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SYNTHESIS AND STRUCTURAL ANALYSIS OF SOME NEW ARYLBROMIDE DECORATED AZOBENZENE DERIVATIVES

ISTVAN KOCSIS[a], NICULINA HĂDADE[a] and ION GROSU[a]*

ABSTRACT. We describe the synthesis and structural analysis of some new bi-functionalized compounds containing azobenzene units decorated with bromoaryl groups. The *trans-cis* equilibrium of the central azobenzene unit, induced by photochemical isomerization, is investigated by NMR experiments.

Keywords: *azobenzene, podands, photoisomerization, cis-trans isomers, NMR*

INTRODUCTION

Controlled dynamics at the molecular level has become a subject of close examination over the last two decades. [1] Structural transitions of a molecule between two or several stable states, triggered by external stimuli (*e.g.* pH, temperature, light) opens new ways for the construction of molecular devices [2], which are the foundation of nanoscale science. [3] To date, the large majority of the existing molecular devices consist of two-state molecular switches. [4, 5].

The aim of our work was to design and synthesize podands which incorporate switchable building blocks and which may be valuable candidates for preparation of photochemically driven molecular devices. One of the most interesting and well studied systems that are used to convert light-energy into "mechanical motion" is based on the photochemical *cis-trans* isomerization of azobenzene derivatives. [6] The isomerisation process can be controlled both by UV light irradiation and thermal relaxation. [6] Thereby, conversion of the thermodynamically stable *trans* configuration to metastable *cis* configuration is achieved using UV light, while heating in the dark or irradiation with visible light of the *cis* isomer yields the thermodynamically stable *trans* form.

Photoisomerisation of azobenzene derivatives found important applications in the synthesis of photoresponsive host-guest systems [7] and polymers [8], as well as in the generation of photoswitchable dynamic

[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos str., RO-400028 Cluj-Napoca, Romania, * igrosu@chem.ubbcluj.ro*

combinatiorial libraries. [9] Moreover, photoisomerisation of azobenzene derivatives has been successfully used to control electronic proprieties [10] or catalysis [11] and to initiate folding/unfolding of oligopeptide chains. [12] In this context, we considered of interest to obtain and to investigate the photochemical properties of some new podands bearing an azobenzene central unit decorated with reactive functional groups. Such compounds might be used for macrocyclization reactions and they seem to be good candidates as building blocks for photochemically controlled molecular devices.

RESULTS AND DISCUSSIONS

Viewing the significance of azobenzene as one of the most familiar unit in the construction of photochemically controlled molecular devices, we focused our attention on the synthesis and structural analysis of new di-functionalised 4,4'-azobenzene derivatives (**I** and **II**, Figure 1).

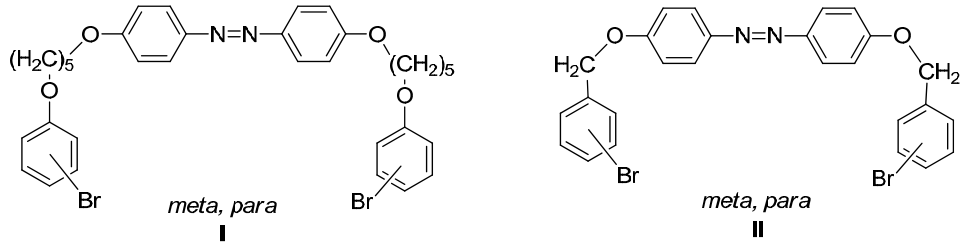
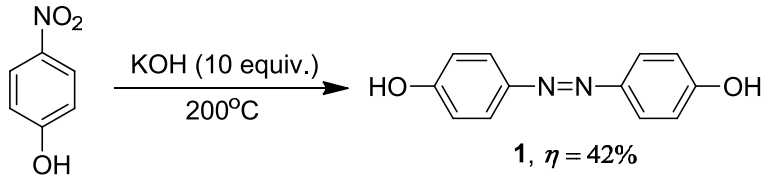


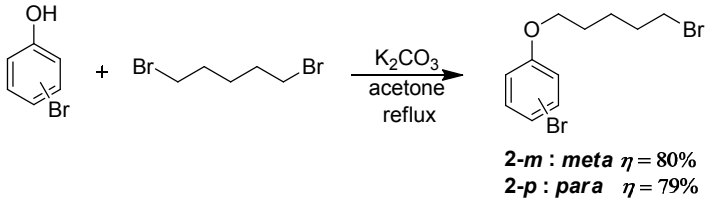
Figure 1. Target azobenzene derivatives **I** and **II**

The *p,p'*-azophenolic unit **1** (Scheme 1) was obtained starting from *p*-nitrophenol, following a previously reported procedure. [13]



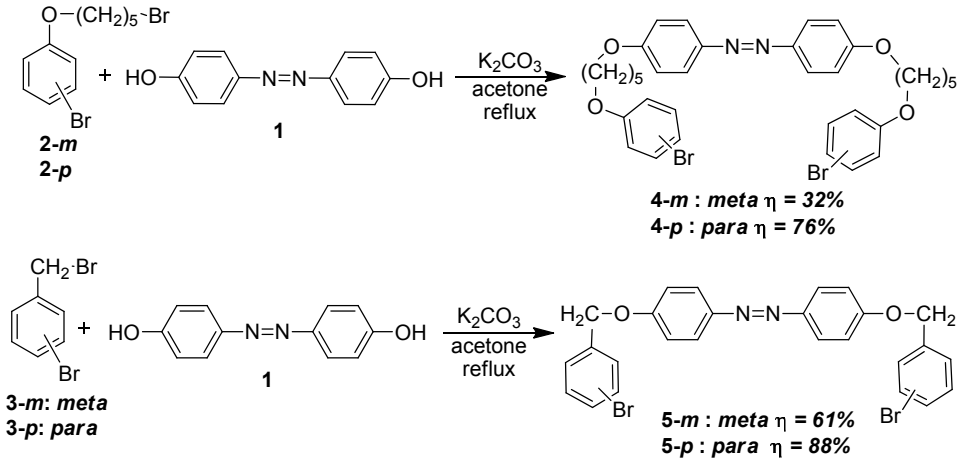
Scheme 1

Next, the dibrominated phenolic ethers **2-*m*** and **2-*p*** (Scheme 2) were obtained in good yields upon treatment of *m*- and *p*-bromophenol respectively with five fold excess of 1,5-dibromopenthane in the presence of potassium carbonate as proton scavenger. A large excess of 1,5-dibromopenthane was used in order to statistically favor the formation of the monosubstituted compounds **2-*m*** and **2-*p***. However, small amounts of disubstituted byproducts (< 6%) also were formed, which were not isolated or investigated.



Scheme 2

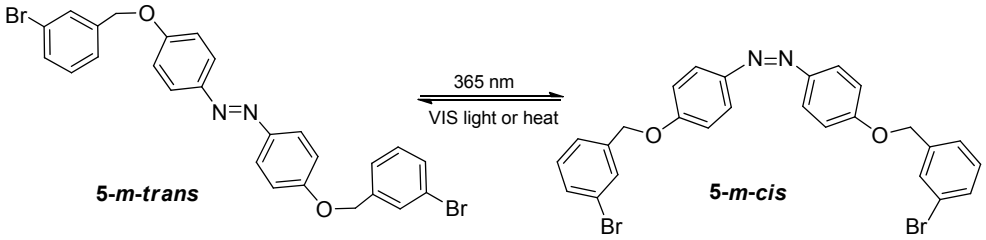
With the building-blocks **1**, **2-*m*** and **2-*p*** in our hands, we proceeded to the synthesis of the target azobenzene derivatives (Scheme 3). Compounds **4-*m*, 4-*p*, 5-*m*** and **5-*p*** were obtained in yields ranging between 32 – 88 % from the reaction of *p,p'*-azophenol **1** with dibromo derivatives **2-*m*, 2-*p*, 3-*m*** and **3-*p*** (dibromo derivatives **3-*m*** and **3-*p*** are commercially available).



Scheme 3

All reaction products were purified by column chromatography and their structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy.

Next, we took a preliminary insight into the photoisomerization process of our azobenzene derivatives. For the present discussion we will refer hereafter to compound **5-*m*** only. The isomerization (trans → cis) (Scheme 4) was achieved at 0 °C by irradiation with UV light (365 nm) and the reaction evolution was monitored by ^{1}H-NMR ($CDCl_3$ on 300 MHz time scale; Figure 2).



Scheme 4

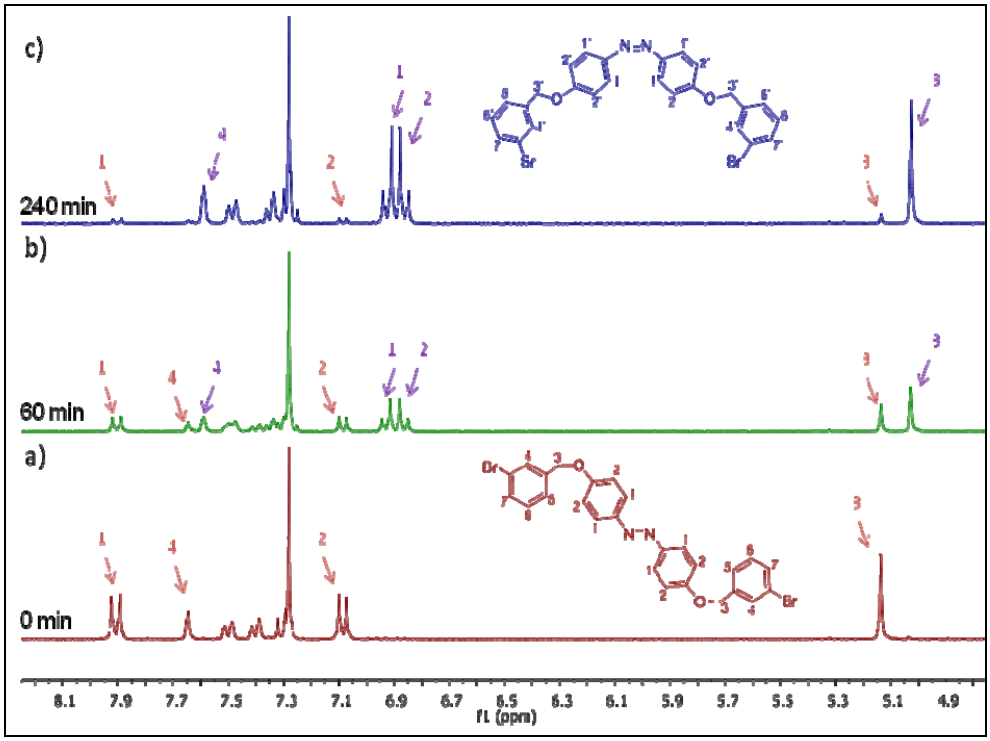


Figure 2. ^{1}H-NMR ($CDCl_3$, 300 MHz, rt) spectra of compound **5-*m***: a) prior to irradiation (*trans* isomer only); b) after 60 min. of irradiation with UV light (365 nm), as a *trans* : *cis* = 1 : 1.6 mixture; c) after 240 min. of irradiation as a *trans* : *cis* = 1 : 11.4 mixture. The atom numbering schemes shown in this figure are used for ^{1}H-NMR assignments and do not correspond to IUPAC numbering rules.

^{1}H-NMR spectrum of **5-*m***, recorded before UV light irradiation (Figure 2a) revealed a single set of signals corresponding to the *trans* isomer. Irradiation with UV light (365 nm) for one hour yielded a mixture of *cis* and *trans* isomers as inferred from the Figure 2b, in a *cis /trans* ratio of 1.6/1 (determined by integration of the singlets at 5.03 ppm and 5.11 ppm corresponding to the CH_2 protons of *trans* and *cis* isomers, respectively). The ^{1}H-NMR spectrum of the *cis* isomer (Figure 2c) shows an identical pattern of signals as the *trans* one, but displaying different chemical shifts. The reaction mixture, after irradiation for four hours displayed a composition of isomers in a ratio *cis/trans = 11.4/1* (inferred from NMR integration). The *trans* isomer of **5-*m*** was totally reformed when **5-*m*-*cis*** was kept under visible light for 24 h.

CONCLUSIONS

In summary, we carried out the efficient synthesis of a new series of *p,p'*-disubstituted azobenzene derivatives containing arylbromine units. For this purpose, the Williamson type reaction between 4,4'-(diazene-1,2-diyl) diphenol and different dibromoderivatives was used. Photoisomerisation studies conducted on compound **5-*m*** and monitored by ^{1}H-NMR spectroscopy showed almost quantitative *trans* to *cis* transformation under UV light irradiation and total *cis* to *trans* conversion under visible light irradiation.

EXPERIMENTAL SECTION

^{1}H and ^{13}C-NMR spectra were recorded at room temperature in $CDCl_3$ or CD_3OD as solvents on a Bruker Advance 300 spectrometer. Multiplicities are abbreviated as follows: br.-broad; *s*-singlet; *d*-doublet; *t*-triplet; *q*-quadruplet; and *m*-multiplet. Melting points were measured with a Kleinfeld Apotec melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was carried out on silica gel 60 F_{254} coated aluminium sheets using UV visualization. Isomerisation studies were realised by UV irradiation using a Vilber Lourmat 12 W UV lamp operating at 254 nm and 365 nm.

Compound **1** was already reported [13] and compounds **3-*m*** and **3-*p*** are commercially available.

*General procedure for synthesis of derivatives **2-m** and **2-p***

A mixture of bromophenol (0.346 g; 0.002 mole), 1,5-dibromopenthane 2.3 g; 0.01 mole) and potassium carbonate (2.76 g; 0.02 mole) in acetone (50 mL) is refluxed overnight. The resulted solid is filtrated and the liquid phase is evaporated *in vacuo*. The residue is chromatographed on silica gel using as mobile phase an elution system of pentane and ethylacetate 90:1 to yield colorless liquids (R.f. = 0.3).

3-bromophenyl, 5'-bromopentylether (2-*m*). Colorless liquid. MW for $C_{12}H_{16}Br_2O$: 336.06 g/mol. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.12 (1H, dd, *J* = 8.1 Hz, *J'* = 7.5 Hz), 7.09 -7.07(1H, m,), 7.06-7.03 (1H, m), 6.82 (1H, ddd, ^{3}J = 8.1 Hz, ^{4}J= 2.3 Hz, $^{4}J'$= 1.3 Hz), 3.94 (2H, t, *J* = 6.3 Hz), 3.44 (2H, t, *J* = 6.6 Hz), 2.01-1.87 (2H, m), 1.81 (2H, cv, *J* = 6.3 Hz), 1.69-1.54 ppm (2H, m). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 159.6, 130.4, 123.6, 117.6, 113.4, 67.7, 33.5, 32.3, 28.2, 24.7 ppm.

4-bromophenyl, 5'-bromopentylether (2-*p*) Colorless liquid. MW for $C_{12}H_{16}Br_2O$: 336.06 g/mol. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.36 (2H, d, *J* = 9 Hz), 6.76 (2H, d, *J* = 9 Hz), 3.92 (2H, t, *J* = 6.3 Hz), 3.43 (2H, t, *J* = 6.9 Hz), 1.93 (2H, m), 1.80 (2H, m), 1.61 ppm (2H, m). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 170.3, 132.1, 116.1, 101.3, 67.8, 33.5, 32.3, 28.2, 24.7 ppm.

*General procedure for synthesis of derivatives **4-m**, **4-p**, **5-m** and **5-p***

A mixture of diphenol **1** (0.214 g; 0.001 mole), bromoderivative **2-*m***, **2-*p***, **3-*m*** or **3-*p*** (0.003 mole), and potassium carbonate (1.38 g; 0.01 mole) in acetone (30 mL) was refluxed overnight. The resulted solid is filtered and the liquid phase is evaporated *in vacuo*. The residue was chromatographed on silica gel.

***Trans*-1,2-bis[4-(7-*m*-bromophenyl-1,7-dioxaheptane-1-yl)phenyl] diazene (4-*m*)** Yellow solid, yield 36%, (pentane/ethylacetate =6:1; Rf = 0.57), m.p. = 125°C. MW for $C_{34}H_{36}N_2O_4$: 696.47 g/mol. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.86 (4H, d, *J* = 9.0 Hz), 7.13 -7.00 (6H, overlapped peaks), 6.98 (4H, d, *J* = 9.0 Hz), 6.84-6.81 (2H, m), 4.06 (4H, t, *J* = 6.3 Hz), 3.98 (4H, t, *J* = 6.0 Hz), 1.92-1.82 (8H, overlapped peaks), 1.65-1.64 ppm (4H, m). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 161.0, 159.8, 146.9, 130.5, 124.3, 123.6, 122.8, 117.7, 114.6, 113.5, 67.9, 29.7, 28.9, 28.9, 22.7 ppm.

***Trans*-1,2-bis[4-(7-*p*-bromophenyl-1,7-dioxaheptane-1-yl)phenyl] diazene (4-*m*)** Yellow solid, yield: 76% (pentane/ethylacetate = 6:1; Rf = 0.57) m.p. = 138°C. MW for $C_{34}H_{36}N_2O_4$:696.47 g/mol. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.87 (4H, d, *J* = 9 Hz), 7.35 (4H, d, *J* = 9 Hz), 6.98 (4H, d, *J* = 9 Hz), 6.77 (4H, d, *J* = 9 Hz), 4.06 (4H, t, *J* = 6 Hz), 3.95 (4H, t, *J* = 6.3 Hz), 1.90 (8H, overlapped peaks), 1.68 ppm (4H, m). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 161.0, 158.1, 146.9, 132.2, 124.3, 116.2, 114.6, 112.7, 68. 0, 67.9, 30.9, 28.9, 22.7 ppm.

***Trans*-1,2-bis[4-(2-*m*-bromophenyl-1-oxaethane-1-yl)phenyl]di azene (5-*m*)** Yellow solid, yield; 61%, (pentane/ethylacetate =6:1; Rf = 0.44), m.p. = 181°C. MW for $C_{26}H_{20}Br_2N_2O_2$: 552.26 g/mol. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.88 (4H, d, *J* = 9.0 Hz), 7.62 (2H, s), 7.47 (2H, d, *J* = 7.8 Hz), 7.37 (2H, d, *J* = 7.8 Hz), 7.27 (2H, t, *J* = 7.8 Hz), 7.06 (4H, d, J = 9.0 Hz), 5.11 ppm (4H, s). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 158.5, 142.7, 138.7, 131.2, 130.3, 130.2, 125.8, 115.0, 87.5, 69.2 ppm.

***Trans*-1,2-bis[4-(2-*p*-bromophenyl-1-oxaethane-1-yl)phenyl]di azene (5-*p*).** Yellow solid. Yield: 88%, (pentane/ethylacetate = 6:1; Rf = 0.44), m.p. = 228°C. MW for $C_{26}H_{20}Br_2N_2O_2$: 552.26 g/mol. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.87 (4H, d, *J* = 8.7 Hz), 7.53 (4H, d, *J* = 8.1 Hz), 7.33 (4H, d, *J* = 8.1 Hz), 7.05 (4H, d, *J* = 8.7 Hz), 5.09 ppm (4H, s). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 170.4, 135.9, 131.8, 129.1, 124.9, 122.1, 115.1, 87.6, 32.4 ppm.

*General procedure for the photoisomerization of derivative **5-m***

A solution of compound **5-m** (10 mg) in deuterated chloroform (1.5 ml) was prepared in a quartz tank. The sollution was cooled at 0 °C using a mixture of water ice and salt. Under magnetic stirring the sollution was subjected to UV irradiation in a darkroom. Each 60 minutes, an aliquot of 0.2 ml was collected in order to prepare the NMR samples. The ^{1}H-NMR spectra (rt) were immediatly recorded. After 4 hours almost the entire quantity of *trans* isomer was transformed into the *cis* one (see Figure 2).

***Cis*-1,2-bis[4-(2-*m*-bromophenyl-1-oxaethane-2-yl)phenyl]di azene (5-*m*-*cis*)**

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.57 (2H, s), 7.46 (2H, d, *J* = 9 Hz), 7.32 (2H, d, *J* = 9 Hz), 7.25 (2H, t, *J* = 9 Hz), 6.90 (4H, d, *J* = 9 Hz), 6.83 (4H, d, *J* = 9 Hz), 5.00 ppm (4H, s). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 157.5, 147.0, 138.7, 131.2, 130.3, 130.2, 125.8, 122.8, 114.8, 87.6, 69.2 ppm.

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