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New Photosensitive Methacrylate Monomers with 4-Aminoazobenzene Type Chromophore Group

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Photosensitive methacrylate monomers, derivatives of azobenzene, were synthesized. The route of syntheses was based on coupling of diazonium salts of sulfathiazole, sulfomethoxazole, sulfadiazine, 4-aminobenzoic acid and 4-nitroaniline with N-alkyl-N-[2-(methacryloyloxy)ethyl]aniline. The *trans*↔*cis* isomerization of the monomers in DMSO solution was investigated by UV-VIS spectroscopy recording their spectra during illumination and thermal recovery periods. It was found that except for nitro derivatives the yield of *trans-cis* isomerization was *ca*. 50% and that the reverse reaction was a result of thermal relaxation. The spectroscopic studies were accompanied by quantum chemical calculations.

Key words: 4-aminoazobenzene derivatives, methacrylate monomers, NLO-phores, E-Z, Z-E isomerization, quantum chemical calculations

Azobenzene group containing compounds are preferred as photosensitive structures and can be utilized in nonlinear optics (NLO) for optical information storage and optical switching materials, because photochemical side reactions, leading to irreversible destruction of the compounds, can be avoided for the majority of them. The azobenzene derivatives with an electron-donating group and an electron-accepting group constitute of π-conjugated system structures showing high first hyperpolarizability, one of the basic requirements for organic NLO materials (NLO-phores) [1]. Well known ability of azobenzene-based compounds for photoinduced reverse *trans*↔cis isomerization reaction [2], *i.e*., photochromic switching between two spectroscopically different forms, make the compounds suitable for optical data storage materials. The most convenient method of using the azobenzene based NLO-phores, from practical point of view, is incorporating them into polymer as fully covalent bonded structure elements in the main or side chain of the polymer macromolcule [1,3–6]. One of the frequently studied type of the azobenzene-based materials in the last decade were acrylate and methacrylate polymers and copolymers containing side-chain azochromophore groups [1,3–24]. The structures of the chromophore monomers used for the synthesis of the (meth)acrylic polymers included derivatives of azobenzene [25], 4-hydroxyazobenzene [9,21,24,25], 4-aminoazobenzene [8,14,15,25] and derivatives of azobenzene, in which one of the phenyl group was replaced by anthraquinonyl [23] or carbazolyl [22] groups.

The aim of our work was synthesis of new NLO-phore containing methacrylate monomers of 4-aminoazobenzene derivative type with different alkyl radical at amino group and constant spacer length (1,2-ethanediyl group) between methacryloyloxy and amino group. The compounds synthesized contained typical, for known methacrylic monomers, NO_2, COOH electron withdrawing groups and electron withdrawing N-substituted sulfonamide group with selected heteroaryl group. Because of foreseen use of the monomers for synthesis of the photoresponsive and NLO-active methacrylic polymers and copolymers, their ability to undergo reverse *trans*↔*cis* photoisomerization was examined spectrophotometrically and by quantum chemical calculations, respectively.

RESULTS AND DISCUSSION

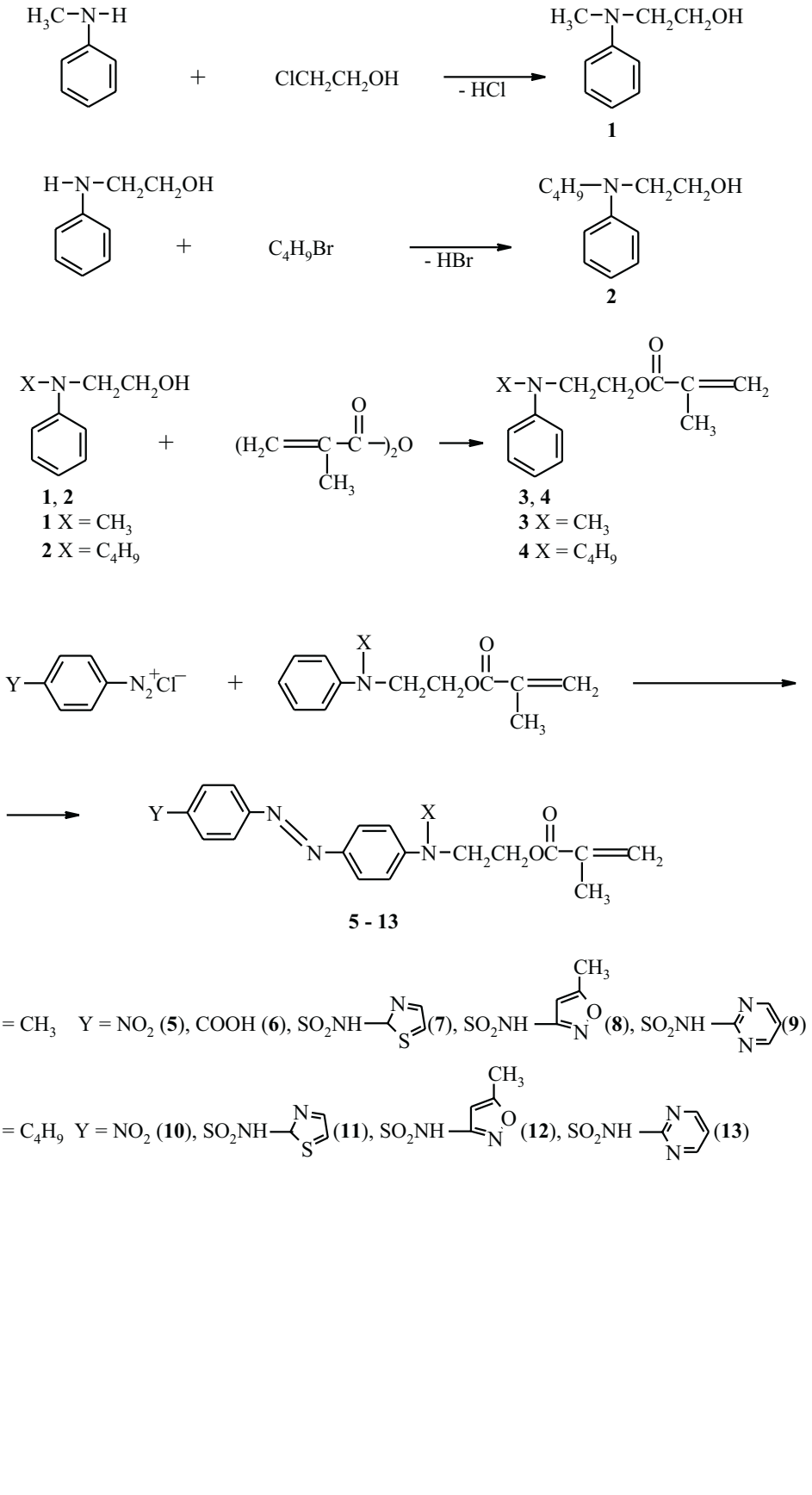
The chromophore containing methacrylates studied were synthesized according to the Scheme. Starting from N-methylaniline or N-(2-hydroxyethyl)aniline corresponding N-methyl (**1**) or N-butyl (**2**) derivatives of the latest aniline were obtained with 55% or 53% yield, respectively. The compounds **3** and **4**, obtained by esterification reaction of **1** and **2** with methacrylic anhydride, were coupled with diazonium salts of 4-nitroaniline, 4-aminobenzoic acid, sulfadiazine, sulfamethoxazole, and sulfathiazole obtaining with 77–93% yield two series (X = CH_3 or X = C_4H_9) of azobenzene based methacrylates (**5**–**13**), *e.g.*, photochromic and NLO-phore group containing methacrylate monomers.

The absorption spectra of the monomers recorded for DMSO solutions, in the absence of external light, for the most of the compounds studied showed maximum absorption peak appearing at *ca.* 446–452 nm. Only for monomers **5** and **10** with NO_2 group the maximum was shifted to *ca.* 494–500 nm. All the compounds showed similar absorption ability expressed by lg ε_{max} *ca.* 4.40–4.55 at the maximum of the absorption bands.

In each series of the monomers, obtained with π-conjugated donor-acceptor system, the electron donating effect of the amino group is the same. The observed bathochromic shift of the absorption band (*ca.* 44–52 nm in both series) of the derivatives containing nitro group (**5**, **10**) depends first of all upon the electron withdrawing power of the acceptor group. The electron withdrawing power of the substituents under study, decreasing in the order NO_2, COOH, and SO_2NH_2 [1], is in good accordance with the observed position of absorption band maximum (Table 1). The structure of the heteroaromatic substituent at nitrogen atom of the sulfonamide group has no significant influence on the position of the maximum.

According to Rau [2], the monomers in question can be classified to "*pseudo-stilbene*" type molecules that means that the azomonomers represent system of two excited states (n→π* or π→π*) with similar energies. High energy π→π* transition is overlapping the low energy n→π* transition that leads to an intensive and symmetric absorption band for *trans* isomer. Overlapping phenomenon of transition state energies can result the same excitation wavelength for both *trans-cis* and

Scheme 1



X = CH_3 Y = NO_2 (**5**), COOH (**6**), SO_2NH–(**7**), SO_2NH–(**8**), SO_2NH–(**9**)

X = C_4H_9 Y = NO_2 (**10**), SO_2NH–(**11**), SO_2NH–(**12**), SO_2NH–(**13**)

cis-trans photoisomerization reactions. It is the case that we observed for illuminated DMSO solutions of **5** and **10** (NO_2 acceptor group), for which no significant changes in the absorption band intensity of the *trans* isomers were recorded (Table 2). According to the results obtained for Disperse Red 1 and Disperse Orange 3 [30], two pseudo stilbene type structures of 4-amino-4′-nitro derivatives of azobenzene, the additional reason of the lack of spectroscopic monitored by us changes in absorption bands of *trans* isomers **5** and **10** during illumination can result from rapid room temperature *cis-trans* isomerization.

Table 1. Yield, melting points and UV-VIS absorption data of synthesized methacrylates.

Compound	Yield %	M.p. °C	λ_{max} nm	lg ε_{max} [a)]
5	84	96–98	494	4.47
6	77	216–219	446	4.40
7	80	210–212	448	4.47
8	88	174–176	452	4.55
9	84	224–226	448	4.47
10	90	73–76	500	4.48
11	93	128–130	448	4.46
12	86	123–125	450	4.54
13	86	192–194	448	4.47

ε_{max} in $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.

Table 2. Yield of *cis* isomer and wavelengths at maximum absorption band of *cis* and *trans* isomers at photostationary state.

Compound	*cis* %	λ_{max} nm	
		cis	*trans*
5	0		494
6	59	380	446
7	45	382	448
8	53	380	452
9	55	380	448
10	0		500
11	41	380	448
12	60	382	450
13	50	382	448

All remaining azomonomers (**6–9** and **11**–**13**) with COOH or N-substituted SO_2NHAr acceptor groups undergo the *trans-cis* isomerization reaction giving 41–60% content of *cis* isomer at photostationary state. The example time depending UV-VIS spectra of illuminated solutions of **9** (*trans-cis* isomerization) and thermal back (in the dark) *cis-trans* isomerization of the same solutions are presented in Fig. 1. The isosbestic points at 380 and 525 nm are characteristic for the existence of two distinct absorbing species in equilibrium with each other in the system studied.

From the data presented in Fig. 1 and in Fig. 2 it is seen that *trans-cis* and *cis-trans* isomerization reactions are kinetically different. The photostationary state have been reached after few seconds of the illumination practically independently of the monomers structure (**6**–**9**,**11–13**). On the contrary, the *cis-trans* isomerization reaction is much slower (reaction times *ca.* 10^2–10^3 times longer), more complex kinetically, and depending on the methacrylates structure (compare curves **7** and **9** in Fig. 2). Generally speaking, except for monomers with nitro group (Y = NO_2), the temporary stability of the *cis* isomer *versus* thermal isomerization for both series of methacrylates depends on the structure of the electron withdrawing group and for sulfonamide type monomers decrease in the order **7** > **9** > **8** (**11** > **13** > **12**), (monomer **6** with carboxy group between **9** and **8**).

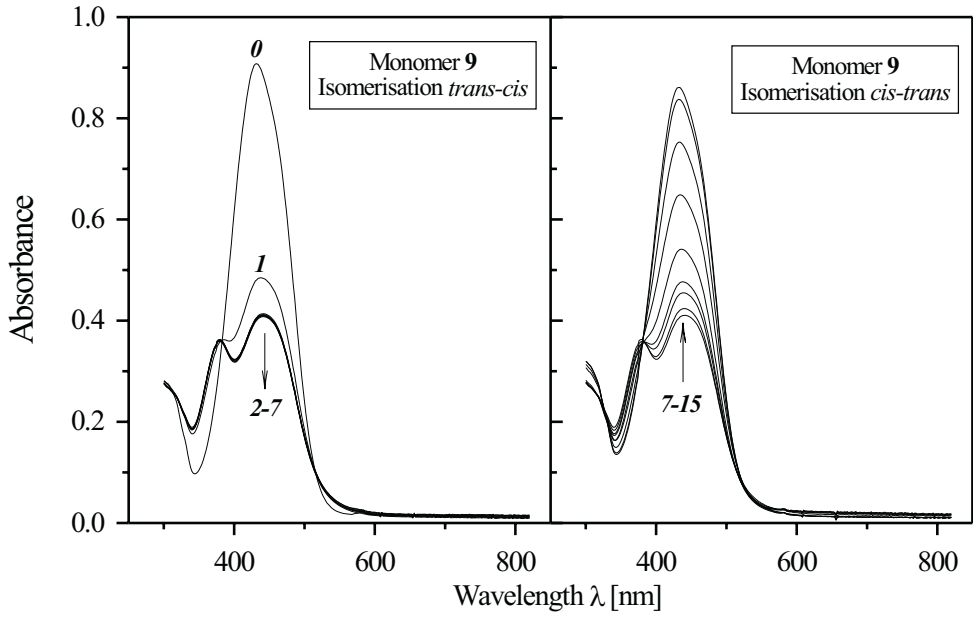


Figure 1. Changes in absorption spectrum during *trans*→*cis* (0–7) and *cis*→*trans* (7–15) isomerization of monomer **9**.

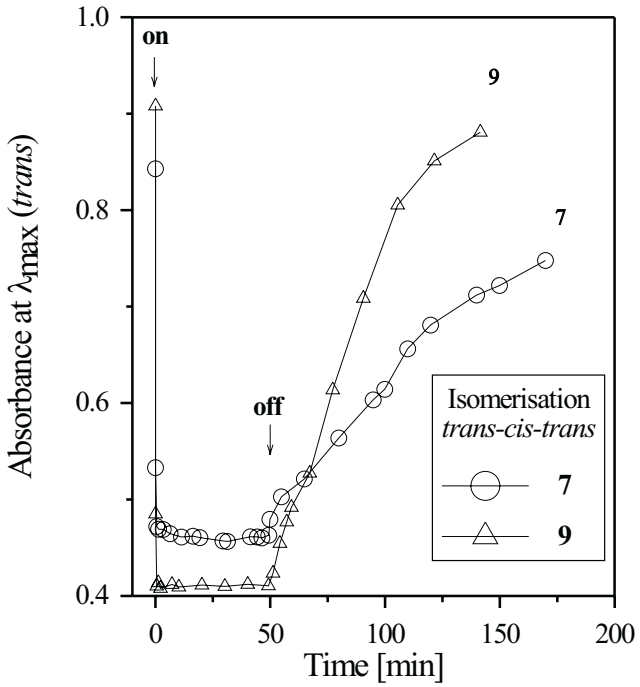


Figure 2. Absorbance at maximum absorption band for *trans* isomer during light induced *trans-cis* isomerization and back dark *cis-trans* isomerization for monomers **7** and **9**.

Applying our earlier used method for evaluation of the agreement between spectroscopic observed photochemical behaviour of the azobenzene derivatives and the theoretically generated by quantum chemical calculations UV-VIS spectra [31], we calculated the spectra for *cis* and *trans* isomers and their mixtures for the methacrylates in question. From the data presented in Fig. 3, for an example compound **7** (monomers **6**–**9** and **11**–**13**), it is seen that calculated maxima of absorption bands for *trans* (***1***) and *cis* (***2***) isomers are hypsochromically shifted by *ca.* 10–15 nm in respect to observed ones. Theoretical absorption band calculated for 1:1 mol/mol mixture of the isomers (curve ***3***) is close in shape to the observed one (curve ***4***).

Investigations of the *trans-cis* isomerization of azobenzene derivatives is not easy as there is a problem with isolation of the *cis* isomer in its pure form and preserve it throughout the measurement procedure. Therefore, it is difficult or in many instances impossible to record experimental spectra of the *cis* form.

In this work, the quantum chemical methods were applied to determine UV-VIS spectra of both *trans* and *cis* form of the most representative monomers. The starting step was optimization of the geometrical structures of the monomers with Gaussian 98 program using *ab initio* RHF (restricted Hartree-Fock) and DFT (density functional theory) options with a split-valence 3-21G basis set. It was found that this relatively simple basis set was satisfactory by compromising the calculation accuracy and computing time. To calculate the UV-VIS spectra of the compounds in question the optimized atomic coordinates from B3LYP/3-21G runs were introduced into

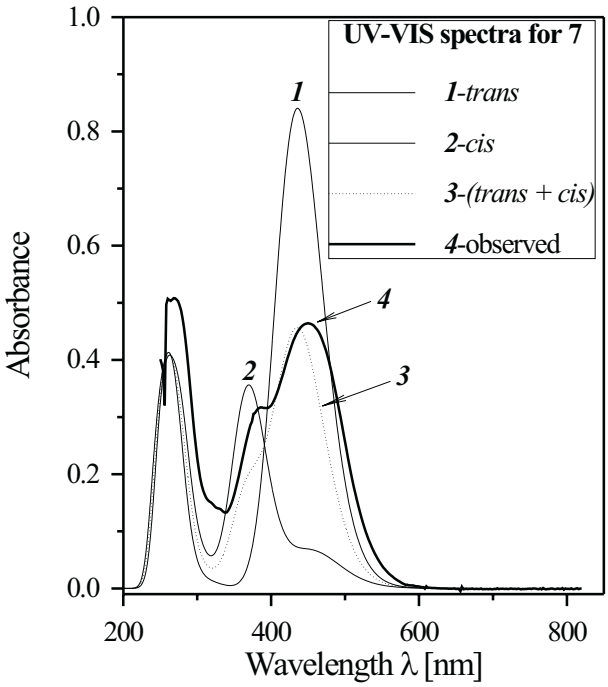


Figure 3. Calculated absorption spectra for isomer *trans* (***1***), *cis* (***2***), 1:1 (mol/mol) mixture of *cis* and *trans* (***3***) and observed spectrum (***4***) at photostationary state of monomer **7**.

INDO1/S semiempirical program [30,31]. The singlet state configuration interaction (CI) was assumed in the space HOMO-30 to LUMO+30 that yielded 900 configurations. The effect of solvent was simulated by self-consistent reaction field (SCRF) using physical data for DMSO; the cavity radius of the solute molecule in solution was obtained from Gaussian calculations. Twenty electronic states were generated, which constituted a set of data: oscillator strength *vs*. energy of the excited state expressed in terms of frequency. This data was converted into a regular spectrum by applying a Gaussian envelope.

In Fig. 3 the calculated spectra were shown for compound **7** and **11**. The spectra were obtained for pure *trans* and *cis* forms and taking these as a base the spectra of 1:1 *trans-cis* mixtures were calculated. The comparison between experimental and calculated spectra of these compounds lead to the conclusion that the agreement between measured and calculated spectra is relatively good. It is to mention that the size of alkyl group at N atom (X substituent) has practically little observable effect on the shape of UV-VIS spectrum.

Fig. 4 shows the calculated and determined spectra for nitro derivative **10**.The experimental and calculated spectrum of the *trans* form is very similar. The shape of the calculated spectrum of the *cis* form is also shown, however, it was not possible to observe a change of the *trans* form spectrum on illumination at room temperature. It may be assumed that at room temperature either the reverse thermal *cis-trans* reaction is relatively fast and it competes with photochemical *trans-cis* isomerization or

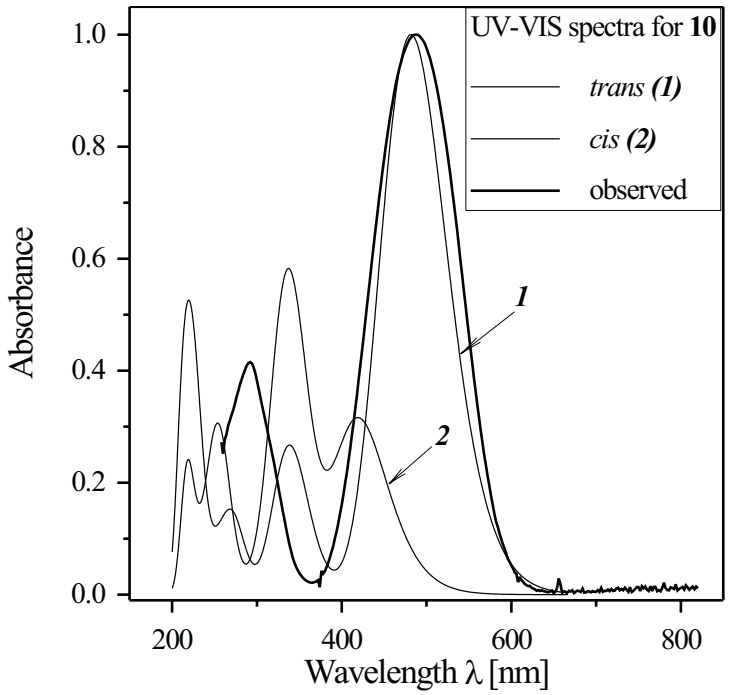


Figure 4. Calculated absorption spectra for isomer *trans* (***1***), *cis* (***2***) and observed absorption spectrum during illumination of monomer **10** with nitro acceptor group.

that absorption bands of *cis* and *trans* forms are too close and at the same time we have to do with contemporaneous photochemical reactions with a net zero observable effect. One experiment was also made with monochromatic light band at maximum absorption of the nitro derivative and in conditions the sulfonamide compounds underwent isomerization, and the nitro ones remained practically unchanged.

Table 3 shows the differences in potential energy, ΔE, between the *trans* and *cis* form of the compounds **5**, **7** and **9**. The values obtained for monomer containing nitro acceptor group are lower as compared with monomers of the sulfonamide type and this may contribute to different behaviour of the former. It is to mention that lower values of ΔE for DFT B3LYP option is a feature of the method and it has been observed previously [31].

Table 3. Potential energy difference, ΔE, of the *trans* and *cis* structures obtained by calculation, in kJ/mol.

Basis set	ΔE Compound		
	5	**7**	**9**
RHF/3-21G	58.9	87.1	85.9
B3LYP/3-21G	46.8	74.7	73.8

The monomers obtained undergo radical polymerization and copolymerization with other methacrylic monomers. The preparation of the polymers and their characteristics will be the subject of a separate publication.

EXPERIMENTAL

Chemicals for synthesis were reagent grade and purchased from Aldrich, Sigma-Aldrich and Merck. DMSO was purified and dried by standard method. Purity of the monomers was checked by TLC method on silica gel 60 F 254 aluminium plates. The spots were visualized in iodine vapour and in UV light. ^{1}H NMR spectra were run on a 300 MHz Bruker Avance DRX-300 spectrometer for solutions in $CDCl_3$ or DMSO-d_6 against TMS as internal reference. UV-VIS spectra were recorded using a Diode Array Hewlett Packard Spectrophotometer 8452A. Illumination of the DMSO solutions of the monomers studied (*ca.* 10^{-5}–10^{-4} M, absorbance 0.8–1.0) was carried out at room temperature, using 150 W halogen lamp and Schott glass filters BG28 and GG giving light power density *ca.* 1.8 mW/cm^2 for evaluation of *trans-cis* isomerization. *Cis-trans* reaction course was controlled spectrophotometrically without illumination (in the dark). The solutions were equilibrated at room temperature in the dark and then illuminated in 1 cm quartz absorption cell. Quantum chemical calculations were carried out at the Wrocław Supercomputer Centre with an IBM R6000 RISC machine using GAUSSIAN 94 and INDO1/S programs [26–28].

Synthesis of N-methyl-N-(2-hydroxyethyl)aniline (1): In a three necked round bottom flask fitted with reflux condenser and mechanical stirrer, 53.6 g (0.50 mole) N-methylaniline, 41.1 g (0.51 mole) 2-chloroethanol, 1.2 g KI and 300 cm^3 *n*-BuOH were placed and refluxed under stirring for 25 hours. After cooling the precipitate was filtered off and the filtrate evaporated under reduced pressure using rotary evaporator to remove solvent. Liquid residue was fractionally distilled and redistilled under reduced pressure using short Vigreux distillation column. Yield: 42 g (55%); b.p.: 102–104°C at 0.6–0.8 mm Hg; n_D^{20} = 1.5700. ^{1}H NMR ($CDCl_3$, TMS): 1.85, br. s, 1H (OH); 3.04, s, 3H (CH_3N-); 3.54, t, ^{3}J = 5.6 Hz, 2H (-OCCH$_2$N-); 3.88, t, ^{3}J = 5.6 Hz, 2H (-OCH$_2$CN-); 6.80–6.90, m, 3H (*ortho* and *para* protons of phenyl ring); 7.25–7.45, m, 2H (*meta* protons of phenyl ring).

Synthesis of N-*n*-butyl-N-(2-hydroxyethyl)aniline (2): In a one neck round bottom flask fitted with reflux condenser and mechanical stirrer, 137.2 g (1.0 mole) N-(2-hydroxyethyl)aniline, 150.7 g (1.1 mole) 1-bromobutane, 1.5 g KI and 200 cm^3 ethanol were placed and refluxed under stirring for 35 hours. The solvent, excess 1-bromobutane and low boiling side products evaporated under reduced pressure using rotary evaporator. The gel like residue was treated with 1.1 mole of 20% aqueous NaOH solution, mixed and refluxed for 15 minutes. Hot organic phase was separated and washed 3 × 150 cm^3 of hot brine, dried over solid KOH and then fractionally distilled and redistilled under reduced pressure using short Vigreux distillation column. Yield: 102.4 g (53%); b.p.: 130–134°C at 1.0 mm Hg; n_D^{20} = 1.5472. ^{1}H NMR ($CDCl_3$, TMS): 0.94, t, ^{3}J = 7.2 Hz, 3H (CH_3CCCN-); 1.34, m, 2H (CCH$_2$CCN-); 1.56, m, 2H ((CCCH$_2$CN-); 1.88, br. s, 1H (OH); 3.30, t, ^{3}J = 7.7 Hz, 2H (CCCCH$_2$N-); 3.45, t, ^{3}J = 5.8 Hz, 2H (-OCCH$_2$N-); 3.77, t, ^{3}J = 5.8 Hz, 2H (-OCH$_2$CN-); 6.64–6.77, m, 3H (*ortho* and *para* protons of phenyl ring); 7.15–7.26, m, 2H (*meta* protons of phenyl ring).

Synthesis of N-methyl- (3) or N-*n*-butyl-N-[2-(methacryloyloxy)ethyl]aniline (4): The syntheses were run according to the method described by Cross *et al.* [17]. N-Methyl- or N-*n*-butyl-N-(2-hydroxyethyl)aniline (0.30 mole), 3.7 g 4-(dimethylamino)pyridine, 0.1–0.2 g BHT or 4-methoxyphenol were dissolved in dry pyridine and then after addition of 54 g (0.35 mole) methacrylic anhydride the resulted mixture was refluxed for 15 minutes. The pyridine was removed under reduced pressure using rotary evaporator. The residue was dissolved in 100 cm^3 ethyl acetate and extracted 3–5 times with 0.1 M aqueous solution of $NaHCO_3$, dried over $MgSO_4$ and evaporated under reduced pressure using rotary evaporator. Crude liquid products **3** and **4** were used for the synthesis of methacrylic monomers **5**–**13**. The structure of the compounds **3** and **4** was confirmed by ^{1}H NMR spectra. Compound **3** ($CDCl_3$, TMS): 1.91, s, 3H (-CH_3C=C); 2.98, s, 3H (CH_3N-); 3.64, t, ^{3}J = 6.0 Hz, 2H (-OCCH$_2$N-); 4.32, t, ^{3}J = 6.0 Hz, 2H (-NCCH$_2$O-); 5.54, s, 1H (-(C)C=CH$_{trans}$); 6.05, s, 1H ((C)C=CH$_{cis}$); 6.68–6.76, m, 3H (*ortho* and *para* protons of phenyl ring); 7.19–7.26, m, 2H (*meta* protons of phenyl ring).

Compound **4** ($CDCl_3$, TMS): 0.95, t, ^3J = 7.2 Hz, 3H (CH_3CCCN-); 1.35, m, 2H (CCH_2CCN-); 1.57, m, 2H ($CCCH_2CN$-); 3.32, t, ^3J = 7.8 Hz, 2H ($CCCCH_2N$-); 3.63, t, ^3J = 6.0 Hz, 2H (-$OCCH_2N$-); 4.32, t, ^3J = 6.0 Hz, 2H (-OCH_2CN-); 5.55, s, 1H (-(C)C=CH_{trans}); 6.05, s, 1H ((C)C=CH_{cis}); 6.69–6.78, m, 3H (*ortho* and *para* protons of phenyl ring); 7.19–7.27, m, 2H (*meta* protons of phenyl ring).

Syntheses of 4-carboxy-4′-[N-methyl-N-(2-methacryloyloxy)ethyl]aminoazobenzene (6), 4-nitro-4′-[N-alkyl-N-(2-methacryloyloxy)ethyl]aminoazobenzenes (5, 10) and 4-N^1-(heteroaryl)sulfonamido-4′-[N-alkyl-N-(2-methacryloyloxy)ethyl]aminoazobenze-nes (7–9, 11–13): General procedure [29]: Mixture of 0.005 mole 4-nitroaniline (for **5**, **10**) [4-aminobenzoic acid for (**6**), sulfathiazole for (**7**, **11**), sulfamethoxazole for (**8**, **12**) and sulfadiazine for (**9**, **13**)] and 1.4 cm^3 of concentrated HCl was stirred and heated to 60–70°C. Into the resulting warm solution or fine dispersion 10 cm^3 water and then 15 cm^3 concentrated acetic acid was added and stirred at 60–70°C to obtain clear solution. To the cooled solution in ice bath at the temperature 0 ÷ +5°C the solution of 0.4 g (0.006 mole) $NaNO_2$ in 1 cm^3 was added dropwise (slowly) under stirring at the temperature below +5°C. 20 min. later a test for excess of nitrous acid was done (iodide-starch paper) and the excess was eliminated by addition of few drops of saturated aqueous solution of sulfamic acid. To the so prepared cold (below +5°C) solution of diazotized starting reagent the cold (below +5°C) solution of 0.0055 mole of N-alkyl-N-[2-(methacryloyloxy)ethyl]aniline in 2-methoxyethanol was added under stirring followed by 5 g (0.06 mole) of sodium acetate and the reaction mixture was carefully mixed. After stirring for 0.5 hour at reaction temperature the resulted reaction mixture was left in refrigerator overnight. Reaction mixture was diluted with 3–5 fold volume of water and coloured precipitate filtered off, washed with water and dried at 60°C. The dried product was crystallised from dimethylformamide. The precipitate was filtered off, washed initially with 50%-vol. DMF-water mixture and then with water and dried at 60°C. Yields and melting points of the methacrylate obtained are listed in Table 1.

4-Nitro-4′-[N-methyl-N-(2-methacryloyloxy)ethyl]aminoazobenzene (5) (84%); m.p. 96–98°C; ^{1}H NMR (DMSO-d_6, TMS): 1.83, s, 3H (-(CH_3)C=C); 3.12, s, 3H (CH_3N-); 3.85, t, ^3J = 5.1 Hz, 2H (-$OCCH_2N$-); 4.34, t, ^3J = 5.1 Hz, 2H (-OCH_2CN-); 5.65, s, 1H (-(C)C=CH_{trans}); 5.97, s, 1H (-(C)C=CH_{cis}); 6.95, d, ^3J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.85, d, ^3J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.94, d, ^3J = 8.9 Hz, 2H (*ortho* protons *vs.* nitro group of nitrophenyl ring); 8.35, d, ^3J = 8.9 Hz, 2H (*ortho* protons *vs.* azo group of nitrophenyl ring). Anal. Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47; N, 15.21. Found: C, 61.76; H, 5.45; N, 15.02.

4-Nitro-4′-[N-*n*-butyl-N-(2-methacryloyloxy)ethyl]aminoazobenzene (10): (90%); m.p. 73–76°C; ^{1}H NMR (DMSO-d_6, TMS): 0.96, t, ^3J = 7.2 Hz, 3H (CH_3CCCN-); 1.38, m, 2H (CCH_2CCN-); 1.58, m, 2H ($CCCH_2CN$-); 1.88, s, 3H (-(CH_3)C=C); 3.50, t, ^3J = 7.2 Hz, 2H ($CCCCH_2N$-); 3.83, t, ^3J = 5.1 Hz, 2H (-$OCCH_2N$-); 4.34, t, ^3J = 5.1 Hz, 2H (-OCH_2CN-); 5.71, s, 1H (-(C)C=CH_{trans}); 6.04, s, 1H (-(C)C=CH_{cis}); 6.96, d, ^3J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.86, d, ^3J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.96, d, ^3J = 8.9 Hz, 2H (*ortho* protons *vs.* nitro group of nitrophenyl ring); 8.38, d, ^3J = 8.9 Hz, 2H (*ortho* protons *vs.* azo group of nitrophenyl ring). Anal. Calcd. for $C_{22}H_{26}N_4O_4$: C, 64.38; H, 6.38; N, 13.65. Found: C, 64.34; H, 6.27; N, 13.66.

4-Carboxy-4′-[N-methyl-N-(2-methacryloyloxy)ethyl]aminoazobenzene (6) (77%): m.p. 216–219°C; ^{1}H NMR (DMSO-d_6, TMS): 1.86, s, 3H (-(CH_3)C=C); 3.12, s, 3H (CH_3N-); 3.85, t, ^3J = 5.1 Hz, 2H (-$OCCH_2N$-); 4.35, t, ^3J = 5.1 Hz, 2H (-OCH_2CN-); 5.67, s, 1H (-(C)C=CH_{trans}); 6.00, s, 1H (-(C)C=CH_{cis}); 6.95, d, ^3J = 8.9 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.86, t, 4H (*ortho* protons *vs.* azo group of aminophenyl ring and *ortho* protons *vs.* sulfonamide group of sulfonamidophenyl ring); 8.11, d, ^3J = 8.1 Hz, 2H (*ortho* protons *vs.* azo group of sulfonamidophenyl ring); 13.0, br. s, 1H (-COOH). Anal. Calcd. for $C_{20}H_{21}N_3O_4$: C, 65.38; H, 5.76; N, 11.44. Found: C, 65.11; H, 5.65; N, 11.27.

4-N^1-(Thiazol-2-yl)sulfonamido-4′-[N-methyl-N-(2-methacryloyloxy)ethyl]aminoazobenzene (7) (80%); m.p. 210–212°C; ^{1}H NMR (DMSO-d_6, TMS): 1.82, s, 3H (-(CH_3)C=C); 3.08, s, 3H (CH_3N-); 3.83, t, ^3J = 5.1 Hz, 2H (-$OCCH_2N$-); 4.33, t, ^3J = 5.1 Hz, 2H (-OCH_2CN-); 5.64, s, 1H (-(C)C=CH_{trans}); 5.97, s, 1H (-(C)C=C_{cis}); 6.86, d, ^3J = 4.6 Hz, 1H (H^5 of thiazole ring); 6.93, d, ^3J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.28, d, ^3J = 4.6 Hz, 1H (H^4 of thiazole ring); 7.80, d, ^3J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.87, d, ^3J = 8.6 Hz, 2H (*ortho* protons *vs.* sulfonamide group of sulfonamidophenyl ring); 7.95, d, ^3J = 8.6 Hz, 2H (*ortho* portons *vs.* azo group of

sulfonamidophenyl ring); 12.65, br. s, 1H (-$NHSO_2$-). Anal. Calcd. for $C_{22}H_{23}N_5O_4S_2$: C, 54.42; H, 4.77; N, 14.42; S, 13.20. Found: C, 54.52; H, 4.72; N, 14.39; S, 12.97.

4-N^1-(Thiazol-2-yl)sulfonamido-4′-[N-*n*-butyl-N-(2-methacryloyloxy)ethyl]aminoazobenzene (**11**) (93%); m.p. 128–130°C; ^{1}H NMR (DMSO-d_6, TMS): 0.95, t, ^{3}J = 7.2 Hz, 3H (CH_3CCCN-); 1.37, m, 2H (CCH_2CCN-); 1.58, m, 2H ($CCCH_2$CN-); 1.88, s, 3H (-(CH_3)C=C); 3.48, t, ^{3}J = 7.2 Hz, 2H ($CCCCH_2$N-); 3.81, t, ^{3}J = 5.1 Hz, 2H (-$OCCH_2$N-); 4.33, t, ^{3}J = 5.1 Hz, 2H (-OCH_2CN-); 5.70, s, 1H (-(C)C=CH_{trans}); 6.04, s, 1H (-(C)C=C_{cis}); 6.89, d, ^{3}J = 4.6 Hz, 1H (H^5 of thiazole ring); 6.95, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.31, d, ^{3}J = 4.6 Hz, 1H (H^4 of thiazole ring); 7.82, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.89, d, ^{3}J = 8.6 Hz, 2H (*ortho* protons *vs.* sulfonamide group of sulfonamidophenyl ring); 7.97, d, ^{3}J = 8.6 Hz, 2H (*ortho* portons *vs.* azo group of sulfonamidophenyl ring); 12.84, br. s, 1H (-$NHSO_2$-). Anal. Calcd. for: $C_{25}H_{29}N_5O_4S_2$: C, 56.91; H, 5.54; N, 13.27; S, 12.15. Found: C, 56.80; H, 5.55; N, 13.07; S, 12.01.

4-N^1-(5-Methylisoxazol-3-yl)sulfonamido-4′-[N-methyl-N-(2-methacryloyloxy)ethyl]amino-azobenzene (**8**) (88%); m.p. 174–176°C; ^{1}H NMR (DMSO-d_6, TMS):1.82, s, 3H (-(CH_3)C=C); 2.29, s, 3H (CH_3 of methylisoxazole ring); 3.08, s, 3H (CH_3N-); 3.83, t, ^{3}J = 5.1 Hz, 2H (-$OCCH_2$N-); 4.33, t, ^{3}J = 5.1 Hz, 2H (-OCH_2CN-); 5.64, s, 1H (-(C)C=CH_{trans}); 5.97, s, 1H (-(C)C=C_{cis}); 6.13, s, 1H (H^4 of methyl-isoxazole ring); 6.93, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.81, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.88, d, ^{3}J = 8.6 Hz, 2H (*ortho* protons *vs.* sulfonamide group of sulfonamidophenyl ring); 7.97, d, ^{3}J = 8.6 Hz, 2H (*ortho* portons *vs.* azo group of sulfonamidophenyl ring); 11.50, br. s, 1H (-$NHSO_2$-). Anal. Calcd. for $C_{23}H_{25}N_5O_5S$: C, 57.13; H, 5.21; N, 14.48; S, 6.63. Found: C, 57.12; H, 5.09; N, 14.29; S, 6.50.

4-N^1-(5-Methylisoxazol-3-yl)sulfonamido-4′-[N-*n*-butyl-N-(2-methacryloyloxy)ethyl]amino-azobenzene (**12**) (86%); m.p. 123–125°C; ^{1}H NMR (DMSO-d_6, TMS): 0.95, t, ^{3}J = 7.2 Hz, 3H (CH_3CCCN-); 1.37, m, 2H (CCH_2CCN-); 1.58, m, 2H ($CCCH_2$CN-); 1.88, s, 3H (-(CH_3)C=C); 2.34, s, 3H (CH_3 of methylisoxazole ring); 3.48, t, ^{3}J = 7.2 Hz, 2H ($CCCCH_2$N-); 3.81, t, ^{3}J = 5.1 Hz, 2H (-$OCCH_2$N-); 4.35, t, ^{3}J = 5.1 Hz, 2H (-OCH_2CN-); 5.70, s, 1H (-(C)C=CH_{trans}); 6.04, s, 1H (-(C)C=C_{cis}); 6.20, s, 1H (H^4 of methylisoxazole ring); 6.95, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.83, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.93, d, ^{3}J = 8.6 Hz, 2H (*ortho* protons *vs.* sulfonamide group of sulfonamidophenyl ring); 8.01, d, ^{3}J = 8.6 Hz, 2H (*ortho* portons *vs.* azo group of sulfonamidophenyl ring); 11.56, br. s, 1H (-$NHSO_2$-). Anal. Calcd. for $C_{26}H_{31}N_5O_5S$: C, 59.41; H, 5.94; N, 13.32; S, 6.10. Found: C, 59.33; H, 5.95; N, 13.13; S, 5.99.

4-N^1-(Pyrimidin-2-yl)sulfonamido-4′-[N-methyl-N-(2-methacryloyloxy)ethyl]aminoazoben-zene (**9**) (84%); m.p. 224–226°C; ^{1}H NMR (DMSO-d_6, TMS): 1.82, s, 3H (-(CH_3)C=C); 3.09, s, 3H (CH_3N-); 3.83, t, ^{3}J = 5.1 Hz, 2H (-$OCCH_2$N-); 4.33, t, ^{3}J = 5.1 Hz, 2H (-OCH_2CN-); 5.64, s, 1H (-(C)C=CH_{trans}); 5.97, s, 1H (-(C)C=C_{cis}); 6.93, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.07, t, ^{3}J = 4.9 Hz, 1H (H^5 of pyrimidine ring); 7.81, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.89, d, ^{3}J = 8.5 Hz, 2H (*ortho* protons *vs.* sulfonamide group of sulfonamidophenyl ring); 8.10, d, ^{3}J = 8.5 Hz, 2H (*ortho* portons *vs.* azo group of sulfonamidophenyl ring); 8.51, d, ^{3}J = 4.9 Hz, 2H (H^4, H^6 of pyrimidine ring); 11.94, br. s, 1H (-$NHSO_2$-). Anal. Calcd. for $C_{23}H_{24}N_6O_4S$: C, 57.49; H, 5.03; N, 17.49; S, 6.67. Found: C, 57.50; H, 5.00; N, 17.27; S, 6.66.

4-N^1-(Pyrimidin-2-yl)sulfonamido-4′-[N-*n*-butyl-N-(2-methacryloyloxy)ethyl]aminoazoben-zene (**13**) (86%); m.p. 192–194°C; ^{1}H NMR (DMSO-d_6, TMS): 0.95, t, ^{3}J = 7.2 Hz, 3H (CH_3CCCN-); 1.37, m, 2H (CCH_2CCN-); 1.58, m, 2H ($CCCH_2$CN-); 1.88, s, 3H (-(CH_3)C=C); 3.48, t, ^{3}J = 7.2 Hz, 2H ($CCCCH_2$N-); 3.81, t, ^{3}J = 5.1 Hz, 2H (-$OCCH_2$N-); 4.33, t, ^{3}J = 5.1 Hz, 2H (-OCH_2CN-); 5.70, s, 1H (-(C)C=CH_{trans}); 6.03, s, 1H (-(C)C=C_{cis}); 6.94, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* amino group of aminophenyl ring); 7.09, t, ^{3}J = 4.9 Hz, 1H (H^5 of pyrimidine ring); 7.82, d, ^{3}J = 9.1 Hz, 2H (*ortho* protons *vs.* azo group of aminophenyl ring); 7.91, d, ^{3}J = 8.5 Hz, 2H (*ortho* protons *vs.* sulfonamide group of sulfonamidophenyl ring); 8.15, d, ^{3}J = 8.5 Hz, 2H (*ortho* portons *vs.* azo group of sulfonamidophenyl ring); 8.55, d, ^{3}J = 4.9 Hz, 2H (H^4, H^6 of pyrimidine ring); 11.98, br. s, 1H (-$NHSO_2$-). Anal. Calcd. for $C_{26}H_{30}N_6O_4S$: C, 59.75; H, 5.79; N, 16.08; S, 6.13. Found: C, 59.47; H, 5.71; N, 15.88; S, 5.98.

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