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Synthesis of Chemically Closely Linked *N*-(1,3-dioxoindan-2-yl)pyridinium Betaine and 1-Amino-4-nitroazobenzene Bichromophore

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Abstract. **Bichromophore 2-[4-(4-nitrophenylazo)-phenylaminopyridinium-1-yl]-1,3-dioxy-2,3-dihydro-1*H*-inden-2-ide (1) has been prepared in order to develop strategy that allows simultaneously to increase the first molecular hyperpolarizability and to adjust the dipole moment of chromophores. Three synthetic roots to its precursor - [4-(4-nitrophenylazo)phenyl]octylpyridin-4-ylamine (2) have been examined. UV-vis and ^{1}H NMR spectra of the synthesized bichromophore and of the two chromophores combined in it are given.**

Keywords: **chromophores, donor-acceptor systems, azocompounds, betaines, substituent effects.**

I. Introduction

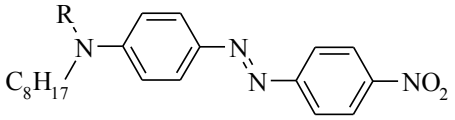
Chromophores, mostly conjugated π-electron systems and metal complexes, are essential components to create nonlinear optical (NLO) devices. Two of chromophore molecular properties, which have high impact on their NLO efficiency in the material, are first molecular hyperpolarizability (β_0) and ground state dipole moment (μ_g). It is typical, that NLO chromophores with high β_0 values have large dipole moments, which prompts them to aggregate in antiparallel configuration in the material at high chromophore loads diminishing the macroscopic EO effect [1]. For practical application it is a challenge to obtain chromophores with high β_0 and low μ_g.

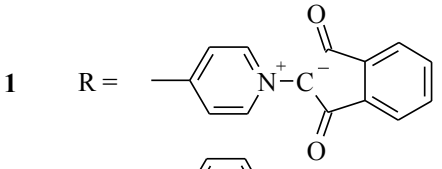
One of the strategies that allow simultaneously to increase β_0 and to adjust dipole moment was to link chemically NLO effective neutral-ground state push-pull chromophore with a zwitterionic chromophore in an antiparallel dipole moment fashion [2]. Using supramolecular approach of this strategy within the host-guest system built from 2-(4-dimethylaminobenzylidene)indan-1,3-dione containing host and zwitterionic *N*-(1,3-dioxoindan-2-yl) pyridinium betaine as a guest, twofold enhancement of NLO efficency was observed [1].

In order to develop the new β_0 and μ_g control approach it was of interest to prepare representative bichromophores, containing in one molecule simultaneously chromophore with neutral and chromophore with zwitterionic ground state. This paper reports synthesis of 2-[4-(4-nitrophenylazo)phenylamino-pyridinium-1-yl]-1,3-dioxy-2,3-dihydro-1*H*-inden-2-ide **(1)** containing chemically closely linked two NLO active chromophores: azo chromophore (neutral in its ground state, but zwitterionic in its charge transfer excited state) and *N*-(1,3-dioxoindan-2-yl) pyridinium betaine (zwitterionic character in its ground state). To increase chromophore solubility the octyl group was attached on nitrogen of the molecule backbone.

II. Results and Discussion

General method available in the literature for the synthesis of *N*-(1,3-dioxoindan-2-yl) pyridinium betaine and its derivatives is the reaction of pyridine or substituted pyridines with 2-dicyanomethyleneindan-1,3-dione oxide [3]. To apply it for obtaining bichromophore **1** unknown [4-(4-nitrophenylazo)phenyl]octylpyridin-4-ylamine **(2)** was required as precursor.





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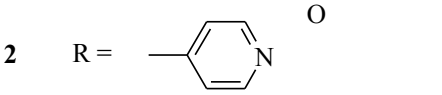
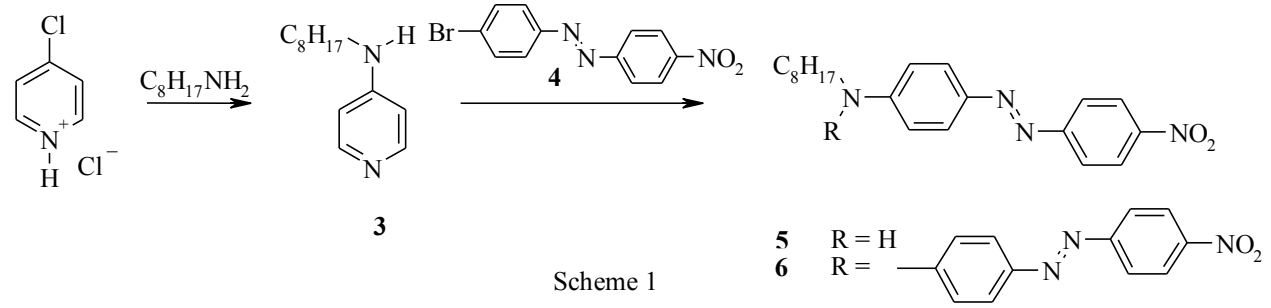
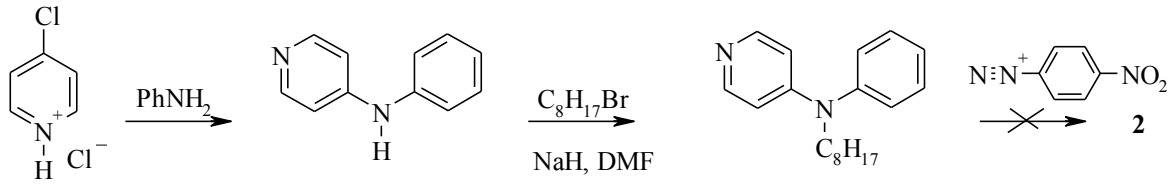


2 R =

We investigated three of synthetic routs to compound **2**. The more straightforward route (Scheme 1) begins with obtaining octylpyridin-4-ylamine (**3**) which is then subjected to arylation by 4-bromo-4'-nitroazobenzene (**4**). Alkylaminopyridines can be prepared by nucleophylic aromatic substitution (S_NAr) of 4-halopyridine derivatives with appropriate aminocompound [4] or in palladium catalyzed amination reaction [5, 6]. For the synthesis of compound **3** we tested several methods described in literature and found out that the simplest way to compound **3** was solvent free heating of *n*-octylamine and 4-chloropyridinium chloride at 180-190 ºC for 3 ½ h. In a similar mode compound **3** was previously obtained from 4-phenoxypyridine or 4-bromopyridine hydrochloride and octylamine hydrochloride [7, 8].



Scheme 1

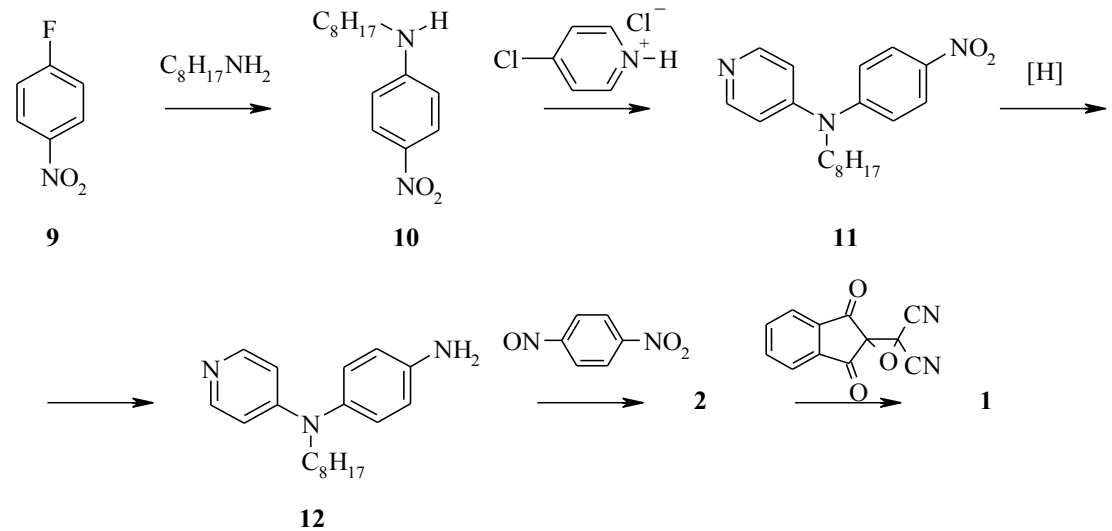


Scheme 2

Unfortunately *N*-arylation of compound **3** with bromoazobenzene **4** under standard Buchwald-Hartwig amination conditions: $Pd(OAc)_2$/Binap catalyst system in the presence of K_2CO_3 as base, did not lead to compound **2,** but unexpectedly gave mixture of two compounds: 4-(4-nitrophenylazo)-phenyloctylamine (**5**) and bis-[4-(4-nitrophenylazo)phenyl]-octylamine (**6**) suggesting, that, since in the migratory insertion step of the generic catalytic cycle of arylation [9, 10] both *N* of aminopyridine **3** can act as nucleophyles, the leaving group has been pyridine.

The second route (Scheme 2) to compound **2** involves arylation of aniline with 4-chloropyridine and subsequent alkylation and azocoupling. Heating aniline and 4-chloropyridinium chloride in acetic acid for 2 days gave phenylpyridin-4-ylamine **(7)** which was treated with NaH and 1-bromooctane in DMF giving octylphenylpyridin-4-ylamine (**8)** in 41% yield. However all our attempts of azo coupling of compound **8** with *p*-nitrobenzene diazonium salts and with even more reactive 2-cyano-4-nitrobenzene diazonium salt also in modified coupling conditions were not successful. The starting compound **8** was identified in the reaction mixture and only trace amount of desired compound **2** was formed. We attribute this failure to too low nucleophility of C-4 in the phenyl residue due to the presence of the pyridyl substituent attached to the amino group. In comparison, diphenylamine forms azocoupling product with *p*-nitrobenzene diazonium chloride, although the reaction is slow [11].

An effective route to compound **2** proves to be the one given in Scheme 3. Nucleophilic aromatic substitution of 1-fluoro-4-nitrobenzene (**9**) with *n*-octylamine in DMSO following a procedure reported in literature [12] afforded 4-nitro-*N*- octylbenzenamine (**10**) in 77% yield. Compound **10** was *N*-arylated by 4-chloropyridine using $Pd(OAc)_2$/Binap catalyst system in the presence of large excess (20 eq) of K_3PO_4 as base and boiling the reaction mixture for 120 h in dioxane.



Scheme 3

Purification of the crude product by column chromatography on silica gel afforded *N*-(4-nitrophenyl)-*N*-octylpyridin-4-amine **(11)** in only 35% yield and 20% of starting compound **10** was recovered. Compound **11** was quantitatively transformed by reduction with $SnCl_2 \cdot 2H_2O$ into *N*-octyl-*N*-(pyridine-4-yl)benzene-1,4-diamine (**12**) which was condensed with 1-nitro-4-nitrozobenzene in acetic acid to yield azo compound **2**. Reaction of compound **2** with 2-dicyanomethyleneindan-1,3-dione oxide proceeded in boiling MeCN for 6 h and compound **1** was obtained as brown crystals, melting above 210 ºC. It was characterized by UV-vis and ^{1}H NMR spectra and the obtained data were consistent with the assigned structure.

UV-vis spectra of compounds **1** and **2** and of compound **5,** betaines of 2-(*N*-4-octylaminopyridinium)indan-1,3-dione (**13**) and 2-(*N*-pyridinium)indan-1,3-dione (IPB) as model compounds are given in Table I.

TABLE I

UV-VIS SPECTRA OF COMPOUNDS **1**, **2**, **5, 13** AND IPB

Com-pound	λ_{max}, nm (lgε), in PhMe[1]	λ_{max}, nm,of CTB in EtOH	Solvatochromic effect[2]
1	315 (4.21), 392 (4.45), 409 (4.46), 466 (4.11)	351	-41[3]
2	294 (4.15), 441 (4.13)	416	-25
5	446 (4.43)	479	+33
13	312 (3.70), 391 (4.42), 406 (4.40)	350	-41
IPB	431 (4.52)[4]	392	-39

[1] charge-transfer bands (CTB) are underlined; [2] λ_{max} EtOH — λ_{max} PhMe of CTB; [3] solvatochromic effect of the first CT band[4;] in hexane

Compound **1** could be considered as $D^{-}A^{+}$-D-π-A type conjugated bichromophore, where $D^{-}A^{+}$ represents zwitterionic IPB chromophore and D-π-A – neutral-ground state azobenzene **5.** Absorption spectrum of IPB in nonpolar media exhibits charge transfer band (CTB, $\lambda_{max\ in\ hexane}$ 431 nm) that is blue shifted with the increase of solvent polarity ($\lambda_{max\ in\ EtOH}$ 392 nm, solvatochromic effect -41 nm) [13], but spectrum of compound **5** shows CTB in the visible region of light ($\lambda_{max\ in\ PhMe}$ 446 nm) that is red shifted upon increasing solvent polarity ($\lambda_{max\ in\ EtOH}$ 479 nm, solvatochromic effect +33 nm).

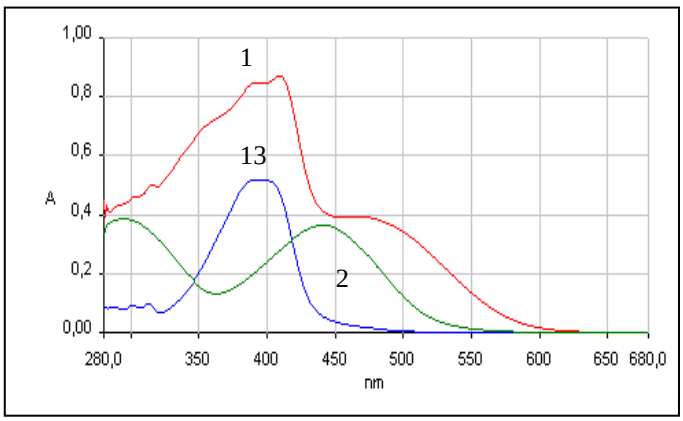
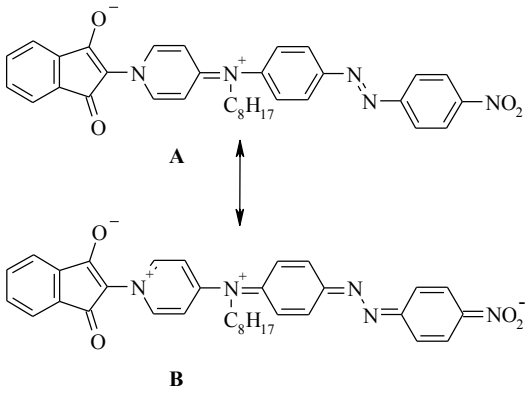


Fig. 1. UV-vis spectra of compounds**1, 2** and **13** in toluene

In the absorption spectra of bichromophore **1** in toluene (Fig. 1) there are two absorption bands, the first with two maxims: at ~400 nm pertaining to the CT in IPB chromophore and at 466 nm – to CT in azobenzene chromophore. The shape of the spectra is similar to the superposed spectra of compounds **13** and **2** rather than IPB and compound **5**, but the second band is broadened, exhibits batochrochromic shift and hyperchromic effect in comparison with the band in the spectra of compound **2.** Incorporation of pyridyl group into the structure of compound **5** significantly affects the electronic structure of neutral-ground-state chromophore fragment (solvatochromic effect changes its sign, from +33 nm of compound **5** to -25 nm to compound **2**).

In the spectra of bichromophore **1** in EtOH there is only one broad band with the maxima at 350 nm thereby UV-vis spectra in EtOH suggest remarkable contribution of mesomeric structure A and B in the structure of bichromophore **1**.



Nonlinear optical coefficients of bichromophore **1** are at estimation.

III. EXPERIMENTAL SECTION

2-Dicyanomethylideneindan-1,3-dione oxide was obtained in accordance with [14], 1-nitro-4-nitrozobenzene from *p*-aminonitrobenzene [15]. Purity of all compounds was checked by TLC method on Merck F_{254} silica plates. The spots were visualized when necessary in UV light and in iodine vapor. Chromatographic separations were carried out on silica gel (Merc, reinst) or Biotage SP1 HPLC using Biotage silicagel cartridges. Melting points were taken on a Stuart apparatus SMP 10 and ^{1}H NMR spectra were obtained on Bruker Avance 300 (300 MHz) spectrometer against TMS as internal reference. UV spectra were recorded using Perkin-Elmer UV/VIS spectrometer Lambda 35. Waters Alliance 2695 HPLC was used with Waters EMD 1000 MS detector, mass spectra obtained in ESI+ mode, cone voltage 30V.

Octylpyridin-4-ylamine (3). The mixture of *n*-octylamine (2.5 mL, 15 mmol) and 4-chloropyridinium chloride (1.5 g, 10 mmol) was heated at 180-190 ºC for 3 ½ h, cooled and the crude product dissolved in water. The concentrated solution of NaOH was added till pH 9 and resulting oily precipitate extracted with *tert*-butyl methyl ether. The ether extract was washed with brine and dried. Solvent was evaporated and the residue was recrystallized from hexane. Yield 1.25 g, (61%),

m.p. 62-4 ºC 1H NMR spectrum, δ, ppm (J, Hz): 8.11 (d, J=6.1, 2H), 6.35 (dd, J=6.1, 1.5, 2H), 4.13 (br., 1H), 3.06 (td, J=7.1, 5.6, 2H), 1.7-1.45 (m, 2H, 1.45-1.11 (m, 10H), 0.82 (t, J=6.9, 2H). Mass spectrum (ESI+), m/z: 207.2 $[M+H]^+$.

4-Bromo-4'-nitroazobenzene (4). Mixture of 4-bromoaniline (1.72 g, 10 mmol) and 1-nitro-4-nitrozobenzene (1.52 g, 10 mmol) in 20 mL acetic acid was heated for 10 min at 100 ºC then allowed to cool to the room temperature. After 1h the precipitate was filtered off, washed with ethanol, dried at 70 ºC and recrystallized from toluene. Yield 1.7 g, (57%), m.p. 208 ºC (203 ºC in [16]).

4-(4-Nitrophenylazo)phenyloctylamine (5) and bis-[4-(4-nitrophenylazo)phenyl]octylamine (6). Palladium acetate (9 mg, 2 mol%), BINAP (30 mg, 2 mol%) and K_2CO_3 (2.2 g, 20 mmol) and abs. toluene (5 mL) were stirred under Ar for 15 min. Compound **3** (0.4 g, 1.9 mmol) and compound **4** (0.5 g, 1.60 mmol) was added and the mixture stirred for 10 h at 100-110 ºC then cooled, filtered, concentrated and chromatographed on silica gel column with toluene as eluent. Compound **5** (0.2 g, R_f 0.5) and compound **6 (**0.15 g, R_f 0.64) were obtained.

Compound **5** 1H NMR spectrum, δ, ppm (J, Hz): 8.26 (d, J=8.9, 2H), 7.84 (d, J=8.9, 2H), 7.80 (d, J=8.8, 2H), 6.58 (d, J=8.8, 2H), 4.28 (br., 1H), 3.17 (m, 2H), 1.65-1.54 (m, 2H), 1.46-1.11 (m, 10H), 0.83 (t, J=6.6, 3H). Mass spectrum (ESI+), m/z: 355.2 $[M+H]^+$.

Compound **6** 1H NMR spectrum, δ, ppm (J, Hz): 8.31 (d, J=8.9, 4H), 7.93 (d, J=8.9, 4H), 7.89 (d, J=8.7, 4H), 7.16 (d, J=8.7, 4H), 3.91-3.81 (m, 2H), 1.7 (dd, J=14.6, 7.3, 2H), 1.39-1.1 (m, 10H), 0.81 (t, J=6.8, 3H). Mass spectrum (ESI+), m/z: 580.4 $[M+H]^+$.

Phenylpyridin-4-ylamine (7). 4-Chloropyridinium chloride (1.5 g, 10 mmol) and aniline (2.3 mL, 25 mmol) in 5 mL of acetic acid was boiled for 48 h, acetic acid was evaporated off and the residue made alkaline with $NaHCO_3$. The precipitate was filtered, dried at 70 ºC and recrystallized from ethanol. Yield 1.1 g, (62%), m.p. 177-178 ºC (179-179.5 ºC in [16]).

Octylphenylpyridin-4-ylamine (8). To a cooled solution of compound **7** (1.6 g, 9.4 mmol) in 10 mL DMF NaH (60% dispersion in oil, 0.38 g, 10 mmol) was added under Ar. The mixture was stirred for ½ h, 1-bromooctane (1.6 mL, 9.4 mmol) was added and the mixture was stirred at 95 to 100 ºC for 24 h. The reaction mixture was poured onto 30 g of ice and extracted with *tert*-butyl methyl ether. The organic layer was washed with water, dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography with the mixture $CHCl_3$/methanol/NH_3 (25:2.5:1) as eluent. Yield of pale yellow oil 1.1 g (41%). 1H NMR spectrum, δ, ppm (J, Hz): 8.10 (dd, J=5.0, 1.5, 2H), 7.45-7.08 (m, 5H), 6.39 (dd, J=5.0, 1.5, 2H), 3.68-3.41 (m, 2H), 1.72-1.43 (m, 2H), 1.21-1.19 (m, 10H), 0.81 (t, J=6.5, 3H). Mass spectrum (ESI+), m/z: 283.4 $[M+H]^+$.

4-Nitro-*N*-octylbenzenamine (10) [12]. 4-Fluoronitrobenzene **(9)** (2.82 g**,** 0.02 mol) was dissolved in 22 mL DMSO and stirred at 75 ºC. Potassium carbonate (3.94 g, 0.028 mol) and octan-1-amine (8 mL, 0.049 mol) were added and stirred at 120 ºC under Ar for 6 h. The reaction mixture was cooled and poured over crushed ice and stirred for ½ h. The yellow precipitate was filtered, washed with water and dried in air. It was purified by eluting through silica gel column using ethyl acetate-hexane (3:1) mixture. Yield 3.84 g (77%), m.p. 52-54 ºC.

***N*-(4-Nitrophenyl)-*N*-octylpyridin-4-amine (11).** To the suspension of 4-chloropyridinium chloride (1.8 g, 12 mmol) in 100 mL abs. dioxane KO*t*Bu (1.36 g, 12 mmol) was added portionwise with intensive stirring and cooling. Compound **10** (2.5 g, 10 mmol), palladium acetate (48.4%. 0.186 g, 0.4 mmol), BINAP (0.25 g, 0.4 mmol) and K_3PO_4 (10 g) were added under Ar and the mixture was stirred at 90 ºC for 60 h. 4-Chloropyridinium chloride (1.8 g) and K_3PO_4 (20 g) additionally were added and the stirring continued at 110 ºC for 60 h. After cooling the mixture was filtered and the solution concentrated. The crude product was purified by eluting through silica gel column using ethyl acetate as eluent. Yield 1.15 g (35%). 1H NMR spectrum, δ, ppm (J, Hz): 8.34 (dd, J=4.9, 1.5, 2H), 8.17-8.12 (m, 2H), 7.18-7.12 (m, 2H), 6.81 (dd, J=4.9, 1.5, 2H), 3.77-3.70 (m, 2H), 1.62-1.60 (m, 2H), 1.31-1.12 (m, 12H), 0.81 (t, J=6.8, 3H). Mass spectrum (ESI+), m/z: 329.2 $[M+H]^+$.

***N*-Octyl-*N*-(pyridin-4-yl)benzene-1,4-diamine (12).** To the solution of nitro compound **11** (1.1 g, 3.4 mmol) in 30 mL ethanol $SnCl_2 \cdot 2H_2O$ (6 g, 27 mmol) was added and the mixture was stirred at 75 ºC for 5 h. After cooling in an ice bath and diluting with 60 mL H_2O, the resulting mixture was made alkaline to pH 9-10 with 40% NaOH solution, and then it was extracted with *tert*-butyl methyl ether. The organic layer was washed with water, dried and evaporated to give 1 g (98%), m.p. 98-100 ºC (100-101 ºC in [18]). Mass spectrum (ESI+), m/z: 298.2 $[M+H]^+$.

[4-(4-Nitrophenylazo)phenyl]octylpyridin-4-ylamine (2). Mixture of compound **12** (0.84 g, 2.8 mmol) and 1-nitro-4-nitrozobenzene (0.43 g, 2.8 mmol) in 6 mL acetic acid was heated at 100 ºC for ½ h, then allowed to cool to the room temperature. Solution was concentrated, the residue made alkaline with $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with water; dried, evaporated and purified by eluting through silica gel column using ethyl acetate as eluent. Compound **2** was recrystallized from ethanol. Yield 0.65 g, (52%), m.p. 80-2 ºC. 1H NMR spectrum, δ, ppm (J, Hz): 8.34-8.30 (m, 4H), 8.24 (dd, J=4.9, 1.5, 2H), 7.31-7.27 (m, 4H), 6.69 (dd, J=4.9, 1.5, 2H), 3.75-3.71 (m, 2H), 1.68-1.61 (m, 2H), 1.31-1.17 (m, 12H), 0.81 (t, J=6.8, 3H). Mass spectrum (ESI+), m/z: 433.3 $[M+H]^+$.

2-[4-(4-Nitrophenylazo)phenylaminopyridinium-1-yl]-1,3-dioxo-2,3-dihydro-1*H*-inden-2-ide (1). 2-Dicyanomethylideneindan-1,3-dione oxide (0.21 g, 0.95 mmol) was added portion wise to the solution of compound **2** (0.41 g, 0.95 mmol) in 5 mL of MeCN at 60 ºC under Ar. The mixture was boiled for 6 h, concentrated and purified by eluting through silica gel column using ethyl acetate as eluent. Compound **1** was recrystallized from ethyl acetate.

Yield 0.18 g, (55%), brown crystals, m.p. 210 - 212 ºC. 1H NMR spectrum, δ, ppm (J, Hz): 9.10 (d, J=7.9, 2H), 8.38 (d, J=9.1, 2H), 8.10 (d, J=8.7, 2H), 8.04 (d, J=7.9, 2H), 7.42-7.(m, 4H), 7.34-7.32 (m, 2H), 6.75 (d, J=7.9, 2H), 3.80-3.76 (m, 2H), 1.73-1.66 (m, 2H), 1.29-1.20 (m, 12H), 0.81 (t, J=6.8, 3H). Mass spectrum (ESI+), m/z: 577.4 $[M+H]^+$, 433.3 $[M\text{-}Ind]^+$.

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Jana Kreicberga, Jekaterina Sirotkina, Guna Bērziņa, Lauma Laipniece, Valdis Kampars. Ķīmiski tuvu saistītu *N*-(1,3-dioksoindan-2-il)piridīnija betaīna un 1-amino-4-nitroazobenzola bihromofora sintēze

Darba mērķis bija sintezēt 2-[4-(4-nitrofenilazo)fenilaminopiridīnij-1-il]-1,3-diokso-2,3-dihidro-1*H*-inden-2-īdu (**1**) - bihromoforu, kurā ķīmiski saistīti divi atšķirīga tipa NLO aktīvi hromofori: jonu tipa (ierosinātā stāvoklī neitrāls) *N*-(1,3-dioksoindan-2-il)piridīnija betaīns un pamatstāvoklī neitrāls (ierosinātā – jonu tipa) 1-amino-4-nitroazobenzols. Bihromofors iegūts dicanometilidenindan-1,3-diona oksīda reakcijā ar [4-(4-nitrofenilazo)fenil]oktilpiridīn-4-ilamīnu (**2**), kura iegūšanai pētīti trīs ceļi. Konstatēts, ka Pd katalizētā reakcijā starp oktilpiridīn-4-ilamīnu un 4-brom-4'-nitroazobenzolu neveidojas savienojums **2,** bet notiek piridīn-aizvietotāja atšķelšanās un 4-(4-nitrofenilazo)feniloktilamīna, kā arī bis-[4-(4-nitrofenilazo)fenil]oktilamīna veidošanās. Iegūts oktilfenilpiridīn-4-amīns, tomēr tas nestājās azosametināšanās reakcijā ar *p*-nitrobenzoldiazonija sāļiem. Savienojums **2** iegūts kondensējot *N*-oktil-*N*-(piridīn-4-il)benzol-1,4-diamīnu ar 1-nitro-4-nitrozobenolu. Savienojuma **1** elektronu spektros toluolā novērojamas abu bihromofora molekulā sasaistīto hromoforu lādiņa pārneses (LP) joslas, azohromofora LP josla ir batohromi nobīdīta un tās ekstinkcijas koeficients samazinājies salīdzinot ar atsevišķa hromofora spektriem. Spektros etanolā novērojama tikai viena, paplatināta LP josla.

Яна Крейцберга, Екатерина Сироткина, Гуна Берзиня, Лаума Лайпниеце, Валдис Кампарс. Синтез химически связаного бетаина *N*-(1,3-диоксоиндан-2-ил)пиридиния и 1-амино-4-нитроазобензола бихромофора

Цель работы была синтезировать бихромофор 2-[4-(4-нитрофенилазо)фениламинопиридиний-1-ил]-1,3-диоксо-2,3-дигидро-1*H*-инден-2-ид (**1**), состоящий из двух разных НЛО активных хромофоров: ионного типа (нейтральный в возбуждённом состоянии) бетаина *N*-(1,3-диоксоиндан-2-ил)пиридиния и нейтрального в основном состоянии (ионного типа в возбуждённом) 1-амино-4-нитроазобензола. Бихромофор получен в реакции оксида дицианометилиден -1,3-диона с [4-(4-нитрофенилазо)фенил]октилпиридин-4-иламином (**2**). Для получения соединения (**2**) было исследовано три метода. В реакции октилпиридин-4-иламина с 4-бром-4-нитроазобензолом, катализируемой Pd, получены 4-(4-нитрофенилазо)фенилоктиламин и бис-[4-(4-нитрофенилазо)фенил]октиламин, а не желаемое соединение (**2**). Полученный октилфенилпиридин-4-амин не вступает в реакцию с солями *n*-нитробензолдиазония для получения соединения (**2**). Соединение (**2**) получено в реакции конденсации *N*-октил-*N*-(пиридин-4-ил)бензол-1,4-диамина с 1-нитро-4-нитрозобензолом. В электронных спектрах соединения **1** в толуоле видны две полосы, которые соответствуют переносу заряда в обоих связанных хромофорах бихромофора. Полоса переноса заряда азосоединения батохромно сдвинута и коэффициент экстинкции уменьшился в два раза по сравнению с отдельно взятым хромофором. В спектре соединения **1** в этоноле видна только одна широкая полоса переноса заряда.