# Synthesis and properties of dimeric naphthalene diimides

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<sup>4</sup>Department of Chemistry, Aleksandras Stulginskis University, Studentų 11, LT-53361 Akademija, Kaunas District, Lithuania New dimeric naphthalene diimides were synthesized via condensation of 1,4,5,8-naphthalene-tetracarboxylic dianhydride with different aromatic amines such as 2-amino-4-*tert*amylphenol and 4-*tert*-butylcyclohexylamine as well as using linking agents such as hydrazine and *p*-phenylenediamine. The unsymmetrical imide synthesis approach was used to prepare intermediate derivatives. The structures of the compounds were characterized by means of <sup>1</sup>H NMR, IR and mass spectrometry. The thermal behavior of the naphthalene diimides was investigated via differential scanning calorimetry. The studies showed that the compounds prepared are amorphous materials with glass transition temperatures from 132 °C to 266 °C. Optical properties of the synthesised naphthalene diimides in solution were studied by UV spectroscopy. All the compounds absorb electromagnetic radiation in the range of 200–400 nm.

Key words: naphthalene diimide, condensation, glass formation, optical properties

# **INTRODUCTION**

During the past decades, considerable attention has been focused on organic low- and high-molecular-weight conjugated systems called organic semiconductors both from the basic research and application standpoint. This is caused by the fact that they can be exploited in organic electronic devices [1, 2, 3–4]. The use of organic materials as the semiconductor layer provides a number of advantages, including lowtemperature process, large-area spin coating, inject printing, etc. [1, 2]. The derivatives of naphthalene tetracarboxylic anhydride are planar, chemically robust and redox-active compounds. They usually have high melting points as well as high thermal stability and assemble in  $\pi$ -stacks in the solid state that enhances the intermolecular  $\pi$ -orbital overlap and facilitates charge transport [1].

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Naphthalene tetracarboxylic dianhydride (NTCDA) and naphthalene tetracarboxylic diimide (NTCDI) derivatives are the most extensively investigated semiconductors for nchannel thin film transistors because of the easy addition of varied substituents to imide or anhydride moieties. They have large electron affinities which improve the electron accumulation to facilitate channel formation of a thin film transistor [2]. However, they have low solubility in common industrial solvents which limits their applications. The aim of this study was synthesis of the derivatives of naphthalene diimides with the improved solubility by introducing various fragments at the terminal positions. The optical, thermal properties and solubility of the materials were examined and compared.

#### EXPERIMENTAL

#### Materials and instrumentation

1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and tetrabutylamonium bromide were purchased from Fluka. 2-amino-4-*tert*-amylphenol, 1-iodhexane, 4-*tert*-butylcyclohexylamine, *p*-phenylenediamine were purchased from Aldrich Chemical Co. Acetone, hexane, diethyl ether, DMF, THF, CH<sub>3</sub>Cl, toluene and methanol were supplied by Poch, Penta, Lachema, Chempur and Aldrich. Compound **A** was prepared as reported [2].

Nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were obtained using a Varian Unity Inova 300 MHz (<sup>1</sup>H). All the data are given as chemical shifts in  $\delta$  (ppm), multiplicity, integration downfield from (CH<sub>3</sub>)<sub>4</sub>Si. Mass (MS) spectra were obtained on a Waters ZQ 2000 (Milford, USA). Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum GX spectrometer. UV spectra were recorded with a Hitachi U-3000 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Q100 TA DSC series thermal analyzer at a heating rate of 20 °C/min under nitrogen flow.

#### Synthesis

# *N*<sup>1</sup>-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (1)

To a stirring solution of 2-amino-4-tert-amylphenol (2.23 g, 12.44 mmol) in DMF (350 ml) 1,4,5,8-naphthalene-tetracarboxylic dianhydride (5 g, 18.64 mmol) was added and the reaction mixture was allowed to reflux for 24 hours in argon atmosphere. Then it was concentrated using a rotary evaporator and precipitated in 1 N HCl, The precipitate was filtered and carefully washed with water. The crude product was additionally washed with diethyl ether. The crude product was purified by silica gel column chromatography. A mixture of acetone and hexane (1/1.5) was used as an eluent. 2.62 g of yellow crystals (49%) were obtained. <sup>1</sup>H NMR spectrum yielded the following chemical shifts (300 MHz, CDCl<sub>2</sub>,  $\delta$ , ppm): 0.75 (t, 3H, J = 7.4 Hz, -CH<sub>2</sub>CH<sub>2</sub>), 1.29 (s, 6H,  $-C(CH_{2})_{2}$ , 1.63 (q, 2H, J = 7.4 Hz,  $-CH_{2}CH_{2}$ ), 6.85 (d, 1H,  $J = 8.5 \text{ Hz}, 6-\text{H}_{\text{ph}}), 7.13 \text{ (d, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 1H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}, 3-\text{H}_{\text{ph}}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H, } J = 2.3 \text{ Hz}), 7.26 \text{ (dd, 2H,$  ${}^{3}J_{\text{HH}} = 8.6 \text{ Hz}, {}^{5}J_{\text{HH}} = 2.3 \text{ Hz}, 5 \text{-H}_{\text{pb}}), 8.82 \text{ (s, 4H, Naph)}. An in-$  frared absorption spectrum yielded the following peaks (KBr window), in cm<sup>-1</sup>:  $\nu$  (OH) 3 348,  $\nu$  (arene C-H) 3077, 3042;  $\nu$  (C-H) 2 963, 2 926, 2 874;  $\nu$  (C=O) 1711;  $\nu$  (C=O<sub>imid</sub>) 1681, 1658;  $\nu$  (C=C in Ar) 1620, 1581, 1511, 1446;  $\nu$  (C-N) 1 342, 1247;  $\gamma$  (Ar) 764.

# $N^{1}$ -(2-hydroxy-5-tert-amylphenyl)- $N^{2}$ -amine-1,4,5,8-naphthalenetetracarboxylic diimide (2)

N<sup>1</sup>-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (1) (3.52 g, 8.2 mmol) and hydrazine hydrate (0.82 ml, 17.38 mmol) in 40 ml of dry DMF were heated up to 110 °C and stirred for 1.5 hours in argon atmosphere. The reaction mixture was concentrated using a rotary evaporator and then precipitated in 1 N HCl, filtered and carefully washed with water. The crude product was purified using silica gel column chromatography. A mixture of acetone and hexane (1/1.5) was chosen as an eluent. 1 g of crystals (29 %) was obtained. <sup>1</sup>H NMR spectrum yielded the following chemical shifts (300 MHz, DMSO,  $\delta$ , ppm):  $0.69 (t, 3H, J = 7.2 \text{ Hz}, -CH_2CH_2), 1.24 (s, 6H, -C(CH_2)_2), 1.59$  $(q, 2H, J = 7.5 \text{ Hz}, -C\underline{H}_2\text{CH}_3), 5.91 (s, 2H, NH_2), 6.94 (d, 1H, CH_2)$  $J = 8.3 \text{ Hz}, 6 \text{-H}_{\text{pb}}), 7.17 (q, 1\text{H}, J = 2.2 \text{ Hz}, 3 \text{-H}_{\text{pb}}), 7.27 \text{ (dd, 1H,}$  ${}^{3}J_{_{\rm HH}} = 8.5 \text{ Hz}, {}^{5}J_{_{\rm HH}} = 2.7 \text{ Hz}, 5 \cdot \text{H}_{_{\rm Ph}}$ ), 8.68 (d, 2H,  $J_{_{\rm AB}} = 9.7 \text{ Hz}$ , Naph), 8.72 (d, 2H,  $J_{_{\rm AB}} = 7.6 \text{ Hz}$ , Naph), 9.43 (s, 1H, OH). An infrared absorption spectrum yielded the following peaks (KBr window), in cm<sup>-1</sup>: v (NH<sub>2</sub>) 3 334, 3 247; v (arene C-H) 3 081; v (C-H) 2 963, 2 875; v (C=O) 1 713; v (C=O<sub>imid</sub>) 1 664; v (C=C in Ar) 1619, 1581, 1514, 1450; v (C-N) 1353, 1249; γ (Ar) 763. MS (APCI<sup>+</sup>, 20 V), m/z: 444 ([M+H]<sup>+</sup>).

# $N^2$ , $N^2$ -bis-(2-hydroxy-5-tert-amylphenyl)- $N^1$ , $N^1$ -bis-1,4,5,8-naphthalenetetracarboxylic diimide (3)

N<sup>1</sup>-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (1) (0.48 g, 1.13 mmol) N<sup>1</sup>-(2-hydroxy-5-tert-amylphenyl)-N<sup>2</sup>-amine-1,4,5,8and naphthalenetetracarboxylic diimide (2) (0.5 g, 1.13 mmol) in 35 ml of dry DMF were heated up to 110 °C and stirred for 78 hours in argon atmosphere. The reaction mixture was concentrated using a rotary evaporator and then precipitated in 1 N HCl, filtered and washed with water. The crude product was purified using silica gel column chromatography. A mixture of acetone and toluene (1/5) was chosen as an eluent. 0.5 g of crystals (52%) was obtained. <sup>1</sup>H NMR spectrum yielded the following chemical shifts (300 MHz, DMSO,  $\delta$ , ppm): 0.71 (t, 6H, J = 7.33 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 1.26 (s, 12H,  $-C(C\underline{H}_3)_3$ , 1.61 (q, 4H, J = 7.35 Hz,  $-C\underline{H}_3CH_3$ , 6.98 (d, 2H, J = 8.5 Hz, 6,6'-H<sub>ph</sub>), 7.27 (d, 1H, J = 2.3 Hz, 3,3'-H<sub>ph</sub>), 7.32 (dd, 2H,  ${}^{3}J_{HH} = 8.6 \text{ Hz}, {}^{5}J_{HH} = 2.3 \text{ Hz}, 5,5'-H_{Ph}$ ), 8.83 (d, 2H, *J* = 7.6 Hz, Naph), 8.96 (d, 2H, *J* = 7.6 Hz, Naph), 9.51 (s, 2H, OH). An infrared absorption spectrum yielded the following peaks (KBr window), in cm<sup>-1</sup>: v (OH) 3 420; v (arene C-H) 3082; v (C-H) 2963, 2875; v (C=O) 1719; v (C=O<sub>imid</sub>) 1679; v (C=C in Ar) 1619, 1582, 1513, 1445; v (C-N) 1 342, 1 316, 1 248; γ (Ar) 764. MS (APCI<sup>+</sup>, 20 V), m/z: 855  $([M+H]^+).$ 

# $N^2$ , $N^2$ -bis-(2-hexylphenyl-5-tert-amylphenyl)- $N^1$ , $N^1$ -bis-1, 4,5,8-naphthalenetetracarboxylic diimide (4)

To a stirring solution of N<sup>2</sup>, N<sup>2</sup>-bis-(2-hydroxy-5-tertamylphenyl)-N<sup>1</sup>,N<sup>1</sup>-bis-1,4,5,8-naphthalenetetracarboxylic diimide (3) (0.15 g, 0.18 mmol) in 4 ml of dry acetone 1-iodhexane (0.26 g, 1.69 mmol), anhydrous potassium carbonate (0.2 g, 1.47 mmol) and tetrabutylamonium bromide (0.05 g, 0.16 mmol) were added. The reaction mixture was stirred for 72 hours at room temperature. The reaction mixture was concentrated using a rotary evaporator. The crude product was purified using silica gel column chromatography. A mixture of acetone and hexane (1/1) was used as an eluent. 0.06 g of crystals (33%) was obtained. <sup>1</sup>H NMR spectrum yielded the following chemical shifts (300 MHz, DMSO, δ, ppm): 0.71 (t,  $6H, J = 7.0 Hz, -CCH_{2}CH_{2}, 0.78 (t, 6H, J = 7.3 Hz, -CH_{2}CH_{2}),$ 1.14-1.05 (m, 8H, 2CH<sub>2</sub>), 1.25-1.15 (m, 4H, CH<sub>2</sub>), 1.32 (s, 12H,  $-C(CH_{2})_{2}$ , 1.55 (q, 4H, J = 7.1 Hz,  $CH_{2}CH_{2}$ ), 1.66 (q, 6H,  $J = 7.4 \text{ Hz}, \overline{\text{CCH}}, \text{CH}_3), 3.98 (t, 4\text{H}, J = 6.4 \text{ Hz}, -\text{OCH}_3, -), 7.04$  $(d, 2H, J = 8.7 \text{ Hz}, 6.6' \text{-H}_{Ph}), 7.25 (d, 1H, J = 2.3 \text{ Hz}, 3.3' \text{-H}_{Ph}),$ 7.40 (dd, 2H,  ${}^{3}J_{\rm HH} = 8.7$  Hz,  ${}^{5}J_{\rm HH} = 2.4$  Hz, 5,5'-H<sub>ph</sub>), 8.94–8.86 (m, 8H, Naph). An infrared absorption spectrum yielded the following peaks (KBr window), in cm<sup>-1</sup>: v (arene C-H) 3081; v (C-H) 2959, 2929, 2871; v (C=O) 1720; v (C=O<sub>init</sub>) 1683; v (C=C in Ar) 1582, 1509, 1444; v (C-N) 1341, 1315, 1246; γ (Ar) 764.

 $N^{1}$ -(4-tert-butylcyclohexyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (5) was prepared according to the similar procedure as 1 using 4-tert-butylcyclohexylamine (1.16 g, 7.47 mmol) instead of 2-amino-4-tert-amylphenol. The crude product was purified by silica gel column chromatography using the mixture of toluene and diethyl ether (vol. ratio 6 : 1) as an eluent to obtain 2.3 g of 5. Yield: 76%. <sup>1</sup>H NMR spectrum yielded the following chemical shifts (300 MHz, CDCl<sub>3</sub>, δ, ppm): 0.91 (s, 9H,  $3 \times CH_3$ ), 1.18–1.12 (m, 2H,  $CH_{2 \text{ cyclo}}$ ), 1.25 (s, 1H, C- $CH_{\text{cyclo}}$ ),  $1.96-1.78 \text{ (m, 6H, 3 \times CH}_{2 \text{ cyclo}}\text{)}, 4.88-4.84 \text{ (m, 1H, N-CH}_{\text{cyclo}}\text{)},$ 8.70 (dd, 4H,  $J_{AB} = 7.6$  Hz,  $J_{AB} = 7.6$  Hz, Naph). An infrared absorption spectrum yielded the following peaks (KBr window), in cm<sup>-1</sup>: v (arene C-H) 3086, 3046; v (C-H) 2946, 2865; ν (C=O) 1793, 1745, 1704; ν (C=O<sub>imid</sub>) 1669, 1659; ν (C=C in Ar) 1626, 1582, 1517, 1479, 1449; ν (C-N) 1333, 1 240; γ (cyclo C-C) 1 019; γ (Ar) 764. MS (APCI<sup>+</sup>, 20 V), m/z:  $405 ([M+H]^+).$ 

 $N^{1}$ -(4-tert-butylcyclohexyl)- $N^{2}$ -phenylenamine-1,4,5,8naphthalenetetracarboxylic diimide (6) was prepared according to the similar procedure as 2 using *p*-phenylenediamine (0.27 g, 2.47 mmol) instead of hydrazine hydrate. The crude product was purified by silica gel column chromatography using the mixture of toluene and diethyl ether (vol. ratio 1 : 1) as an eluent to obtain 0.41 g of **6**. The yield was 67%. <sup>1</sup>H NMR spectrum yielded the following chemical shifts (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 0.92 (s, 9H, 3 × CH<sub>3</sub>), 1.25–1.15 (m, 6H, 2 × CH<sub>2 cyclo</sub>, 2 × CH<sub>cyclo</sub>), 1.92–1.85 (m, 4H, 2 × CH<sub>2 cyclo</sub>), 5.32 (s, 2H, -NH<sub>2</sub>), 6.68 (d, 2H, J = 8,6 Hz, 9,10-H<sub>ph</sub>), 7.03 (d, 2H,  $J_{\rm HH} = 8.0$  Hz, 6,7-H<sub>ph</sub>), 8.70 (s, 4H, Naph). An infrared absorption spectrum yielded the following peaks (KBr window), in cm<sup>-1</sup>: v (NH<sub>2</sub>) 3 434, 3 370; v (arene C-H) 3 077, 3 046; v (C-H) 2 946, 2 864; v (C=O) 1 715; v (C=O<sub>imid</sub>) 1 669; v (C=C in Ar) 1 580, 1 499, 1 449; v (C-N) 1 365, 1 350;  $\gamma$  (cyclo C-C) 979;  $\gamma$  (Ar) 769, 747. MS (APCI<sup>+</sup>, 20 V), m/z: 495 ([M+H]<sup>+</sup>).

 $N^2$ ,  $N^2$ -*bis*-(4-tert-butylcyclohexyl)- $N^1$ ,  $N^1$ -*bis*-1, 4, 5, 8-*naph-thalenetetracarboxylic diimide* (7) was prepared according to the similar procedure as 3 using 5 (0.05 g, 0.1 mmol) and 6 (0.04 g, 0.1 mmol). The crude product was purified by silica gel column chromatography using the mixture of toluene and acetone (vol. ratio 5 : 1) as an eluent to obtain 0.04 g of 7. Yield: 45%. <sup>1</sup>H NMR spectrum yielded the following chemical shifts (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 0.94–0.90 (m, 18H,  $6 \times CH_3$ ), 1.26–1.22 (m, 4H,  $4 \times CH_{cyclo}$ ), 1.19–1.13 (m, 16H,  $8 \times CH_{2cyclo}$ ), 6.69 (d, 2H, J = 8.8 Hz, 3,4-H<sub>ph</sub>), 7.03 (d, 2H,  $J_{HH} = 8.7$  Hz, 1,2-H<sub>ph</sub>), 8.71 (s, 8H, Naph). An infrared absorption spectrum yielded the following peaks (KBr window), in cm<sup>-1</sup>: v (arene C-H) 3 069; v (C-H) 2 944, 2 863; v (C=O) 1 709; v (C=O<sub>imid</sub>) 1 662; v (C=C in Ar) 1 580, 1 515, 1 447; v (C-N) 1 343; γ (cyclo C-C) 978; γ (Ar) 768. MS (APCI<sup>+</sup>, 20 V), m/z: 882 ([M+H]<sup>+</sup>).

#### **RESULTS AND DISCUSSION**

N<sup>1</sup>-(2-hydroxy-5-tert-amylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (1) and N<sup>1</sup>-(4-tertbutylcyclohexyl)-1,4,5,8-naphthalenetetracarboxylic-1,8anhydride-4,5-imide (5) were synthesized by the reaction of 1,4,5,8-naphthalene-tetracarboxylic dianhydride and 2-amino-4-tert-amylphenol or 4-tert-butylcyclohexylamine, respectively. Compounds 2 and 6 were obtained by the reaction of the corresponding anhydride with hydrazine hydrate or *p*-phenylenediamine, respectively. They are readily soluble in organic solvents and have a primary amino group. Bichromophoric naphthalene diimides 3 and 7 were prepared under mild reaction conditions (120 °C, 78 h) from naphthalene anhydrides 1 or 5 and amines 2 or 6, respectively. The alkyl derivative of naphthalenetetracarboxy diimide was obtained after the alkylation of 3 with 1-iodhexane in acetone with tetrabutylammonium bromide as phase-transfer catalyst (PTC) (Scheme).

The structures of the intermediate and the target derivatives were confirmed by <sup>1</sup>H NMR, IR and mass spectrometries. The main purpose of introducing branched alkyl chains was to increase the solubility in common organic solvents. The derivatives are soluble in solvents such as chloroform, THF, acetonitrile, dimethylformamide, etc.

The absorption bands due to OH groups at 3348 and 3420 cm<sup>-1</sup> are present in the IR spectra of condensation products 1 and 3, respectively, and the absorption bands due to the amino group at 3334, 3247 cm<sup>-1</sup> are present in the IR spectrum of product 2 and at 3434, 3370 cm<sup>-1</sup> in the IR spectrum of **6**. The absorption bands of alkyl groups in the range



Scheme. Synthetic routes to naphthalene imides 1-7

from 2 946 to 2 863  $\text{cm}^{-1}$  are present in the IR spectra of these compounds.

The signals in the <sup>1</sup>H NMR spectra of all the newly synthesized compounds can be assigned to the characteristic hydrogen atoms. The triplet of two protons at 3.98 ppm and two triplets of six protons at 0.78 and 0.71 ppm observed in the <sup>1</sup>H NMR spectra show the presence of 2-hexylphenyl-5-*tert*amylphenyl fragment in molecule 4 in such a way proving the formation of symmetrical diimide. The structures of the target compounds were also confirmed by mass spectrometry. The mass spectrum of dimer **3** are presented in Fig. 1. The mass spectrum signal of molecular ion is at m/z of 855.

Thermal properties of the synthesized compounds were examined by the DSC technique. The glass transition and melting temperatures of the materials are summarized in the Table. After the synthesis, derivative 3 was isolated as crystalline material, showing melting point at 280 °C during



Fig. 1. Mass spectrum of 3

Table. Thermal characteristics of naphthalenetetracarboxy diimide-based materials

Compound	<i>T<sub>m</sub></i> , °C <sup>1</sup>	<i>T<sub>q</sub></i> , °C <sup>1</sup>
3	280	266
4	-	132
7	-	159

<sup>1</sup> Scan rate 20 °C/min, N<sub>2</sub> atmosphere.



Fig. 2. TGA curve of 7 recorded at the heating rate of 10 °C/min in N, atmosphere



Fig. 3. UV absorption spectra of dilute THF solutions of 3 and A

the first DSC scan. We did not manage to obtain diimides 4 and 7 in the crystalline form, therefore we could state that the attached alkyl chains prevent packing of the molecules into crystal lattices, and the materials exist in the amorphous state. Only glass transitions were observed at 132 °C and 159 °C during the first DSC scans of 4 and 7, respectively. Compounds 3, 4 and 7 showed high  $T_g$  (132–266 °C), which are predetermined by the rigidity of the naphthalene tetracarboxy diimide moiety.

Thermogravimetry was used to analyze the thermostability of the synthesized compounds. Fig. 2 shows the TGA curve of compound 7. It is evident that the thermal degradation of 7 occurs in two stages. Derivative 7 starts to decompose only at temperatures higher than 400 °C. This observation confirms a very high thermal stability of the synthesized compounds. It is obvious that imides containing cyclohexyl units start to decompose by N-C bond fission. The weight loss in the first step is ca. 15%, which corresponds to the loss of approximately one tertbutylcyclohexyl unit. The second stage of the thermal degradation of compound 7 starts at the temperatures higher than 600 °C.

The dilute solution of the synthesized naphthalenetetracarboxy diimide derivatives absorb electromagnetic radiation in the range of 200–400 nm. The UV absorption spectrum of the dilute THF solution of compound **3** is given in Fig. 3. For the comparison the spectrum of the model compound **A** is shown. The spectra of **3** and **A** are very similar. This observation shows that two naphthalene diimide moieties in **3** behave like independent chromophores, i. e. there is no enhancement in conjugation to a considerable degree after joining two naphthalene diimide chromophores by N-N bonding.

### CONCLUSIONS

Four new glass-forming naphthalenetetracarboxy diimide dimeric derivatives were synthesized using the unsymmetrical imide synthesis approach. The structures of the synthesized derivatives were confirmed by <sup>1</sup>H NMR, IR and mass spectrometries. Their thermal transitions were studied by differential scanning calorimetry and their optical properties were explored by UV absorption spectrometry. All the synthesized compounds form glasses with the glass transition temperatures ranging from 132 °C to 266 °C. It was shown that alkyl chains attached to the molecule allowed for alkylated compound to exist in the glassy state. The electronic interaction between two naphthalene diimide chromophores coupled of by N-N bond is negligible as it was shown by UV absorption spectroscopy.

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### DIMERINIŲ NAFTALENDIIMIDŲ SINTEZĖ IR SAVYBĖS

#### Santrauka

Kondensacijos būdu iš 1,4,5,8-naftalentetrakarboksi dianhidrido ir 2-amino-4-*tret*-amilfenolio arba 4-*tret*-butilcikloheksilamino sintetinant asimetrinius imidus ir juos jungiant su hidrazino hidratu arba *p*-fenilendiaminu buvo gauti naftalentetrakarboksidiimidų dimerai. Junginių struktūros įrodytos <sup>1</sup>H BMR, IR spektroskopijos ir masių spektrometrijos būdais. Diferencinės skenuojamos kalorimetrijos metodu buvo ištirtos dimerinių naftalendiimidų terminės savybės. Susintetinti junginiai gali būti transformuoti į kietą amorfinę būseną, kurių stiklėjimo temperatūra išsidėsto intervale nuo 132 °C iki 266 °C. UV spektroskopijos metodu buvo ištirtos naftalendiimidų praskiestų THF tirpalų optinės savybės. Gauti junginiai absorbuoja UV spinduliuotę 200–400 nm bangų ilgio intervale.