SYNTHESIS OF ORGANIC GLASSES CONTAINING AZOCHROMOFORE

AZOHROMOFORUS SATUROŠU ORGANISKO STIKLU SINTĒZE

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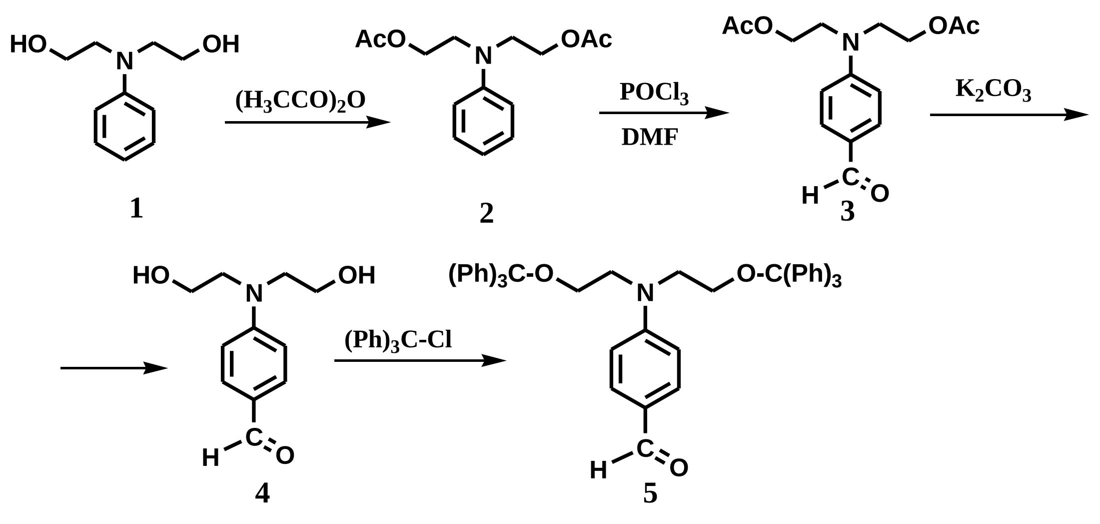
Introduction

Push-pull type chromophores containing compounds where electron acceptor group is conjugated with electron donor group *via* azogroup bridge are object of intense research as active component in nonlinear optic (NLO) materials. The ability of amorphous azochromophore containing compounds to form a surface relief grating after exposure to laser radiation can be used to create different high density data storage systems [1-4]. One of main parameters for successful experiments in given research is ability of synthesized materials to form thin amorphous layers and ability to absorb electromagnetic radiation at necessary wavelength. Thin amorphous layers can be formed not only by polymer type compounds but also by some molecular compounds – organic glasses.

Results and discussion

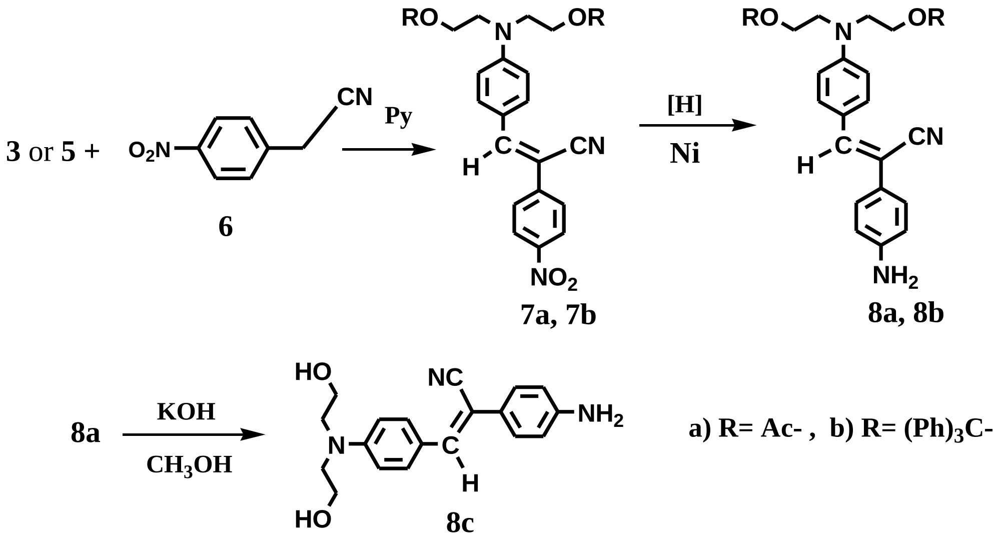
Our goal was to synthesize different type of push-pull azochromophore containing molecular compounds where electron donating aminogroup was connected with azogroup via conjugated stylbene bridge, and to determine the ability of obtained compounds to form amorphous thin layers. Target products were acquired using Mill's reaction. Intermediate compounds **8a-c** were obtained as shown in scheme 1 and 2. 4-bis(2-Hydroxyethyl)aminobenzaldehyde (**4**) was obtained according to scheme 1 [5-7] and aldehyde **5** *via* tritilation of compound **4**.

Scheme 1



Aldehydes **3**, **5** condensation products with 4-nitrobezylcyanide (**6**), after catalytic hydrogenation, yielded amines **8a** and **8b**.

Scheme 2



6

7a, 7b

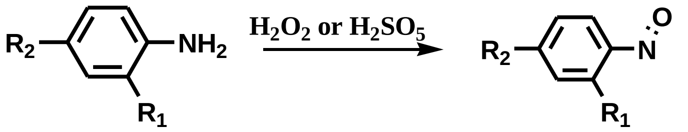
8a, 8b

8c

a) R= Ac- , b) R= $(Ph)_3C$-

Nitrosoarenes **10a-b** were synthesized by oxidation of anilines **9a-b** with hydrogen peroxide in the presence of catalytic amounts of Mo(VI) oxide or its salts [8], according to scheme 3. 2-Bromo-4-nitroaniline (**9c**) was selectively obtained using system $KBr/NaBO_3/MoO_3$ [9], but corresponding nitroso product **10c** was synthesized by oxidation of **9c** with Caro's acid [10-12].

Scheme 3



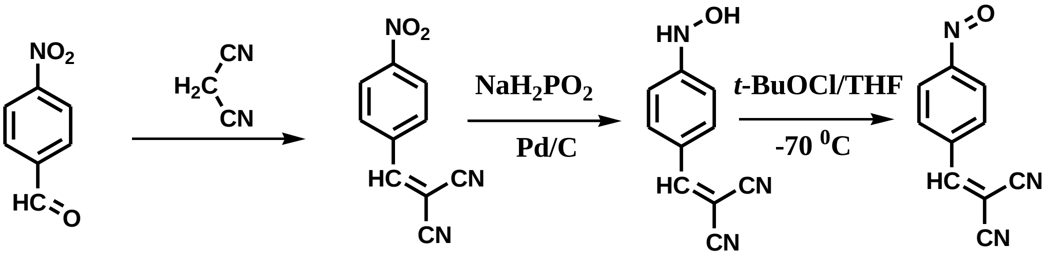
9a, 9b, 9c

10a, 10b, 10c

a) R_1= -H, R_2= -NO_2 b) R_1= -H, R_2= -Ac c) R_1= -Br, R_2= -NO_2

According to scheme 4, synthesis of (4-nitrosobenzylidene)malononitrile (**10d**) was realized following: 4-nitrobenzaldehyde (**11**) and malononitrile condensation product **12** was reduced over Pd/C with sodium hypophosphite. Obtained hydroxylamine **13** then was oxidized with t-butylhypochlorite, which was synthesized according to literature [13].

Scheme 4



11

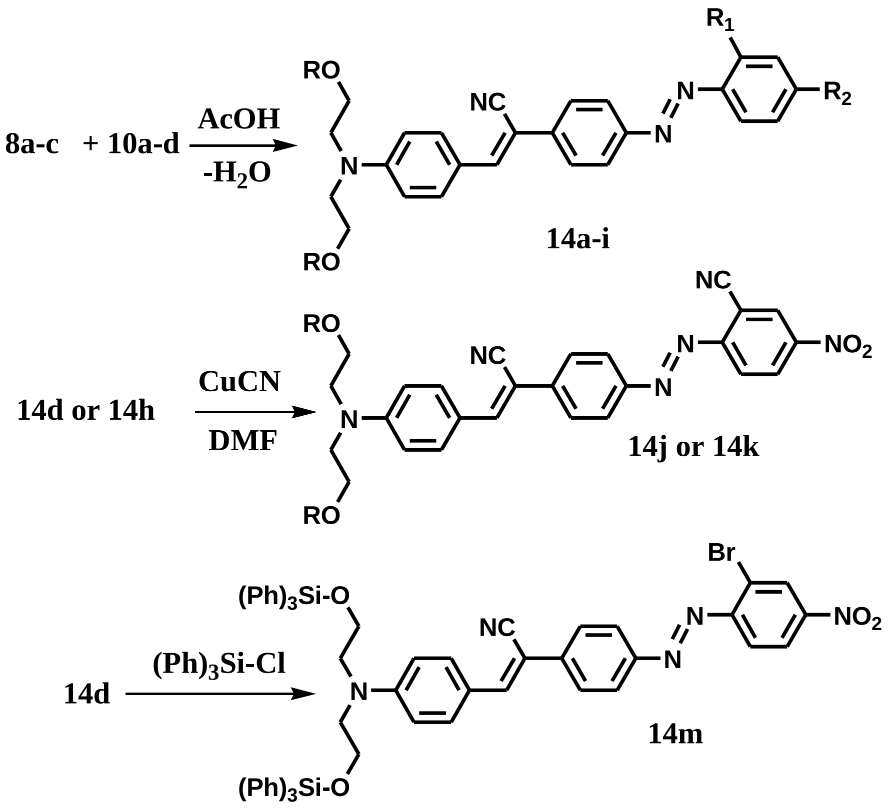
12

13

10d

Condensations of nitrosoarenes **10a-d** and amines **8a-c** were carried out in acetic acid, according to scheme 5. Products and their electron absorption spectra maximums at visible wavelength electromagnetic radiation are shown in table 1.

Scheme 5

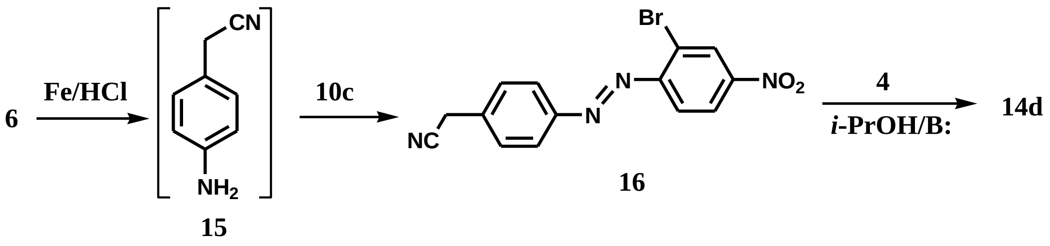


d) R=-H, R_1= -Br, R_2= -NO_2 **j) R= -H, k) R= -C(Ph)$_3$**

h) R=-C(Ph)$_3$, R_1= -Br, R_2= -NO_2

Compound **14d** was also acquired using alternative synthesis route as shown in scheme 6. Reduction product of 4-nitrobenzylcyanide (**6**), without isolation of crystalline amine **15**, was condensated with nitroso compound **10c**. Synthesis yielded active methylene group containing product **16** what was further reacted with 4-bis(2-hydoxyethyl)amino-benzaldehyde (**4**) to yield azochromophore **14d**.

Scheme 6



Azochromophores **14g**, **14h** were obtained using both condensation of amine **8b** with nitrosoarenes **10a**, **10c** and alkylation of compounds **14c** and **14d** with tritylchloride. Reaction of **14d** with triphenylchlorosilane yielded compound **14m**.

Products **14j** and **14k** were obtained by substitution of bromine atom with cyano group [14]. The presence of cyano group in electron acceptor part of molecule caused batochromic shift of the electron absorbance maximum by approximately 20nm.

Table 1
Synthesized azochomophore containing compounds and their electron absorption spectra maximums at visible part of spectra.

Compound	**Substitutes**			**λ_{max} (nm) / lgε (DMF)**
	R	**R_1**	**R_2**	
14a	-Ac	-H	$-NO_2$	496 / 4.68
14b	-Ac	-Br	$-NO_2$	510 / 4.65
14c	-H	-H	$-NO_2$	495 / 4.58
14d	-H	-Br	$-NO_2$	511 / 4,64
14e	-H	-H	$-CH=C(CN)_2$	438 / 4.60
14f	$-C(Ph)_3$	-H	-Ac	470 / 4.53
14g	$-C(Ph)_3$	-H	$-NO_2$	494 / 4.55
14h	$-C(Ph)_3$	-Br	$-NO_2$	510 / 4.54
14i	$-C(Ph)_3$	-H	$-CH=C(CN)_2$	469 / 4.58
14j	-H	-CN	$-NO_2$	533 / 4.11
14k	$-C(Ph)_3$	-CN	$-NO_2$	533 / 4.52
14m	$-Si(Ph)_3$	-Br	$-NO_2$	509 / 4.47

Electron absorption spectra maximums of the synthesized compounds, depending on structure of electron acceptor fragment, vary from 440-530nm. The electron absorption curves are wide and at certain concentration they surpass 630nm mark, what makes these compounds as perspective materials for holographic recording with He-Ne laser. Azochromophore containing compounds where substitute **R** is triphenylmethyl group (**14f**, **14g**,**14h**, **14i** and **14k**) or triphenylsilyl group (**14m**) form thin glassy layers from volatile solvents (chloroform or methylene chloride).

Experimental

IR spectra of synthesized compounds were taken in paraffin oil on Nicolet 5700 FT-IR spectrometer. UV-VIS spectra were recorded on a Perkin Elmer Lamda 35 spectrometer. Products were characterized by ^{1}H-NMR with Bruker WH90/DS spectrometer at 90MHz and with Varian VRX-Unity spectrometer at 200MHz. Chemical shift of ^{1}H-NMR was referenced to tetramethylsilane (TMS) at 0 ppm.

4-[N,N-di(Trityloxyethyl)amino]benzaldehyde (5).

4-[N,N-di(Hydroxyethyl)amino]benzaldehyde (**4**) (3.0 g, 14.3 mmol) and trytilchloride (12.0 g, 0.43 mmol) are dissolved in 200 mL of dry pyridine and refluxed for 2h. The reaction mixture is then evaporated under reduced pressure till 80 mL volume and poured into 300 mL of isopropanol. Obtained white precipitate is then filtrated and washed with isopropanol (3x50 mL) and methanol (3x50 mL). Yield: 9.13g (92 %). ^{1}H-NMR (200MHz, $CDCl_3$) δ, ppm: 3.28 (4H, t, ^3J=5.3Hz), 3.62 (4H, t, ^3J=5.7Hz), 6.82 (2H, d, ^3J=8.9Hz), 7.10-7.40(30H, m), 7.62(2H, d, ^3J=8.9Hz), 9.67(1H, s).
IR (ν, cm^{-1}): 3072, 3021, 2737, 1681, 1598, 1558, 1523, 1355, 1318.

4-Nitrosoacetophenone (10b).

4-Aminoacetophenone (**9b**) (13.5g, 0.1mol) is suspended into 200ml of methanol and dissolved by heating. During intensive stirring, 100 mL of distilled water is added. The resulting suspension is cooled till room temperature, and H_2O_2 (85 mL– 30%, 7.5 eqv), MoO_3 (1.44 g, 1 mol%) are added, after what the mixture is intensively stirred at room temperature. After 3 days the heterogenic suspension is diluted with 70 mL of ethanol and 30 mL of water. Approximately after 10 days when the mixture contains 90% of product (TLC, toluene/ethyl acetate = 2/1), the suspension is filtered. The product is washed with water and small amount of methanol. Further purification is made by column chromatography (silica gel, toluene). Yield: 11.2g (75 %) of yellow substance, m.p. 110 ºC (111 ºC

[15]). ^{1}H-NMR (200MHz, DMSO) δ, ppm: 2.64 (3H, s), 8.00 (2H, d), 8.22 (2H, d, ^{3}J=8,30Hz).

3-{4-[bis(2-Acetoxyethyl)amino]phenyl}-2-(4-nitrophenyl)acronitrile (7a).
4-Nitrobenzylcyanide (**6**) (5.6g, 34.6mmol) and 4-(di[acetoxyethyl]-amino)benzaldehyde (**3**) (10.0 g, 34.1 mol) under heating are dissolved in 200 mL of isopropanol and 3 drops of morpholine are added after what solution is refluxed for 4 h. The mixture is cooled and orange needle-shaped crystals are filtered (7.2 g). The filtrate is repeatedly refluxed until all of starting substances have reacted (TLC, toluene/ethyl acetate = 2/1). Additional 3.3 g of product are obtained. After crystallization from toluene, 9.6 g (65 %) of needle-shaped crystals are yielded, m.p. 129-130 ºC. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 1.93 (6H, s), 3.66 (4H, t, ^{3}J=5.1Hz), 4.16 (4H, t, ^{3}J=5.0Hz), 6.88 (2H, d, ^{3}J=11.1Hz), 7.91 (4H, d, ^{3}J=8.2Hz), 8.12 (1H, s), 8.27 (2H, d, ^{3}J=11.2Hz). IR(ν, cm^{-1}): 3100, 3072, 3035, 1736, 1612, 1596, 1579, 1512, 1403, 1377, 1363, 1340. Elemental analysis for $C_{23}H_{23}N_3O_6$, calculated %: C 63.15, H 5.30, N 9.61. Found %: C 63.00, H 5.37, N 9.61. UV-VIS (DMF): λ_{max}=448 nm, lgε=4.56.

3-{4-[bis(2-Trityloxyethyl)amino]phenyl}-2-(4-nitrophenyl)acronitrile (7b).
Aldehyde **5** (7.1 g, 10.2 mmol) and 4-nitrobenzylcyanide (**6**) (2.0 g, 12.3 mmol) are dissolved into 150 mL of pyridine. The solution is refluxed for 6h and evaporated under reduced pressure till 50 mL volume. The concentrated solution is poured into 200 mL of isopropanol, orange precipitate is filtrated and washed with methanol. Yield: 6.1g of orange powder which is used to obtain amine (**8b**) without further purification and characterization.

2-(4-Aminophenyl)-3-{4-[bis(2-acetoxyethyl)amino]phenyl}acronitrile (8a).
In a round flask, 1.6 g of activated Raney nickel is suspended into 20 mL of THF and the system is three times deaerated. Then under atmosphere pressure hydrogen is supplied and 4.3 g (9.8 mmol) of nitroproduct **7a** in 70 mL of THF and 10 mL of acetic acid is added. Deareation is repeated. After 3 h when all the starting substance have reacted (TLC control, toluene/ethyl acetate =2/1), the mixture is filtrated through layer of silica gel what is suspended in THF. The filtrate is then concentrated under reduced pressure till 1/3 of volume and 150 mL of isopropanol are added. The resulting solution is evaporated till 40 mL volume and cooled, obtained precipitate is filtered. Yield after crystallization from isopropanol: 2.6 g (65%) of yellow crystals, m.p. 123-124 ºC. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 1.93 (6H, s), 3.62 (4H, t, ^{3}J=6.1Hz), 4.13 (4H, t, ^{3}J=5.9Hz), 5.38 (2H, s), 6.56 (2H, d, ^{3}J=9.1Hz), 6.80 (2H, d, ^{3}J=9.9Hz), 7.18 (2H, d, ^{3}J=9.8Hz), 7.42 (1H, s), 7.67 (2H, d, ^{3}J=9.0Hz). IR(ν, cm^{-1}): 3439, 3355, 3233, 3061, 3032, 2198, 1725, 1637, 1607, 1581, 1522, 1366, 1354, 1319. Elemental analysis for $C_{23}H_{25}N_3O_4$, calculated %: C 67.80, H 6.18, N 10.31. Found %: C 67.66, H 6.20, N 10.18. UV-VIS (DMF): λ_{max}=329 nm, lgε=4,25, λ_{max}=383 nm, lgε=4.44.

2-(4-Aminophenyl)-3-{4-[bis(2-trityloxyethyl)amino]phenyl}acronitrile (8b).
Reduction of nitroproduct **7b** is analogical as in case of amine **8a**. Obtained amine **8b** is purified by column chromatography (silica gel, DCM). Yield: 79%. ^{1}H-NMR (200MHz, $CDCl_3$) δ, ppm: 3.24 (4H, d, ^{3}J=5.66Hz), 3.54 (4H, d, ^{3}J=5.84), 3.72 (2H, s), 6.45 (2H, d, ^{3}J=9.05Hz), 6.64 (2H, d, ^{3}J=8.60Hz), 7.10-7.35 (32H, m), 7.39 (1H, s), 7.61 (2H, d, ^{3}J=8.89Hz). IR(ν, cm^{-1}): 3444, 3360, 3083, 3054, 3031, 2206, 1604, 1583, 1523, 1408, 1320. UV-VIS (DMF): λ_{max}=389 nm, lgε=4.51.

2-(4-Aminophenyl)-3-{4-[bis(2-hydroxyethyl)amino]phenyl}acronitrile (8c).
Acylated compound **8a (**5.0g, 12.3 mmol) under intensive stirring are dissolved in 150 mL of methanol, slowly solution of 1.38 g KOH in 30 mL of methanol is added. During deacylation precipitate of product **8c** occurred. The suspension are left to stir for 12 h. The product is filtered and repeatedly washed with water and methanol. Further purification is accomplished by extraction in Soxhlet apparatus which is filled with silica gel using toluene/ethyl acetate 1/1 as solvent. Yield: 3.5 g (88%). ^{1}H-NMR (200MHz, DMSO) δ, ppm.: 3.49 (4H, t, ^{3}J=3.3Hz), 3.56 (4H, t, ^{3}J=3.3Hz), 4.78 (2H, t, ^{3}J=3.5Hz), 5.40 (2H, s), 6.61 (2H, d, ^{3}J=8.4Hz), 6.76 (2H, d, ^{3}J=8.8Hz), 7.33 (2H, d, ^{3}J=7.2Hz), 7.44 (1H, s), 7.73 (2H, d, ^{3}J=8.8Hz). IR (ν, cm^{-1}): 3459, 3357, 3211, 2207, 1629, 1607, 1585, 1521, 1356. UV-VIS (DMF): λ_{max}=332 nm, lgε=4.12, λ_{max}=390 nm, lgε=4.41.

3-{4-[bis(2-Acetoxyethyl)amino]phenyl}-2-{4-(4-nitrophenyl)diazenyl]phenyl}acronitrile (14a). 4-Nitro-nitrosobenzene (**10a**) (0.84 g, 5.5 mmol) and amine **8a** (2 g, 4.9 mmol) are suspended into 30 mL of acetic acid. The solution is heated for 30 min. The mixture is cooled and the brown precipitate is filtered. The product is washed repeatedly with acetic acid and methanol. Yield after crystallization from acetic acid: 1.55 g (60%) of dark purple crystals. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 1.96 (6H, s), 3.76 (4H, t, ^{3}J=6.0Hz), 4.25 (4H, t, ^{3}J=6.0Hz), 6.97 (2H, d, ^{3}J=9.0Hz), 8.06 (9H, m), 8.47 (2H, d, ^{3}J=9.2Hz). IR (ν, cm^{-1}): 2920, 2852, 2216, 1736, 1612, 1576, 1528, 1516, 1460. Elemental analysis for $C_{29}H_{27}N_5O_6$, calculated %: C 64.32, H 5.03, N 12.93. Found %: C 64.18, H 5.19, N 12.95. UV-VIS (DMF): λ_{max}=496 nm, lgε=4.68.

3-{4-[bis(2-Acetoxyethyl)amino]phenyl}-2-{4-(2-bromo-4-nitrophenyl)diazenyl]phenyl}-acronitrile (14b). Compound synthesized similar to **14a** from 2-bromo-4-nitrosobenzene (**10c**) (1.14 g, 4.9 mmol) and amine **8a** (2.0 g, 4.9 mmol). Yield 2.1 g (68 %) of dark brown crystals. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 1.98 (6H, s), 3.73 (4H, t, ^{3}J=6.0Hz), 4.20 (4H, t, ^{3}J=6.0Hz), 6.89 (2H, d, ^{3}J=9.2Hz), 7.96 (8H, m), 8.33 (1H, d, ^{3}J=8.2Hz), 8.67 (1H, s). IR (ν, cm^{-1}): 3096, 2924, 2212, 1736, 1608, 1572, 1522, 1460. Elemental analysis for $C_{29}H_{26}BrN_5O_6$, calculated %: C 56.14, H 4.22, N 11.29. Found %: C 56.12, H 4.40, N 11.00. UV-VIS (DMF): λ_{max}=510 nm, lgε=4.65.

3-{4-[bis(2-Hydroxyethyl)amino]phenyl}-2-{4-(4-nitrophenyl)diazenyl]phenyl}acronitrile (14c). Common method: arylamine **8c** condensation with nitrosoarenes **10a**, **10c** and **10d**.
4-Nitro-nitrosobenzene (**10a**) (0.745 g, 4.9 mmol) and amine **8c** (1.55 g, 4.9 mmol) are suspended into 50 mL of acetic acid and 3 mL water. Suspension under intensive stirring is heated at 70 ºC for 3 h. After cooling the reaction mixture, the precipitate is filtered and washed repeatedly with acetic acid and methanol. Crude product is purified by crystallization from DMSO or by extraction with Soxhlet apparatus which is filled with silica gel, using ethyl acetate as solvent. Yield: 0.8 g (37 %) dark purple needle-shaped crystals. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 3.57 (8H, m), 4.82 (2H, t, ^{3}J=5.6Hz), 6.86 (2H, d, ^{3}J=9.0Hz), 7.93 (4H, t), 8.04 (3H, t), 8.10 (2H, d, ^{3}J=8.7Hz), 8.44 (2H, d, ^{3}J=8.8Hz). IR (ν, cm^{-1}): 3336, 2920, 2212, 1612, 1574, 1512, 1488. Elemental analysis for $C_{25}H_{23}N_5O_4$, calculated %: C 65.63, H 5.07, N 15.31. Found %: C 64.16, H 5.27, N 14.89. UV-VIS_ (DMF): λ_{max}=495 nm, lgε=4.58.

{4-[(2-Bromo-4-nitrophenyl)diazenyl]phenyl}acetonitrile (16). 4-Nitrobenzylcyanide (3.1 g, 19,1 mmol) and iron powder (6.1 g, 0.11 mol) are suspended into 100 mL of ethanol 1.5 mL of concentrated hydrochloric acid are added to the suspension and the mixture is refluxed for 3 h. Dark red solution is evaporated under reduced pressure till 30 mL volume. To the dense suspension 100 mL of ethyl acetate are added and solution is then filtrated through silica gel/ethyl acetate layer after what silica gel is washed with additional 100 mL of ethyl acetate. The ethyl acetate solution then is washed with water (3x50 mLl) and dried over $MgSO_4$ after what it is evaporated under reduced pressure. Light yellow oil **15** (1.41 g, 10.7 mmol) is obtained which is then dissolved into 15 mL of acetic acid and 2-bromo-4-nitrosobenzene (2.5 g, 10.8 mmol) is added. The reaction mixture is heated at 50 ºC for 2 h after what product is precipitated, filtered and washed with methanol (3x50 mL). Yield after crystallization from acetic acid: 2.4 g (37 %) of light brown powder. ^{1}H-NMR (200MHz, DMSO) δ, ppm: 4.18 (2H, s), 7.59 (2H, d, ^{3}J=8.30), 7.71 (1H, d, ^{3}J=8.85), 7.95 (2H, d, ^{3}J=8.31), 8.30 (1H, dd, ^{3}J=8.84Hz, ^{4}J=2.30Hz), 8.56 (1H, d, ^{4}J=2.24 Hz). IR (ν, cm^{-1}): 3108, 3078, 3058, 2250, 1605, 1519, 1418, 1348, 1326. UV-VIS (DMF): λ_{max}=340 nm, lgε=4.42, λ_{max}=716 nm, lgε=3.85.

3-{4-[bis(2-Hydroxyethyl)amino]phenyl}-2-{4-(2-bromo-4-nitrophenyl)diazenyl]phenyl}-acronitrile (14d).
a) Same procedure as in synthesis of **14c** from 2-bromo-4-nitro-nitrosobenzene **10c** (1.2 g, 8.0 mmol) and amine **8c** (2.0 g, 6.2 mmol). Yield 1.5 g (45 %) of brown crystals.
b) synthesized by condensation of active methylene group containing compound **16** with aldehyde **4** in solution of isopropanol and using catalytic amounts of morpholine. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 3.57 (8H, m), 4.83 (2H, t, ^{3}J=3.5Hz), 6.85 (2H, d, ^{3}J=8.4Hz), 7.77 (1H, d, ^{3}J=8.4Hz), 7.90 (4H,

d), 8.01 (3H, t), 8.34 (1H, d, ^{3}J=8.2Hz), 8.63 (1H, s). IR (ν, cm^{-1}): 3527, 3334, 2211, 1611, 1574, 1515, 1399, 1338, 1318. Elemental analysis for $C_{25}H_{22}BrN_5O_4$, calculated %: C 55.98, H 4.13, N 13.06. Found %: C 55.57, H 4.16, N 12.90. UV-VIS (DMF): λ_{max}=388 nm, lgε=4.08, λ_{max}=511nm, lgε=4.64.

{4-[{4-[2-(bis(2-Hydroxyethyl)aminophenyl)-1-cyanovinyl]phenyl}diazenyl]-benzylidene}malononitrile (14e).
Same procedure as in synthesis of **14c** from 4-nitrosobenzylidenemalononitrile (**10d**) (1.5 g, 8.0 mmol) and amine **8c** (2.0 g, 6.2 mmol). Yield after crystallization from DMF/acetonitrile solution: 1.0 g (33 %) of purple powder. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 3.55 (8H, m), 4.81 (2H, s), 6.85 (2H, d, ^{3}J=8.8Hz), 7.8-8.2 (11H, m), 8.44 (1H, s). Elemental analysis for $C_{29}H_{24}N_6O_2$, calculated %: C 71.30, H 4.95, N 17.20. Found %: C 71.55, H 5.03, N 16.97. UV-VIS (DMF): λ_{max}=438 nm, lgε=4.59.

3-{4-[bis(2-Trityloxyethyl)amino]phenyl}-2-{4-(4-acetylphenyl)diazenyl]phenyl} acronitrile (14f).
Amine **8b** (1.0 g, 1.2 mmol) and 4-nitrosoacetophenone **10b** (0.19 g, 1.3 mmol) are dissolved in 25 mL of methylene chloride and stirred at room temperature for 4 h. After that the resulting solution is used in column chromatography (silica gel, DCM). Clean fractions are collected (approximately 70 mL) and 150 mL of isopropanol are added. The solution is evaporated under reduced pressure till 100 mL volume and the product is filtered and washed with methanol (3x50 mL) and then dried in vacuum. Yield: 1.0 g (93 %) of bright red crystals. ^{1}H-NMR (200MHz, $CDCl_3$) δ, ppm: 2.61 (3H, s), 3.27 (4H, t, ^{3}J=5.74Hz), 3.58 (4H, t, ^{3}J=5.60Hz), 6.50 (2H, d, ^{3}J=9.17Hz), 7.10-7.40 (30H, m), 7.44 (1H, s), 7.73 (2H, d, ^{3}J=8.87Hz), 7.74 (2H, d, ^{3}J=8.78Hz), 7.93 (2H, d, ^{3}J=8.65Hz), 7.95 (2H, d, ^{3}J=8.74Hz), 8.06 (2H, d, ^{3}J=8.70Hz). IR (ν, cm^{-1}): 3081, 3016, 2979, 2200, 1677, 1606, 1573, 1518, 1413, 1350. UV-VIS (DMF): λ_{max}=329 nm, lgε=4.18, λ_{max}=470 nm, lgε=4.533.

3-{4-[bis(2-Trityloxyethyl)amino]phenyl}-2-{4-(4-nitrophenyl)diazenyl]phenyl} acronitrile (14g).
a) azochromophore **14c** (0.82 g, 1.8 mmol) and tritylchloride (1.2 g, 4.3 mmol) are dissolved in 30 mL of dry pyridine. Mixture is heated for 2 h. Solvent is evaporated under reduced pressure. The solid is dissolved into 50 mL of methylene chloride and 100 mL of isopropanol are added. The solution is evaporated under reduced pressure till 70 mL volume, precipitate is filtered, washed with methanol and dried in vacuum. Product is purified by column chromatography (silica gel, DCM) Yield: 1.54 g (91 %) dark brown powder.
b) same procedure as in synthesis of **14a** from amine **8b** (0.63 g, 0.78 mmol) and 4-nitrosonitrobenzene **10a** (0.14 g, 0.92 mmol). Yield: 0.68 g (93 %). ^{1}H-NMR (200MHz, $CDCl_3$) δ, ppm: 3.28 (4H, t, ^{3}J=5.23Hz), 3.58 (4H, t, ^{3}J=5.78Hz), 6.51 (2H, d, ^{3}J=8.89Hz), 7.10-7.40 (30H, m), 7.45 (1H, s), 7.74 (2H, d, ^{3}J=9.01Hz), 7.76 (2H, d, ^{3}J=8.79Hz), 7.96 (2H, d, ^{3}J=8.68Hz), 7.99 (2H, d, ^{3}J=9.06Hz), 8.33 (2H, d, ^{3}J=9.03Hz). IR (ν, cm^{-1}): 2211, 1608, 1578, 1519, 1490, 1406, 1362, 1337. Elemental analysis for $C_{63}H_{51}N_5O_4$, calculated %: C 80.35, H 5.46, N 7.43. Found %: C 79.97, H 5.63, N 7.58. UV-VIS (DMF): λ_{max}=352 nm, lgε=4.25, λ_{max}=494 nm, lgε=4.55.

3-{4-[bis(2-Trityloxyethyl)amino]phenyl}-2-{4-(2-bromo-4-nitrophenyl)diazenyl]phenyl}-acronitrile (14h).
a) Same procedure as in synthesis of **14g** according to method a) from azochromophore **14d** (0.71 g, 1.3 mmol) and tritylchloride (0.84 g, 3.0 mmol). Yield: 1.25 g (94 %) dark purple crystals.
b) Same procedure as in synthesis of **14a** from amine **8b** (0.67 g, 0.83 mmol) and nitrosoarene **10c** (0.23 g, 1.0 mmol). Yield: 0.74 g (87 %). ^{1}H-NMR (200MHz, $CDCl_3$) δ, ppm: 3.28 (4H, t, ^{3}J=5.18Hz), 3.58 (4H, t, ^{3}J=5.56Hz), 6.51 (2H, d, ^{3}J=9.07Hz), 7.10-7.40 (30H, m), 7.48 (1H, s), 7.75 (2H, d, ^{3}J=8.60Hz), 7.78 (2H, d, ^{3}J=8.65Hz), 8.00 (1H, d, ^{3}J=9.05Hz), 8.06 (2H, d, ^{3}J=8.60Hz), 8.64 (1H, dd, ^{3}J=9.03Hz, ^{4}J=2.44Hz), 8.64 (1H, d, ^{4}J=2.38Hz). IR (ν, cm^{-1}): 2204, 1607, 1574, 1520, 1489, 1449, 1413, 1352, 1344. Elemental analysis for $C_{63}H_{50}BrN_5O_4$, calculated %: C 74.11, H 4.94, N 6.88. Found %: C 73.63, H 5.10, N 7.19. UV-VIS (DMF): λ_{max}=382 nm, lgε=4.29, λ_{max}=510 nm, lgε=4.54.

{4-[{4-[2-(bis(2-Trityloxyethyl)aminophenyl)-1-cyanovinyl]phenyl}diazenyl]-benzylidene}malononitrile (14i).

Same procedure as in synthesis of **14g** according to method a) from compound **9e** (0.31 g, 0.63 mmol) and tritylchloride (0.42 g, 1.5 mmol). Repeated chromatographic purification needed using ethyl acetate as eluent. Yield: 0.08 g (13 %) dark purple powder. ^{1}H-NMR (200MHz, $CDCl_3$) δ, ppm: 3.32 (4H, t, ^{3}J=5.31Hz), 3.64 (4H, t, ^{3}J=5.68Hz), 6.55 (2H, d, ^{3}J=9.1Hz), 7.10-7.40 (30H, m), 7.51 (1H, s), 7.75-7.85 (5H, m), 7.95-8.01 (6H, m). IR (ν, cm^{-1}): 3087, 3020, 2966, 2221, 1607, 1578, 1519, 1490, 1406, 1364. UV-VIS (DMF): λ_{max}=362 nm, lgε=4.26, λ_{max}=469 nm, lgε=4.58.

3-{4-[bis(2-Hydroxyethyl)amino]phenyl}-2-{4-(2-cyano-4-nitrophenyl)diazenyl]phenyl}-acronitrile (14j).

Azochromophore **14d** (1.5 g, 2.8 mmol) is dissolved into 50 mL of DMF, then CuCN (0.75 g, 8.4 mmol) is added and solution is heated for 3 h. After that the mixture is poured into 200 mL of water and precipitate is filtered. Purification is accomplished by extraction in Soxhlet apparatus which is filled with silica gel using toluene/ethyl acetate 2:1 as solvent. Yield: 0.7 g (52 %) of black powder. ^{1}H-NMR (90MHz, DMSO) δ, ppm: 3.58 (8H, m), 4.83 (2H, t, ^{3}J=5.3Hz), 6.88 (2H, d, ^{3}J=8.4Hz), 7.77 (1H, d, ^{3}J=8.6Hz), 8.00 (4H, d), 8.11 (3H, t), 8.34 (1H, d, ^{3}J=8.6Hz,), 9.00 (1H, s). IS (ν, cm^{-1}): 3526, 3322, 2210, 1610, 1573, 1514, 1398, 1338. Elemental analysis for $C_{26}H_{22}N_6O_4$, calculated %: C 71.30, H 4.95, N 17.20. Found %: C 70.68, H 4.87, N 16,83%. UV-VIS (DMF): λ_{max}=400 nm, lgε=4.17, λ_{max}=533 nm, lgε=4.11.

3-{4-[bis(2-Trityloxyethyl)amino]phenyl}-2-{4-(2-cyano-4-nitrophenyl)diazenyl]phenyl}-acronitrile (14k).

Azochromophore **14h** (0.43 g, 0.42 mmol) and CuCN (0.19 g, 1.9mmol) are dissolved into 7 mL of DMF and solution is heated at 120 ºC for 3 h. When all of **14h** have reacted (TLC control, DCM) solvent is evaporated under reduced pressure and solid is dissolved into minimal amount of ethyl acetate. Solution is filtered through silica gel layer and filtrate is evaporated. The solid is purified by column chromatography (silica gel, DCM). Yield: 0.29 g (71 %) dark brown crystals. ^{1}H-KMR (200MHz, $CDCl_3$) δ, ppm: 3.28 (4H, t, ^{3}J=5.87Hz), 3.58 (4H, t, ^{3}J=5.55Hz), 6.51 (2H, d, ^{3}J=8.86Hz), 7.10-7.40 (30H, m), 7.48 (1H, s), 7.75 (2H, d, ^{3}J=8.85Hz), 7.78 (2H, d, ^{3}J=8.67Hz), 8.00 (1H, d, ^{3}J=8.97Hz), 8.07 (2H, d, ^{3}J=9.06Hz), 8.46 (1H, dd, ^{3}J=9.09Hz, ^{4}J=2.34Hz), 8.65 (1H, d, ^{4}J=2.28Hz). IR (ν, cm^{-1}): 2234, 2206, 1608, 1567, 1530, 1518, 1418, 1363, 1344. Elemental analysis for $C_{64}H_{50}N_6O_4$, calculated %: C 79.48, H 5.21, N 8.69. Found %: C 79.42, H 5.36, N 8.99. UV-VIS (DMF): λ_{max}=384 nm, lgε=4.32, λ_{max}=533 nm, lgε=4.52.

3-(4-(bis(2-(Triphenylsilyloxy)ethyl)amino)phenyl)-2-(4-((2-bromo-4-nitrophenyl) diazenyl)phenyl)acrylonitrile (14m).

0,3 g (0.54 mmol) of 3-(4-(bis(2-Hydroxyethyl)amino(phenyl)-2-(4-(2-bromo-4-nitrophenyl) diazenyl)-phenyl)acrylonitrile (**14d**) was dissolved in dry pyridine. Triethylamine (0.16 g, 1,62 mmol) and triphenylsilyl chloride (0.47 g, 1,62 mmol) were added to the solution. The mixture was stirred at room temperature for 2 h and then poured into isopropyl alcohol (50 mL). Purple precipitate was filtered and purified by column chromatography over silica gel using DCM/petroleum ether (2:1) as eluent. Yield: 0.5 g (89 %). ^{1}H NMR ($CDCl_3$): δ, ppm: 3.43 (4H, t, ^{3}J=6.51Hz), 3.84 (3H, t, ^{3}J=6.26Hz), 6.21 (2H, d, ^{3}J=8.99Hz), 7.21-7.54 (31H, m), 7.59 (2H, d, ^{3}J=8.99Hz), 7.73 (1H, ^{3}J=8.61Hz), 7.76 (2H, d, ^{3}J=8.61Hz), 8.00 (2H, d, ^{3}J=8.61Hz), 8.19 (1H, dd, ^{3}J=6.65Hz, ^{4}J=2.34Hz), 8.57 (1H, d, ^{4}J=2.34Hz). UV-VIS (DMF): λ_{max}=510nm, lgε=4.47.

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V. Kokars, A. Maļeckis, K. Traskovskis. Azohromoforus saturošu organisko stiklu sintēze.

Sintezēta rinda „push-pull" tipa organisko stiklu. Iegūtie savienojumi, 3-{4-[bis(2-tritiloksietil)amino]fenil}-2-{4-(4-acetilfenil)diazenil]fenil}- akrilnitrils, 3-{4-[bis(2-tritiloksietil)amino]fenil}-2-{4-(4-nitrofenil)- diazenil]-fenil}akrilnitrils, 3-{4-[bis(2-tritiloksietil)amino]fenil}-2-{4-(2-brom-4-nitrofenil)diazenil]fenil} akrilnitrils, {4-[{4-[2-(bis(2-tritiloksietil)aminofenil)-1-cianovinil]fenil}diazenil] benzilidēn} malonnitrils, 3-{4-[bis(2-tritil-oksietil)amino]fenil}-2-{4-(2-ciano-4-nitrofenil)diazenil]fenil} akrilnitrils un 3-{4-(bis(2-(trifenilsililoksi) etil) *amino)fenil)-2-(4-((2-brom-4-nitrofenil)diazeni)-fenil}-akrilonitrils, raksturojas ar intensīvu elektronu absorbciju gaismas spektra redzamajā daļā un tie no viegli gaistošiem šķīdinātājiem (hloroforms vai metilēnhlorīds) spēj veidot plānas amorfas kārtiņas.*

V. Kokars, A. Maļeckis, K. Traskovskis. Synthesis of organic glasses containing azochromophore.
Series of push-pull type organic glasses were synthesized. Obtained compounds, 3-{4-[bis(2-trityloxyethyl)amino]phenyl}-2-{4-(4-acetylphenyl)diazenyl]phenyl} acronitrile, 3-{4-[bis(2-trityloxyethyl)amino]phenyl}-2-{4-(4-nitrophenyl)diazenyl]phenyl} acronitrile, 3-{4-[bis(2-trityloxyethyl)amino]phenyl}-2-{4-(2-bromo-4-nitrophenyl)diazenyl]phenyl}- acronitrile, 3-{4-[{4-[2-(bis(2-trityloxyethyl)aminophenyl)-1-cyanovinyl-] phenyl}-diazenyl]- benzylidene}malononitrile, 3-{4-[bis(2-trityloxyethyl)amino]phenyl}-2-{4-(2-cyano-4-nitro- phenyl)-diazenyl]phenyl}- acronitrile and 3-{4-(bis(2-(triphenylsilyloxy) ethyl) amino)phenyl)-2-(4-((2-bromo-4-nitrophenyl)diazenyl)-phenyl}-acrylonitrile, show intensive electron absorbance in visible part of spectra and also can form thin glassy layers from volatile solvents (chloroform or methylene chloride).

В. Кокарс, А. Малецкис, К. Трасковскис. Синтез органических стеклообразных соеднений содержащих азохромофоры.
Синтезирован ряд „push-pull” типа стеклообразных соеднений. Полученные соединения, 3-{4-[бис(2-тритилоксиэтил)амино]фенил}-2-{4-(4-ацетилфенил)диазенил]фенил}акроилнитрил, 3-{4-[бис(2-тритилоксиэтил)амино]фенил}-2-{4-(4-нитрофенил)диазенил]фенил}акроилнитрил, 3-{4-[бис(2-тритилоксиэтил)амино]фенил}-2-{4-(2-бром-4-нитрофенил)диазенил]фенил} акроилнитрил, 3-{4-[бис(2-тритилоксиэтил)амино]фенил}-1-циановинил-]фенил}-диазенил]бензилиден}малоннитрил, 3-{4-[бис(2-тритилоксиэтил)амино]фенил}-2-{4-(2-циано-4-нитро-фенил)диазенил]фенил}акроилнитрил и 3-{4-[бис(2-(трифенилсилил)этил)амино]фенил}-2-{4-(2-бром-4-нитро-фенил)диазенил]фенил} акроилнитрил, имеют интенсивные полосы поглощения в видимой области спекра и способны образовыватъ из легколетучих растворителей (хлороформ или метиленхлорид) устойчивую аморфную плёнку.