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Synthesis and optical properties of new isomeric azo-containing bis(2-hydroxybenzaldehydes) with tetrafluorobenzene units

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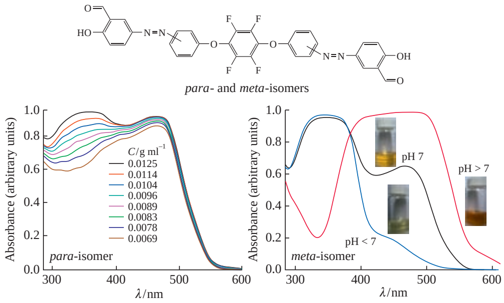
By means of diazotization of isomeric diamines containing tetrafluorobenzene units and the further azo-coupling of the obtained diazonium salts with 2-hydroxybenzaldehyde, new bis-bifunctional azo-monomers have been synthesized. Photo-optical and thermal properties of the synthesized compounds have been estimated.



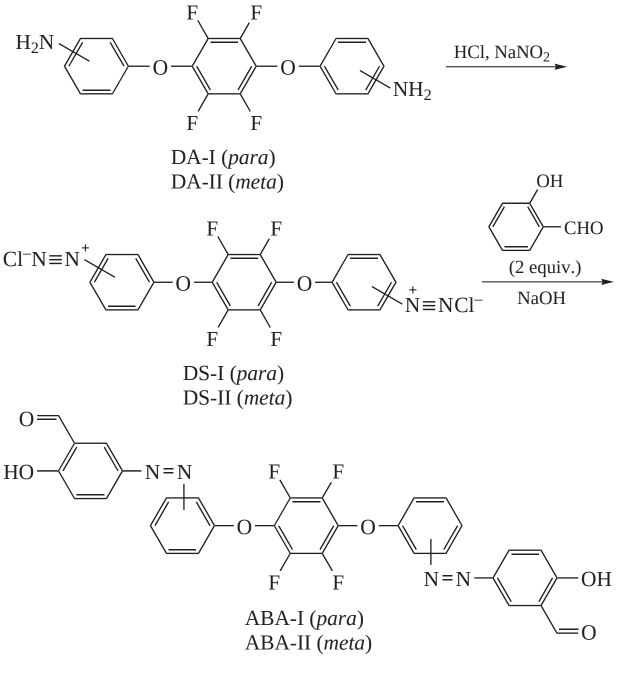
Azo compounds are capable of changing their properties upon UV or visible spectrum impact on an azo group.[1,2] The ability of the azo groups to transfer a charge from an electron-donating group to an electron-withdrawing one is a principal factor of practical application of these compounds, *e.g.*, in optical data storage devices, switches, holographic gratings, materials with nonlinear optical and liquid crystal properties.[3–9]

Azo-containing polymers (APs) based on azo-containing monomers find broad applications.[10,11] In these polymers, azo groups can be located both in a side[12,13] and in a backbone chains.[7,14] Notwithstanding the considerable quantity of azo-containing monomers described, all of them are bifunctional, as a rule.[15] This fact restricts the possibilities of designing APs that possess the required properties. The synthesis of the azo-containing bis-bifunctional (*i.e.* tetrafunctional) monomers would allow one to expand significantly the AP range. This can make it possible to adjust their properties by means of AP modification at the expense of the second functional group. Hence, the synthesis of azo monomers containing aldehyde groups and *ortho*-oriented hydroxy groups is a promising direction in macromolecular chemistry. Moreover, such functional group combination within a monomer can provide polymers capable of forming metal complexes and undergoing tautomerization.[16,17]

It is worth to mention, that APs have some disadvantages, namely, poor solubility and azo chromophore aggregation, which exerts a negative impact on their photo-optical properties.[18] One of the ways to overcome these problems is incorporation of isomeric[19] or perfluoroaromatic units into a monomer (and a polymer thereafter).[20] Fluorinated APs are characterised by the improved optical, electro-optical properties and appropriate solubility, along with the high thermostability.[21] By means of isomeric component variation one can control electro-conformational structure of the polymer chain, which is responsible for polymer solubility and azo chromophore aggregation.[15]

The purpose of the current work was to obtain new monomers, isomeric azo-containing bis(2-hydroxybenzaldehydes) (ABAs) with tetrafluorobenzene units, and to study their physicochemical and optical properties. In the literature there is no information on ABAs bearing fluorinated aromatic units, though diazotisation of perfluoroaromatic diamines is well known.[15] Herein, we synthesized isomeric ABAs with tetrafluorobenzene units (ABA-I and ABA-II) based on diazotisation of fluorine-containing diamines DA-I and DA-II with the following azo-coupling of diazonium salts DS-I and DS-II with salicylaldehyde (Scheme 1).

The obtained in high yields monomers ABA-I and ABA-II are yellow powders (for the experimental details, see Online Supplementary Materials). The solubility test has shown that ABA-I and ABA-II are dissolved well in the highly polar aprotic solvents such as DMF, *N*,*N*-dimethylacetamide (DMA) and



Scheme 1

DMSO. It is worth to mention that the non-fluorinated *para*-connected ABA analogue, synthesized for the first time, is only partially dissolved in the above solvents (see Online Supplementary Materials). Therefore, nonfluorinated *para*-linked azobenzene derivative was not studied further in this work.

The structures of the synthesized compounds ABA-I and ABA-II have been proved by ^{1}H, ^{19}F and ^{13}C NMR, FTIR and UV spectroscopy. In the ^{1}H NMR spectra, two singlets at ~11.57 and ~10.35 ppm correspond to pairs of protons for the hydroxyl and aldehyde groups, respectively. In the ^{13}C NMR spectra, signals at 190.39–196.60 ppm belong to aldehyde group, and those at 163.65–169.80 ppm relate to carbon atoms connected to the hydroxyl groups. ^{19}F NMR spectra contain one singlet from 4 equivalent fluorine atoms.

FTIR spectra of compounds ABA-I and ABA-II manifest stretching vibrations of the hydroxyl groups at 3600–3100 cm^{-1} and a band at 1668–1662 cm^{-1} characteristic of the aldehyde group. The other bands at 1508–1492 and 1026–989 cm^{-1} are attributed to C=C aromatic ring group and C–F group, respectively.

The UV spectra of ABA-I and ABA-II in DMA contain two absorption maxima at 347–356 and 464–467 nm. The first maximum points out the π–π* transition of the azobenzene unit.[2] The second one, most likely, testifies to the presence of hydrazo form and hydrogen-bonded complex, which are formed in highly polar solvents (Figure 1).[22] Interestingly, the UV absorption intensity of ABA-I at 464–467 nm is much higher than that of ABA-II.

Hydroxy azo-containing compounds are known of performing tautomeric transitions from the more stable azo form into the less stable hydrazo one.[23] The choice of a solvent, the acidity of a medium, the type of a substituent and its position in regard to the azo group play a significant role in transferring a charge and, correspondingly, establishing the equilibrium between tautomeric forms.[17] Herewith, the equilibrium shift to one of the tautomeric forms is accompanied with the absorption maximum band shift, which affects the colour and chemical properties of azo compounds.[24]

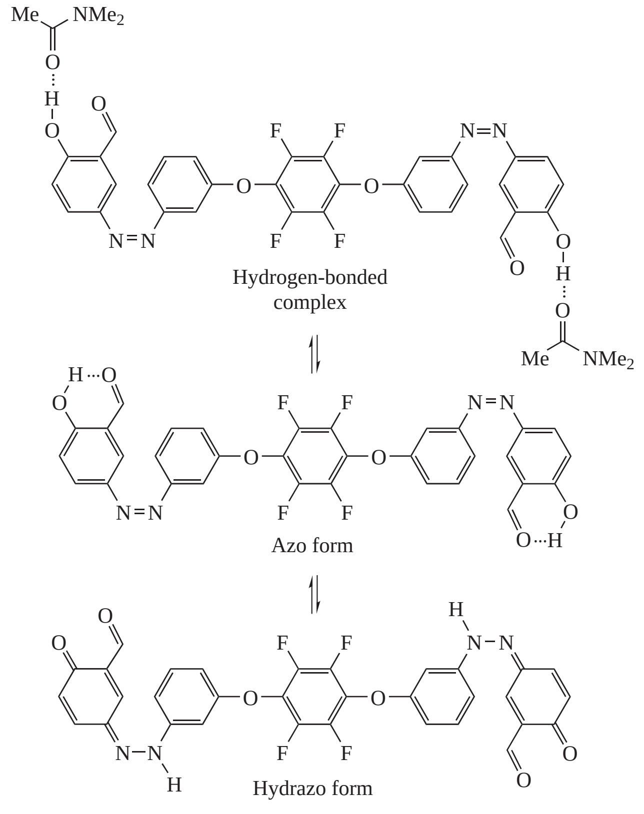


Figure 1 Formation of the hydrazo form and hydrogen-bonded complex of ABA-II in DMA.

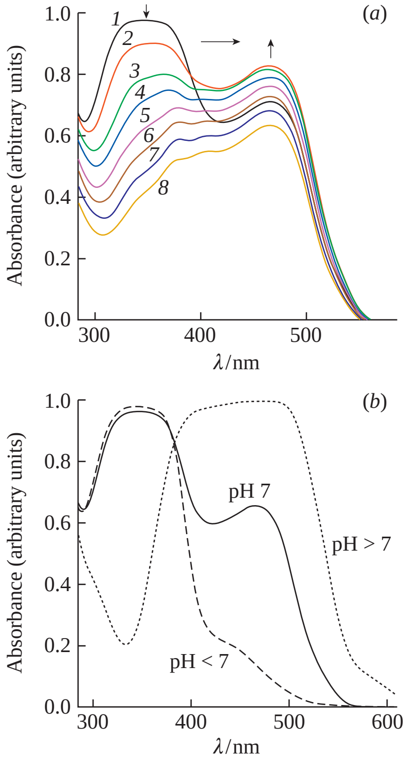


Figure 2 UV-VIS spectra of ABA-II at (*a*) concentrations of (*1*) 0.0125, (*2*) 0.0104, (*3*) 0.0083, (*4*) 0.0073, (*5*) 0.0062, (*6*) 0.0054, (*7*) 0.0046 and (*8*) 0.0040 g cm^{-3} and (*b*) different pH values in DMA.

The presence of tautomeric transitions for the synthesized ABA monomers is confirmed by the changes in UV absorption maxima when their concentration in DMA solution is reduced.[14,22] For instance, a decrease in concentration of ABA-II leads to the equilibrium shift towards hydrazo form and hydrogen-bonded complex. As a result, the UV absorption maximum shifts to the long-wavelength area [Figure 2(*a*)]. The hydrogen-bonded complex absorption maximum shifts bathochromically even greater in comparison with the hydrazo form.[25] The analogous effect is observed for ABA-I (Figure S6, see Online Supplementary Materials).

Variation in the pH values of the ABA-I and ABA-II solutions in DMA affects the UV absorption maximum. In alkaline medium, the UV absorption maxima shift to the red region (470–476 nm) and the solutions acquire a saturated yellow colour. On the contrary, in acidic medium, the UV absorption maximum shifts to the short-wavelength area (344–347 nm) and the solution becomes colourless [Figure 2(*b*)]. Such a way of the UV absorption maxima distribution is connected with the formation of the ionic form in the alkaline medium and azo form in the acidic one (Figure S8).[22,25]

The ^{1}H NMR spectroscopic data additionally confirm the ability of ABA to undergo tautomerism. No characteristic signal of the hydroxyl group proton of ABA-I is observed in neutral medium (DMSO-d_6), which testifies to the formation of a solvate complex between ABA-I and a solvent. In acidic medium, this singlet appears at 11.57 nm, which indicates the equilibrium shift towards the azo form (Figure S9).

Investigation of the *trans–cis* photoisomerization of ABA-I and ABA-II in DMA has shown that their UV spectra do not change after the UV irradiation. Such a phenomenon can be caused by the very rapid *cis–trans* isomerization of bis-azobenzene dyes.[26]

Nevertheless, the capacity of the obtained ABA-I and ABA-II for reversible intramolecular charge transfer under the impact of external factors (solution polarity and concentration, pH of a medium) provides opportunities for using them as molecular switches, indicators of the pH of a medium, anionic sensors and antibacterial drugs.[5,17,23,27,28]

According to the TGA data, the decomposition temperature of ABA-I (265 °C) and ABA-II (300 °C), corresponding to a mass loss of 5%, conforms to the azo group decomposition. Due to these properties the above monomers can be used in the high-temperature polycondensation reactions. Rapid mass loss of ABA-I and ABA-II occurs on heating above 370 °C, as a result of the aromatic ether bonds breaking (Figure S10).[29]

In conclusion, the novel herein obtained azo-containing bis(2-hydroxybenzaldehydes) with tetrafluorobenzene units turned to be well soluble in aprotic polar solvents. Their properties make them promising for design of other analogous monomers, which can find application in dyes manufacturing, optoelectronics, construction of logical schemes, optical data storage devices, as catalysts and chemical sensors.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.11.020.

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