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Synthesis of *bis*-azobenzene derivatives with reactive bromohexyl unit and carboxylic acid group based on Disperse Yellow 7

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RESEARCH ARTICLE

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ABSTRACT

In this work, two types of azobenzene derivatives based on Disperse Yellow 7 (DY7, 4-[4-(phenylazo)phenylazo]-*o*-cresol) were synthesized, which are *bis*-azobenzenes bearing flexible functional 6-bromohexyl chain or carboxylic acid moiety. The first one was synthesized by alkylation of DY7 with an excess of 1,6-dibromohexane in the presence of a mild base (K_2CO_3). The second one (azo dye with carboxylic acid functionality) was obtained by the alkaline hydrolysis of the ester bond of the newly obtained DY7 derivative with the ethoxycarbonyl group. The synthesized compounds were characterized by different spectral analytical techniques such as ^{1}H NMR, ^{13}C NMR, FT-IR, and UV-Vis. They can be employed for the synthesis of a wide variety of azo-based materials, which may be suitable for photochromic systems and molecular electronics applications.

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1. Introduction

Azobenzene-based compounds have been targeted as crucial building blocks of numerous functional smart materials such as photoresponsive molecular switches, molecular shuttles, data storage devices, sensors, nonlinear optical systems, and liquid crystals [1-5]. Azobenzenes (AB) are switchable compounds that exhibit reversible *E-Z* (*trans-cis*) photoisomerization. Photoisomerization from a *cis-* (*Z-form*) to a *trans-* (*E-form*) conformation is reversible by photochemical and thermal pathways [6,7]. It is essential that the isomerization of azobenzene units proceeds with a large structural change that affects the dipole moment and geometry (Figure 1a). Thus, azobenzene derivatives can exhibit a photomechanical effect in bulk materials [8-11].

Note that most of the reported azobenzene-containing compounds have only non-conjugated AB units (mono-AB). The different AB derivatives can exist in *Z*-state for many hours in the dark [6,12]. At the same time, irradiation of photochromic components containing two (or more) AB units leads to a mixture of three isomers *E/E*, *E/Z*, and *Z/Z* at the photostationary state (Figure 1b) [13,14]. Next, systems with multi-AB groups back-isomerize instantaneously [15].

Typically, the organic azo-based chromophores have been incorporated into a polymer backbone (via both covalent and noncovalent binding), the polyhedral oligomeric silsesquioxane core, and others silica-based particles that have better processability and optical properties (i.e. reduced chromophore aggregation) than small molecules [3,12,16-18]. Importantly, that besides photoisomerization, the formation of surface relief gratings in the films, photoinduced orientation, photoactuation are also possible in AB-functionalized polymers [12]. By increasing the number of photochromic groups in *bis*-AB, such as Disperse Yellow 7 (DY7, 4-[4-(phenylazo)phenylazo]-*o*-cresol), it is possible to achieve higher and more stable photoinduced birefringence than the corresponding mono-azo-functionalized systems [15,19,20]. Thus, *bis*-AB-based materials are preferable for photoorientation. Moreover, a high degree of conjugation in para-substituted *bis*-AB allows conductance, which can be precisely regulated by fast and reversible

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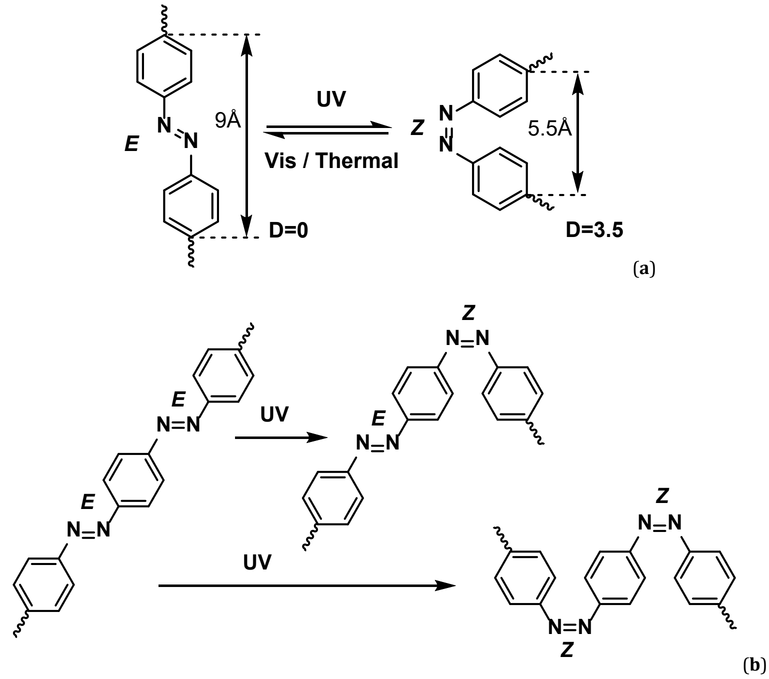


Figure 1. Photochemical isomerization of mono-azobenzene (**a**) and *bis*-azobenzene (**b**) with conjugated AB units derivatives. The *trans* (*E*)- and *cis* (*Z*)-forms are very different in shape, size, and polarity (*D* - Dipole moment).

light-induced switching [21]. Next, liquid crystal molecules were prepared based on *bis*-AB having alkyl moieties [22] as well as, for example, *bis*-AB dyes were applied as cross-linkers for photocontrol of peptide structure [23]. Thus, the synthesis of new chromophores containing π-conjugated *para*-azobenzene units and an appropriate functional group for further synthetic manipulation (attachment/functionalization) is crucial for the development of new azo-based structures with extensive and versatile applications. In this context, flexible bromohexyl unit and highly polar carboxylic acid group are promising functional moieties. Since bromoalkylated azo dyes, these compounds are widely used for directly incorporating azo chromophore groups into the side chains of polymers [24] or as substrates for subsequent organic transformation [25]. The carboxylic functions are the principal groups employed in organic building blocks [26]. The presence of COOH groups not only allows further conjugation of the corresponding dyes with different scaffolds, but they, thanks to their strong and highly directional H-bonding, are extremely important in the supramolecular chemistry [27]. The supramolecular strategy may simplify the route for the preparation of azo materials since such materials can be prepared by non-covalently introducing AB groups into the medium [12].

Therefore, the development of synthetic routes for the preparation of new reactive *bis*-AB chromophores is significant importance. To the best of our knowledge, the *bis*-azobenzene derivatives based on DY7, containing a flexible functional 6-bromohexyl chain or aliphatic carboxylic acid moiety have not been reported yet. Hence, the current work represents an approach to the design of a reactive *bis*-azobenzene dye possessing a flexible alkyl chain with reactive bromine as well as *bis*-azobenzene containing a functional acetic acid fragment.

2. Experimental

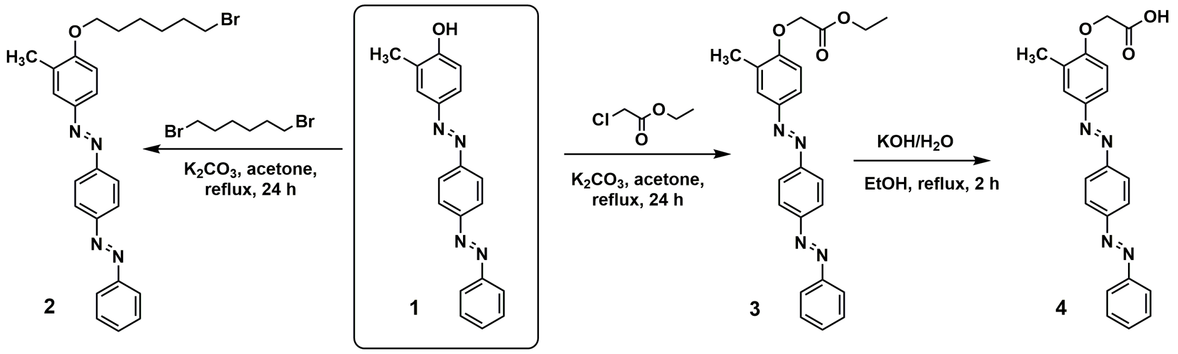
2.1. Materials and measurements

Disperse Yellow 7 (95%), 1,6-dibromohexane (96%), ethyl chloroacetate (99%) were purchased from Sigma-Aldrich and used as received. The other reagents and solvents were purified by well-established techniques. NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer at room temperature in deuterated solvents CDCl$_3$ or DMSO-d_6. Chemical shifts are reported relative to chloroform (δ = 7.25 ppm for ^{1}H NMR and δ = 77.00 ppm for ^{13}C NMR) or DMSO-d_6 (δ = 2.50 ppm for ^{1}H NMR). Fourier transform infrared (FT-IR) spectra (4000-400 cm^{-1}) of synthesized compounds were recorded on a TENSOR 37 spectrometer using KBr pellets. The UV/Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer.

2.2. Azo dyes synthesis

2.2.1. Synthesis of 1-(4-((6-bromohexyl)oxy)-3-methyl phenyl)-2-(4-(phenyldiazenyl)phenyl)diazene (2)

A 50 cm^3 three-necked flask equipped with an oil bath, a mechanical stirrer, a cold-water condenser, an argon inlet/outlet, and a thermometer was charged with compound DY7 (Dye 1, 4-[4-(phenylazo)phenylazo]-*o*-cresol) (1.00 g, 3.16 mmol), 6-dibromohexane (3.85 g, 15.8 mmol), potassium carbonate (0.66 g, 4.74 mmol) and acetone (15 cm^3). The mixture was stirred and heated under reflux for 24 h. Then, the mixture was cooled to room temperature and the inorganic salt was removed via filtration. The filtrate poured dropwise into ice water to precipitate the product. The resulting orange solid was purified by precipitation from chloroform solution into hexane (Scheme 1). Yield: 75%. M.p.: 89-92 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, δ, ppm): 1.55 (s, 4H, -CH$_2$-), 1.87-1.93 (m, 4H, -CH$_2$-), 2.31 (s, 3H, -CH$_3$), 3.43 (t, 2H, J_1 = 6.7, J_2 = 7.1 Hz, -CH$_2$-), 4.07 (t, 2H, J_1 = 5.8, J_2 = 6.2 Hz, -CH$_2$-), 6.93 (d, 1H, J = 8.3 Hz, Ph), 7.48-7.55 (m, 3H, Ph), 7.81-7.84 (m, 2H, Ph), 7.95 (d, 2H, J = 8.3 Hz, Ph), 8.00-8.06 (m, 4H, Ph). ^{13}C NMR (CDCl$_3$, 125 MHz, δ, ppm): 16.41 (-CH$_3$), 25.76, 28.17, 29.09 (-CH$_2$-), 38.93 (-CH$_2$Br), 68.06 (-OCH$_2$-), 110.46, 122.98, 123.32, 123.73, 123.80, 124.57 (Ar-C),127.63 (C-CH$_3$), 129.09, 131.21 (Ar-C), 146.50, 152.70, 153.13, 153.98 (Ar-C-N), 160.26 (Ar-C-O).



Scheme 1

FT-IR (KBr, ν, cm^{-1}): 2850-3050 (CH), 1601, 1499 (C=C$_{arom}$), 1250 (C-O-C), 1144 (C-O), 648 (C-Br). UV/vis (CHCl$_3$, λ_{max}, nm): 385.

2.2.2. Synthesis of ethyl 2-(2-methyl-4-((4-(phenyldiazenyl) phenyl)diazenyl)phenoxy)acetate (3)

A 50 cm^3 three-necked flask equipped with an oil bath, a mechanical stirrer, a cold-water condenser, an argon inlet/outlet, and a thermometer was charged with dye **1** (1.00 g, 3.16 mmol), ethyl chloroacetate (0.58 g, 4.74 mmol), potassium carbonate (0.66 g, 4.74 mmol) and acetone (12 cm^3). The mixture was stirred and heated under reflux for 24 h and filtered. The filtrate was poured into ice-cold water. The separated ester was extracted with ether and dried over anhydrous magnesium sulfate. Excess ether was removed by distillation, and the remaining crude ester was used to prepare the corresponding carboxylic acid **4** (Scheme 1). Yield: 80%. M.p.: 139-142 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, δ, ppm): 1.31 (t, 3H, -CH$_3$), 2.39 (s, 3H, Ar-CH$_3$), 4.29 (q, 2H, J= 7.1 Hz, -COOCH$_2$-), 4.73 (s, 2H, -OCH$_2$CO-), 6.82 (d, 1H, J = 7.9 Hz, Ar-H), 7.49-7.55 (m, 3H, Ar-H), 7.79-7.82 (m, 2H, Ar-H), 7.95 (d, 2H, J = 7.5 Hz, Ar-H), 8.00-8.06 (m, 4H, Ph). FT-IR (KBr, ν, cm^{-1}): 2850-3060 (CH), 1728 (C=O), 1597, 1491 (C=C$_{arom}$), 1248 (C-O-C), 1109 (C-O), 1032 (O-C-C). UV/vis (CHCl$_3$, λ_{max}, nm): 387.

2.2.3. Synthesis of 2-(2-methyl-4-((4-(phenyldiazenyl) phenyl)diazenyl)phenoxy)acetic acid (4)

A mixture of dye **3** (1.00 g, 2.48 mmol), 20 wt% KOH aqueous solution (15 cm^3) and ethanol (20 cm^3) was reflux for 2 h. The mixture was then poured into HCl (1 N, 50 cm^3) with stirring. The product was filtered, then washed with water and purified by boiling out with ethanol (Scheme 1). Yield: 90%. M.p.: >200 °C. ^{1}H NMR (DMSO-d_6, 500 MHz, δ, ppm): 2.30 (s, 3H, Ar-CH$_3$), 4.85 (s, 2H, -CH$_2$-), 7.06 (d, 1H, J = 7.8 Hz, Ar-H), 7.59-7.62 (m, 3H, Ar-H), 7.80-7.82 (m, 2H, Ar-H), 7.93 (d, 2H, J = 6.2 Hz, Ar-H), 8.02-8.08 (m, 4H, Ar-H). FT-IR (KBr, ν, cm^{-1}): 2500-3300 (OH), 2850-3060 (CH), 1745 (C=O), 1597, 1489 (C=C$_{arom}$), 1248 (C-O-C), 1113 (C-O). UV/vis (CHCl$_3$, λ_{max}, nm): 387.

3. Results and discussion

A broader application of *bis*-AB-functionalized materials depends on the successful synthesis of new *bis*-AB-based chromophores with highly reactive groups. For the synthesis of *bis*-azo-containing dyes with reactive bromohexyl unit and carboxylic acid group, commercially available DY7 (dye **1**) was chosen as the initial precursor (Scheme 1).

The attachment of the bromohexyl substituent into the structure of DY7 was achieved by the reaction of a 5-fold excess of 1,6-dibromohexane with dye **1** in the presence of K$_2$CO$_3$ in acetone. The excess of the 1,6-dibromohexane was used to ensure the formation of the mono-substitution product **2** [28]. The developed method of synthesis of dye **4** containing the carboxylic group is based on etherification of compound **1** with ethyl chloroacetate followed by the alkaline hydrolysis of the ester group of the newly obtained scaffold **3**. The hydrolysis was performed in ethyl alcohol-water solvent. Importantly, that compounds with aliphatic carboxylic acid-based units are more reactive than compounds with aromatic carboxylic acid-based units [29]. This might facilitate the later conjugation of the obtained dye **4** with polymers or other scaffolds in subsequent applications.

The yield of products was 75-90%. The *bis*-AB dyes **2**, **3** and **4** are orange or brown in color. The dyes **2** and **3** are readily soluble in common organic solvents such as CHCl$_3$, tetrahydrofuran, dimethylformamide (DMF), dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO). The azo dye **4**, due to the presence in its structure of the highly polar carboxylic acid group, is soluble only in polar aprotic solvents such as DMF, DMAc and DMSO. The ^{1}H NMR spectra of the synthesized dyes **2**, **3**, and **4** correspond to the proposed structures (Figures 2-4).

The conjugation of bromohexyl substituent to DY7 was confirmed by the presence of both sets of signals from the corresponding AB fragment (the resonance peaks from aromatic protons in the range δ 6.9-8.0 ppm as well as a singlet at δ 2.31 ppm for the methyl group) and alkyl unit (four methylene proton signals in the range of δ 1.5 to 4.1 ppm) (Figure 2). Note that the signal from central -CH$_2$- (protons *a* in Figure 2) at δ ~1.55 ppm of the alkyl group overlaps with the signal given by the trace water in deuterated chloroform. Next, the ethyl proton signals at δ 1.31 and 4.28 ppm (Figure 3), originating from the ethoxycarbonyl group of dye **3**, fully disappeared after alkaline hydrolysis of the ester bond in the ^{1}H NMR spectrum of carboxylic acid derivative **4**, as shown in Figure 4. The COOH signal of dye **4** is not seen because of the exchange of the OH protons with at least protons of the residual water in DMSO-d_6 solution. Similar to the ^{1}H NMR spectrum of dye **2**, peaks due to the AB fragment of DY7 were also observed in the ^{1}H NMR spectra of dyes **3** and **4**. Overall, the chemical shifts and peak integrations of all the protons in the azo chromophores are in excellent agreement with their expected structures.

The excellent solubility in the organic solvents of azo dye **2** with alkyl chain and reactive bromine makes it possible additionally to investigate the structure of the dye by ^{13}C NMR spectroscopy (Figure 5). The corresponding ^{13}C NMR spectrum of *bis*-AB **2** indicated that the hydrogen atom from the hydroxyl group of the initial dye **1** was substituted by the alkyl chain such as the 6-bromhexyl unit.

The structures of the prepared *bis*-AB dyes were further confirmed by FT-IR spectroscopy (Figure 6).

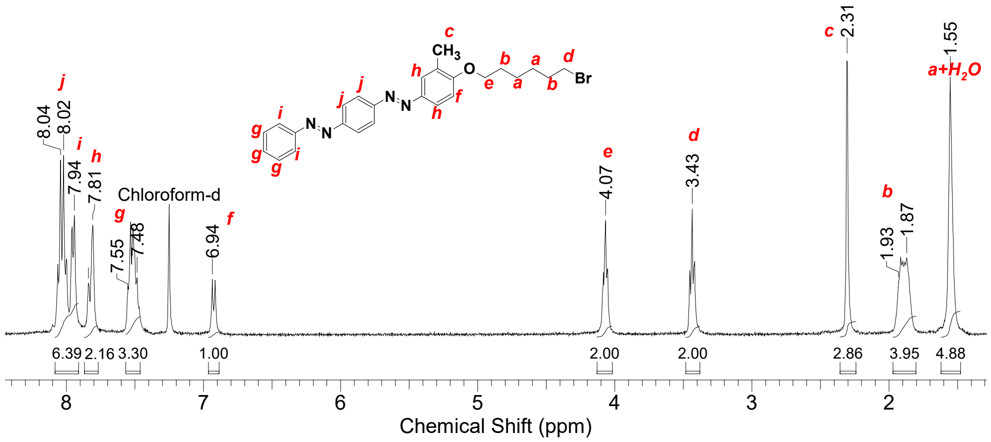


Figure 2. ^{1}H NMR spectrum of azo dye **2**.

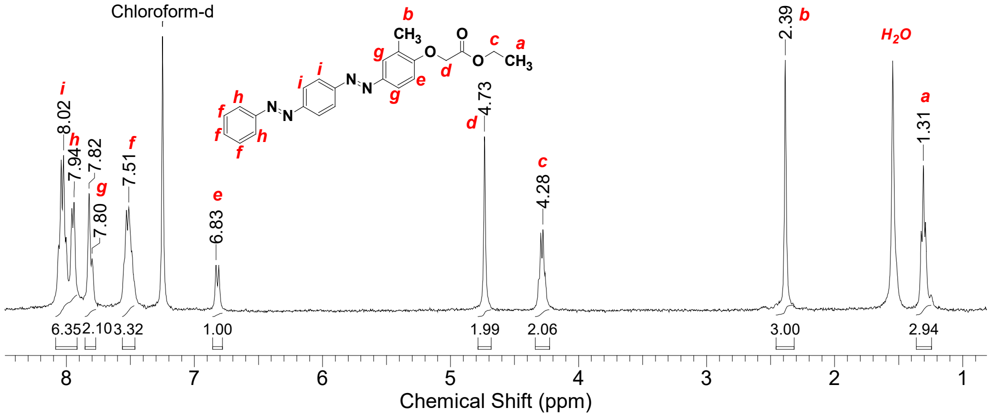


Figure 3. ^{1}H NMR spectrum of azo dye **3**.

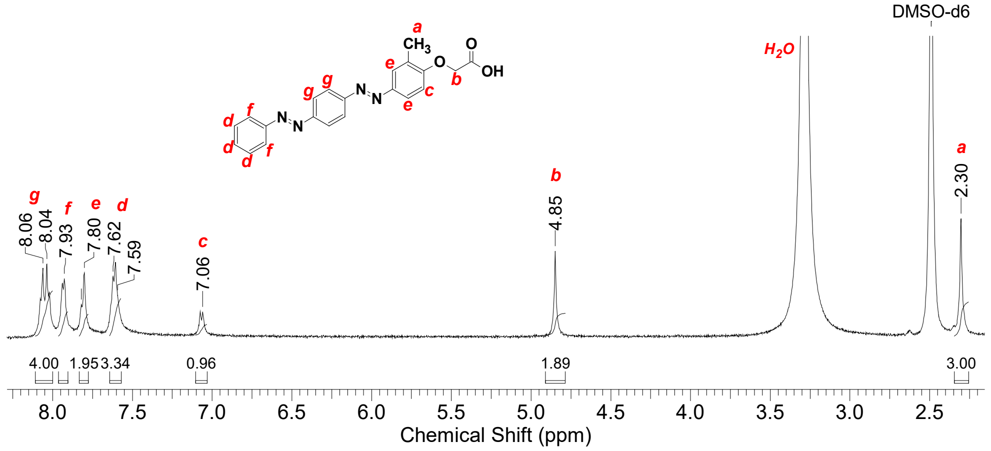


Figure 4. ^{1}H NMR spectrum of azo dye **4**.

The FT-IR spectra of all dyes show the characteristic absorptions in the regions 1248-1250, 1489-1601 (at least two bands in each spectrum in this region) and 2800-3100 cm^{-1}, which correspond to C-O-C, C=C$_{\text{arom}}$ and CH groups [30,31]. The absence of intense bands of ethyl groups connected with oxygen (-O-C-C) of the ester intermediate **3** in the FT-IR spectrum of the obtained dye **4** at the 1032 cm^{-1} indicates that these groups have been removed during the hydrolysis reaction. According to Figure 6, the comparison between the two spectra of dye **3** and dye **4** shows a chemical shift at a wavelength of 1728 cm^{-1}, which refers to C=O group in ester-based dye **3** to a wavelength of 1745 cm^{-1} of C=O group in acid-based dye **4**. The FT-IR spectrum of dye **4** also has a very broadband with a developed structure (due to the overlap with CH absorption bands) in the region 3300-2500 cm^{-1}. This band is associated with OH stretching vibrations of COOH group.

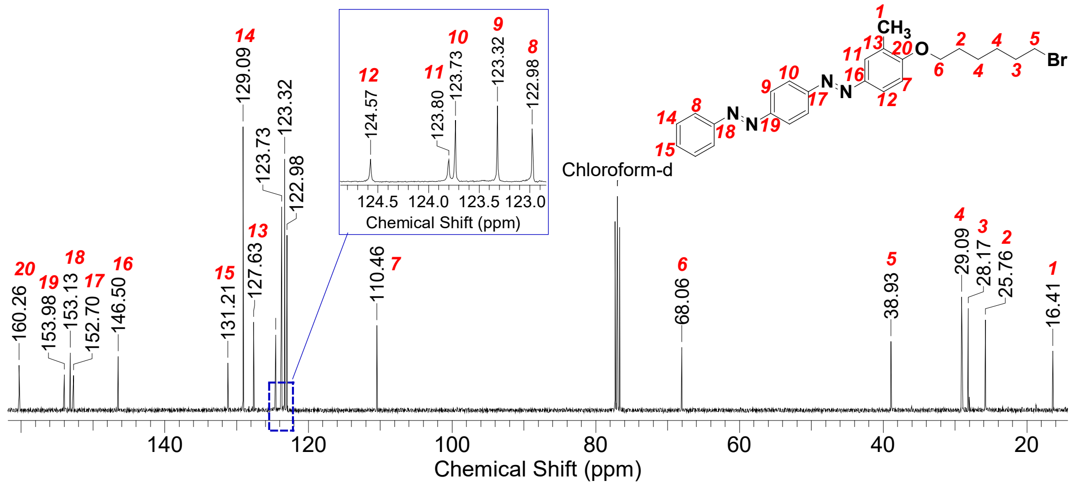


Figure 5. ^{13}C NMR spectrum of azo dye **2**.

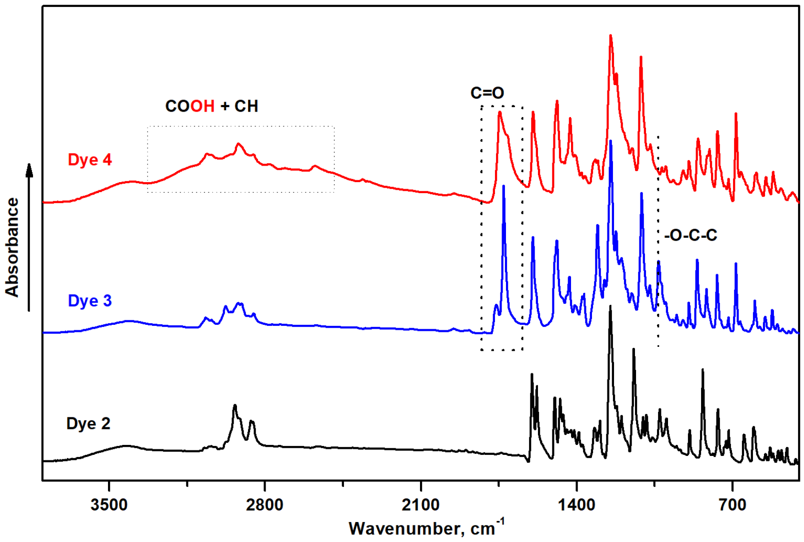


Figure 6. FT-IR spectra of azo dyes **2**, **3** and **4**.

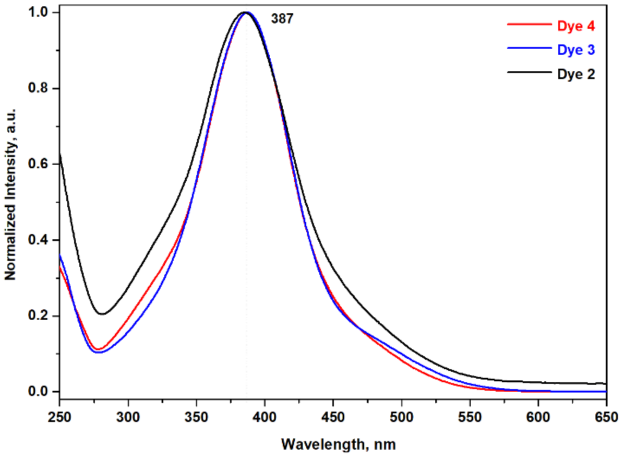


Figure 7. UV/Vis absorbance spectra of azo dyes **2**, **3** and **4** in $CHCl_3$.

The great breadth of this band resulting from the intramolecular and intermolecular hydrogen bond interactions of dye **4** with carboxylic acid functionality [32].

Figure 7 presents the UV-visible spectra of dyes **2**, **3**, and **4** in $CHCl_3$. The spectra of these *bis*-AB chromophores show absorption maxima, corresponding to the π-π* transition, at about 387 nm, being red-shifted ~40 nm as compared to the absorption maximum of mono-azobenzene dyes with similar structures. Thus, mainly, mono-azobenzene dyes have a typical azobenzene absorbance with a strong π-π* band at 348 nm and a weaker n-π* transition at around 430 nm [25,33]. The n-π* transition for azo dyes **2**, **3**, and **4** appears as a shoulder of a main peak at around 470 nm (Figure 7).

Overall, the structural design of the *bis*-azobenzenes **3** and **4** extends the possibility of using such compounds to build up functional azobenzene-based polymer systems. The detailed synthesis and properties of different azo-containing systems based on the obtained *bis*-AB chromophores will be reported in due course.

4. Conclusion

In summary, the Br-terminated *bis*-azobenzene dyes comprising flexible hexenyloxy fragments as well as *bis*-azobenzene with COOH functionality were synthesized. For the synthesis of dye with the carboxylic acid group, *bis*-azobenzene intermediate with the ethoxycarbonyl moieties was firstly obtained. All dyes were synthesized from commercially available Disperse Yellow 7 possessing the π-conjugation between the two AB units. The structures of the synthesized compounds were indicated by FT-IR, ^{1}H and ^{13}C NMR, and UV/vis spectrometry techniques. The presence of functional groups and *bis*-AB functionality in such chromophores opens the possibility of their further chemical modification and their use in macromolecular and supramolecular chemistry for the synthesis of a wide range of new photochromic materials with targeted optical properties.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
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