in common organic solvents such as acetone, chloroform and THF.

The synthesized hydrazones absorb light in the 240–460 nm region. The UV-Vis absorption spectra of dilute

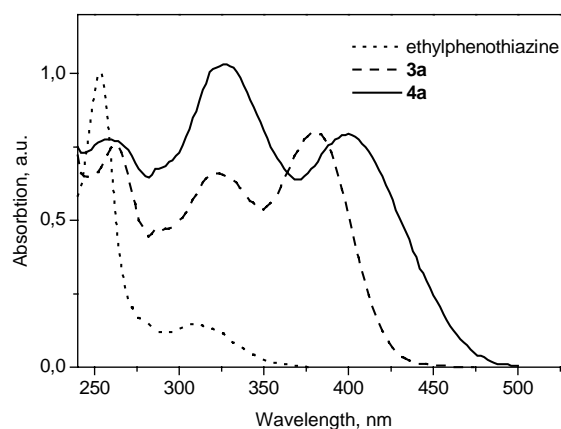


Fig. 2. UV-Vis absorption spectra of dilute solutions ( $\text{CHCl}_3$ ,  $2 \times 10^{-5}$  mol/l) of hydrazones **3a**, **4a** and 10-ethylphenothiazine.

solutions of hydrazones **3a** and **4a** in chloroform are shown in Fig. 2. For the comparison the UV-Vis spectrum of dilute 10-ethylphenothiazine solution is presented. The spectrum of **3a** exhibits a strong bathochromic shift with respect to the spectrum of 10-ethylphenothiazine. This observation shows that the molecules of the hydrazone are  $\pi$ -conjugated through the lone electron pairs of the nitrogen atoms and that the  $\pi$ -electrons are delocalized in these molecules. The absorption spectrum of hydrazone **3b** containing the same chromophore is identical to that of **3a**. The lowest energy absorption bands of dihydrazones **4a–b** are shifted bathochromically by ca. 20 nm with respect to the corresponding bands monohydrazones **3a–b**. This observation

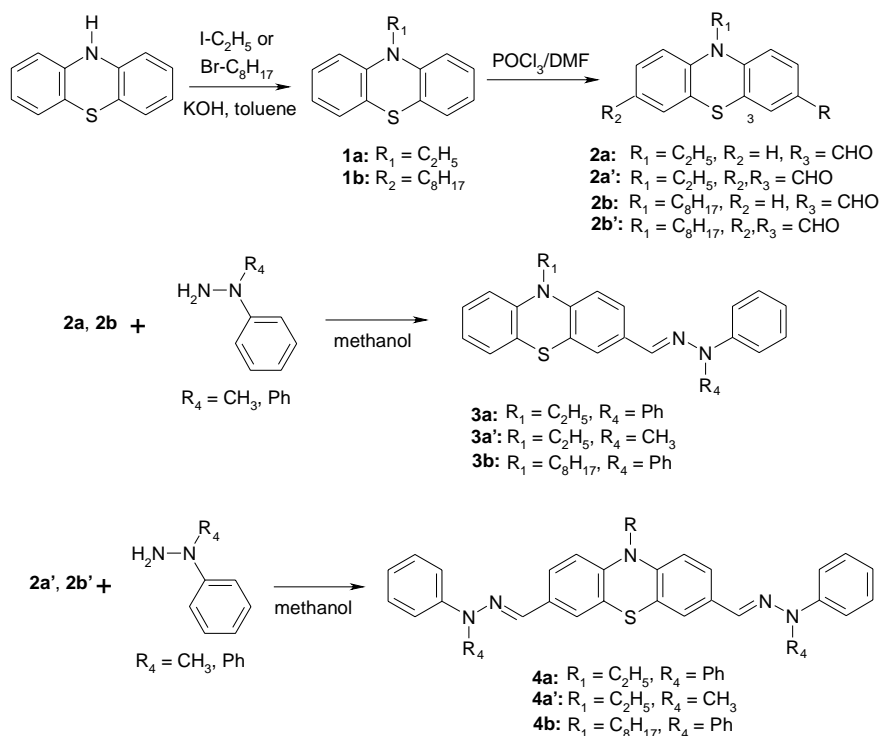


Fig. 1. Synthetic route to 10-substituted phenothiazinylhydrazones.

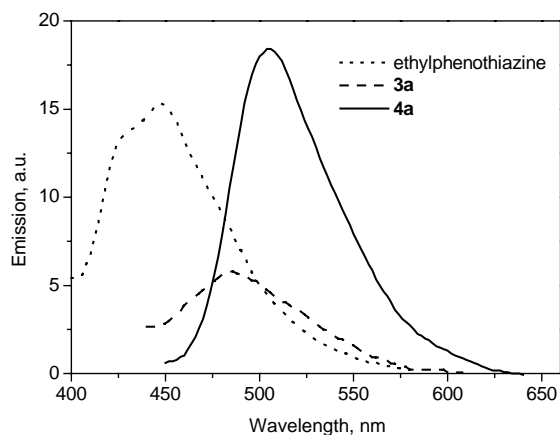


Fig. 3. Fluorescence spectra dilute THF solutions ( $2 \times 10^{-5}$  mol/l) of hydrazones **3a**, **4a**, and 10-ethylphenothiazine ( $\lambda_{\text{ex}} = 300$  nm).

shows that the systems  $\pi$ -conjugated electrons are extended in the molecules of dihydrazones and therefore more effective charge transport can be expected in the films of these compounds. The lowest energy absorption bands of diphenylsubstituted hydrazones **3a** and **4a** are by several nanometers shifted to the longer wavelengths with respect of the corresponding methylphenyl substituted hydrazones **3a'** and **4a'**.

All the synthesized hydrazones emit light when excited with UV light. Their emission spectra do not depend on the excitation wavelength. The fluorescence spectra of dilute THF solutions of some hydrazones synthesized are shown in Fig. 3. For the comparison the fluorescence spectrum of dilute solution of 10-ethylphenothiazine is presented. The fluorescence maxima of all the synthesized hydrazones are shifted bathochromically with respect to the spectrum of 10-ethylphenothiazine. The emission maxima of diphenyl substituted monohydrazones **3a** and **3b** are observed at 487 nm, while the maximum of methylphenyl substituted monohydrazone **3a'** is observed at 475 nm. The emission maxima of diphenyl substituted dihydrazones **4a**, and **4b** are observed at 507 nm, while that of methylphenyl substituted dihydrazone **4b'** is as observed at 494 nm.

The thermal characteristics of the hydrazones synthesized were determined by DSC and are summarized in Table 1. All the compounds reported in this presentation can be trans-

Table 1  
Thermal characteristics of phenothiazine based hydrazones

Compound	$T_m$ ( $^{\circ}\text{C}$ )	$T_{\text{cr}}$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )
<b>3a</b>	128 <sup>a</sup>	–	40
<b>3a'</b>	150 <sup>a</sup>	–	33
<b>3b</b>	–	–	23
<b>4a</b>	–	–	–
<b>4a'</b>	221 <sup>b</sup>	155	78
<b>4b</b>	–	–	58

<sup>a</sup> Only in the first heating run.

<sup>b</sup> Second heating run.

formed in to the amorphous state. **3a** and **3a'** were isolated as crystalline compounds. In the first DSC heating run they showed melting signals with the melting points at 128 and 150  $^{\circ}\text{C}$ , respectively. The second heating run revealed only glass transition. Compound **4a'** was isolated as an amorphous compound, however the morphological stability of its glass seems to be rather low. The first DSC heating run of this compound revealed only glass transition at 78  $^{\circ}\text{C}$ , however during recooling with 10  $^{\circ}\text{C}/\text{min}$  rate it crystallized and the second heating run revealed melting at 221  $^{\circ}\text{C}$ . Compound **4a** was isolated as an amorphous compound however the DSC apparatus used was not sensitive enough to establish its glass transition temperature ( $T_g$ ).  $T_g$  of the synthesized hydrazones strongly depends on the chemical structure of the molecules. The dihydrazones **4a'** and **4b** exhibit higher  $T_g$  than monohydrazones **3a–3b**.  $T_g$  of the hydrazones also depends on the nature and length of the substituents at the nitrogen atoms of phenothiazine and hydrazone moieties. For example,  $T_g$  of hydrazone **3b** having ethylhexyl substituent at the nitrogen atom of phenothiazine unit is by 17  $^{\circ}\text{C}$  lower than that of the corresponding hydrazone having ethyl group at the same position (**3a**).  $T_g$  of hydrazone **3a'** having methyl substituent at the nitrogen atom of hydrazone unit is by 7  $^{\circ}\text{C}$  lower than that of the corresponding hydrazone (**3a**) having phenyl substituent at the same position. Hydrazones **3a**, **3a'**, **3b** and **4b** form stable glasses and show no evidence for recrystallization in the DSC experiments on both heating and cooling with 10  $^{\circ}\text{C}/\text{min}$ .

Amorphous thin films on substrates can be prepared by the casting technique from the solutions of the synthesized hydrazones, however their morphological stability differs depending on the structure of the compounds. The photoelectric properties of the hydrazones were studied using such films. The ionisation potentials ( $I_p$ ), established by the electron photoemission technique, measured for all the synthesized hydrazones are presented in Table 2.

The  $I_p$  values of phenothiazine based dihydrazones **4a–b** are lower by ca. 0.10–0.20 eV than those of monohydrazones **3a–b**. Thus the extension of the system of conjugated  $\pi$ -electrons the molecules of phenothiazine-based hydrazones, leads to decrease the ionisation potentials.  $I_p$  value of methyl substituted dihydrazone **4a'** is a little lower than that of the corresponding phenyl substituted dihydrazones **4a** and **4b**. The similar observation was earlier reported for carbazole-based dihydrazones [12].  $I_p$  values of phenothiazine-based dihydrazones are by ca. 0.1 eV lower

Table 2  
Ionisation potentials of phenothiazine based hydrazones

Compound	$I_p$ (eV)
<b>3a</b>	5.40
<b>3a'</b>	5.41
<b>3b</b>	5.40
<b>4a</b>	5.25
<b>4a'</b>	5.20
<b>4b</b>	5.29

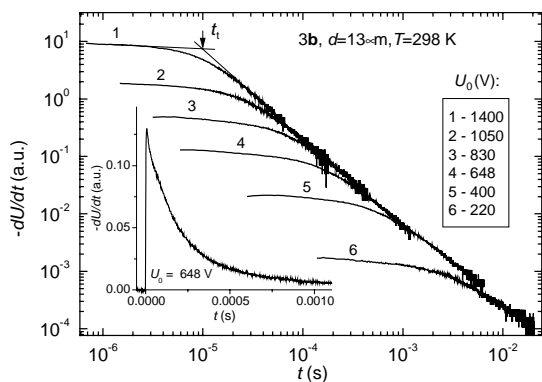


Fig. 4. XTOF transients for the amorphous film of compound **3b**.

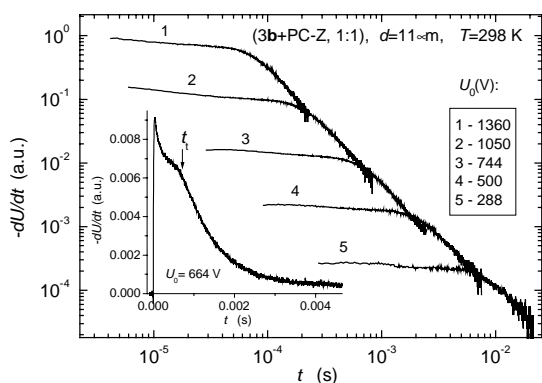


Fig. 5. XTOF transients for the film of the 50% solid solution of **3b** in PC-Z.

than those of the earlier reported corresponding carbazole-based dihydrazones [12].

The hole mobilities of the amorphous films of 5–14  $\mu\text{m}$  thickness of the pure compounds or of their solid solutions in PC-Z were measured by XTOF technique. Figs. 4 and 5

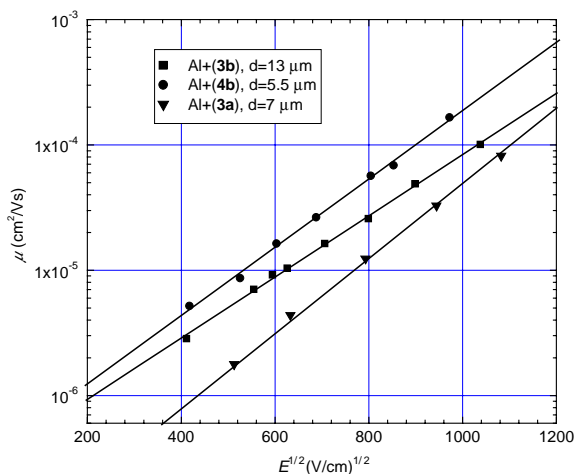


Fig. 6. Electric field dependencies of the hole drift mobilities of the amorphous films of hydrazones **3a**, **3b** and **4b**, at 25 °C.

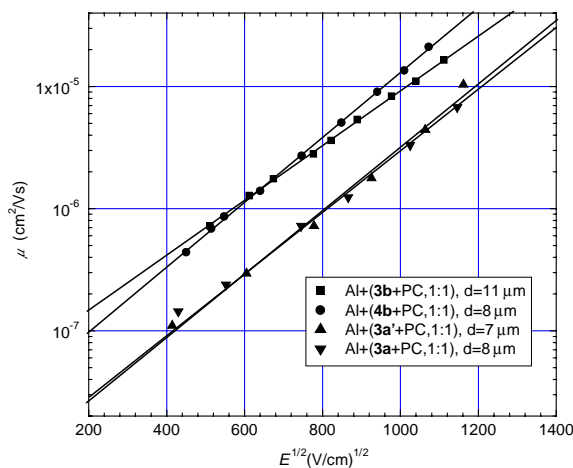


Fig. 7. Electric field dependence of the hole drift mobility of the solid solutions of hydrazones **3a**, **3a'**, **3b** and **4b** in PC, at 25 °C.

show examples of XTOF transients for the amorphous films of compound **3b** and of its 50% solid solution in PC-Z. It is evident that the solid solution of **3b** in PC-Z shows non-dispersive transport of charge carriers while dispersive transport is characteristic of the amorphous film of pure **3b**.

Fig. 6 shows the electric field dependence of the hole drift mobilities of the amorphous films of hydrazones **3a**, **3b** and **4b**. Compound **4b**, have the largest system of the conjugated  $\pi$ -electrons among these hydrazones, exhibited the highest hole drift mobility. It exceeded  $10^{-4} \text{ cm}^2/(\text{V s})$  at high electric fields.

The morphological stability of the amorphous films of compounds **4a** and **4a'** obtained by the casting technique was rather low and the films tended to crystallize soon after casting. Therefore it was impossible to measure hole mobilities in these films. The electric field dependencies of hole drift mobilities of the solid solutions in PC of hydrazones **3a**, **3a'**, **3b** and **4b** is presented in Fig. 7. The solid solutions of the synthesized hydrazones in PC exhibited hole drift mobilities are by one or two orders of magnitude lower than amorphous films of the pure compounds. **4a** and **4a'** tended to crystallize from their solid solutions in PC and therefore we did not manage to measure hole drift mobilities in these systems.

#### 4. Conclusions

A series of phenothiazine-based mono- and dihydrazones were synthesized. Their optical, thermal and photoelectrical properties have been studied. The ionization potentials of the phenothiazine-based hydrazones measured by electron photoemission technique range from 5.2 to 5.41 eV. The hole drift mobilities in the amorphous films and the solid solutions in bisphenol-Z polycarbonate of the synthesized hydrazones were studied by the time of flight technique. The highest room temperature charge mobilities were observed



in the amorphous film of 10-(2-ethylhexyl)-10*H*-3,7-phenothiazine dicarbaldehyde bis(*N,N*-diphenylhydrazone) which exceeded  $10^{-4} \text{ cm}^2/(\text{V s})$  at high electric fields.

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