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Synthesis and characteristics of azo chromophores for nonlinear-optical application

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Abstract

Synthesis and characterization of three incombustible and thermostable chromophores, 1,1-dichloro-2,2-bis(4-hydroxyphenylo)-ethane derivatives were done. These compounds contain azo bonds with substituted thiazole ring as side groups. The static hyperpolarizability β_0 and second-order hyperpolarizability γ_0 were calculated. The structures of obtained monomers were confirmed by elemental analysis, infrared, ^{1}H NMR and ultraviolet spectroscopies. Design of nonlinear-optical polymers with included chromophores was also performed.

Keywords: Azo chromophores; NLO; Hyperpolarizability

1. Introduction

There are no literature reports about chromophores which are products of chlorobisphenole II (1,1-dichloro-2,2-bis(4-hydroxyphenylo)ethane) and derivatives of 2-aminothiazole or 2-aminobenzothiazole coupling as special monomers for nonlinear-optical polymer synthesis. However, the literature data indicate that heterocyclic systems, included in chromophore structures, have advantageous influence on NLO properties of polymers [1–3]. It has been shown that very large nonlinearity can be achieved by employing heteroatomic rings, such as substituted 1,3-azoles as conjugating units since they have lower aromatic stabilization energy upon charge separation than do benzene ring [4].

It is well known that polyarylates or copolyarylates obtained by polycondensation with interfacial catalyst of bisphenol A, izo- and terephtaloyl chlorides show excellent mechanical and physico-chemical properties. Additionally, incorporating halogens into polymer chain result in reduction of combustibility and increase in thermostability of polymer. Hence polyarylates with included 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethane due to presence in macromolecule chlorine atom become incombustible [5].

In this paper, synthesis and characteristics of three azo chromophores (Fig. 1) containing 6-methylbenzothiazole, benzothiazole or 5-nitrothiazole ring are described. These compounds are potential candidates for nonlinear-optical polyarylates syntheses. For these compounds values of first- and second-order hyperpolarizabilities were determined. The full characterization of the obtained compounds was also done.

2. Experimental

These compounds were synthesized by the following method. The 14.4 g 2-amino-5-nitrothiazole (0.1 mol) was dissolved in 80 ml 6 N HCl. A rusty solution was cooled in the ice bath. Seven grams of $NaNO_2$ dissolved

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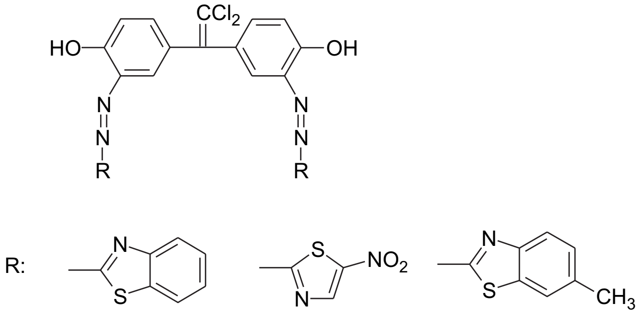

Fig. 1. The structure of chromophores.

in 4 ml H_2O was slowly added to cooled 2-amino-5-nitrothiazole solution with intense stirring. The mixture was cooled for 10 min. The diazonium salt solution was then slowly added to 14.34 g 1,1-dichloro-2,2,-bis-(4-hydroxy-phenyl)-ethene (0.051 mol) dissolved in 208 ml acetic acid. The solution color changed from rusty to red. Clear solution was cooled for 30 min, and then 100 g sodium acetate in 300 ml H_2O was added. 1,1-Dichloro-2,2-bis-[3-(5-nitrothiazolilo-2-azo)-4-hydroxy-phenylo]ethene (CHBISF **1**) precipitate we obtained was filtered, purified in $NaOH_{aq}$, acidified in 4 N HCl and crystallized from ethanol. The yield of the reaction was 58%. Anal. calcd for $C_{20}H_{14}Cl_2N_8S_2$ (%): C, 40.48; H, 1.70; Cl, 11.95; N, 18.82; S, 10.81; found: C, 40.20; H, 1.80; Cl, 11.60; N, 18.45; S, 10.62. ^{1}H NMR: $\delta = 5.50$ (bs, 2H, OH); 6.80–7.02 (m, 2H, Ar); 7.17–7.38 (m, 4H, Ar); 8.68 (s, 1H, $Ar_{thiazole}$); IR (KBr): 3432 cm^{-1}, 1608 cm^{-1}, 1505 cm^{-1}, 1433 cm^{-1}, 1224 cm^{-1}.

The 1,1-dichloro-2,2-bis-[3-(5-methylbenzothiazolyl-2-azo)-4-hydroxy-phenyl]ethene (CHBISF **2**) was prepared by the same procedure as that of CHBISF **1**, using 5.28 g (0.04 mol) 2-amino-5-methylobenzothiazole dissolved in the mixture of acids: 17 ml acetic acid and 10 ml concentrated sulfuric acid, 1.52 g $NaNO_2$ in 3 ml H_2O, 4.56 g (0.02 mol) 1,1-dichloro-2,2,-bis-(4-hydroxy-phenyl)-ethene in 81.3 ml acetic acid, 80 g sodium acetate in 240 ml H_2O. The precipitate was purified by dissolving in $NaOH_{aq}$ and acidified in 4 N HCl giving brown precipitate, then filtered, dried and crystallized from ethanol. The yield of the reaction was 56%. Anal. calcd for $C_{30}H_{20}Cl_2N_6S_2$ (%): C, 57.05; H, 3.19; Cl, 11.23; N, 13.31; S, 10.15; found: C, 57.20; H, 3.30; Cl, 11.10; N, 13.25; S, 10.25. ^{1}H NMR: $\delta = 2.52$ (s, 2H, CH_3); 5.0 (bs, 2H, OH); 6.80 (d, 2H, Ar, $J = 8.8$ Hz); 7.10–7.26 (m, 4H, Ar); 7.92 (s, 2H, $Ar_{thiazole}$), 8.10 (s, 2H, $Ar_{thiazole}$); IR (KBr): 3352 cm^{-1}, 1614 cm^{-1}, 1511 cm^{-1}, 1424 cm^{-1}, 1343 cm^{-1}, 1302 cm^{-1}.

The 1,1-dichloro-2,2,-bis-[3-(benzothiazolyl-2-azo)-4-hydroxy-phenyl]-ethene (CHBISF **3**) was prepared by the same procedure as that of CHBISF **1**, using 6.0 g (0.04 mol) 2-aminobenzothiazole dissolved in the mixture of acids: 18.7 ml acetic acid + 11 ml concentrated sulfuric acid. Dense rusty solution was obtained. After adding diazonium salt to 4.56 g (0.02 mol) 1,1-dichloro-2,2,-bis-(4-hydroxy-phenyl)-ethene solution in 81.3 ml acetic acid the solution color changed from dark violet to cherry. The obtained precipitate was filtered, purified in $NaOH_{aq}$, acidified in 4 N HCl and crystallized from ethanol. The yield of the reaction was 48%. Anal. calcd for $C_{28}H_{16}Cl_2N_6S_2$ (%): C, 55.72; H, 2.67; Cl, 11.75; N, 13.93; S, 10.63; found: C, 55.62; H, 2.74; Cl, 11.68; N, 13.85; S, 10.70. ^{1}H NMR: $\delta = 5.50$ (sb, 2H, OH); 6.80 (m, 2H, Ar); 7.10–7.19 (m, 4H, Ar); 7.47–7.53 (m, 4H, Ar); 7.88 (d, 2H, Ar, $J = 8.8$ Hz). IR (KBr): 3452 cm^{-1}, 1612 cm^{-1}, 1499 cm^{-1}, 1427 cm^{-1}, 1314 cm^{-1}, 1218 cm^{-1}, 1177 cm^{-1}.

3. Measurement

^{1}H NMR spectra were recorded on a Perkin Elmer (200 MHz) spectrometer in chloroform-d solution with TMS as internal standard. IR spectra were taken on a Carl Zeiss Jena M80 spectrometer. Melting points were not corrected. The reaction was controlled by TLC. A Milton Roy Spectronic Genesis 5 UV–vis spectrophotometer was used to record the UV–vis spectral data. Elemental analysis was carried out on an Eager 300 microelement analyzer. TGA and DTA were performed on a MOM derivatograph. A heating rate of 5 °C/min under argon was used.

4. Results and discussion

A possibility of the application of the chromophores as special monomers in nonlinear-optical polymer synthesis depends mainly on values of chromophore hyperpolarizability [6,7]. These values can be estimated by theoretical calculations. In our research the compounds' geometry optimization, hyperpolarizability and dipole moment calculation were performed using an HF method with 6–21 G basis set included in Gaussian 03 program. The values of first-order hyperpolarizability were evaluated from the following formula:

$$\beta_{av} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

where $\beta_i = \beta_{iii} + 1/3\left(\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji})\right)$, calculation of second-order hyperpolarizability was performed by MOPAC93 package utilizing semi-empirical PM3 method. Results are listed in Table 1.

Table 1
Results of theoretical calculations

Compound	Dipole moment (D)	β_0 (esu)	γ_0 (esu)
CHBISF **1**	6.11	1.76×10^{-29}	2.41×10^{-27}
CHBISF **2**	3.64	1.17×10^{-29}	4.32×10^{-27}
CHBISF **3**	2.70	5.41×10^{-30}	2.17×10^{-27}

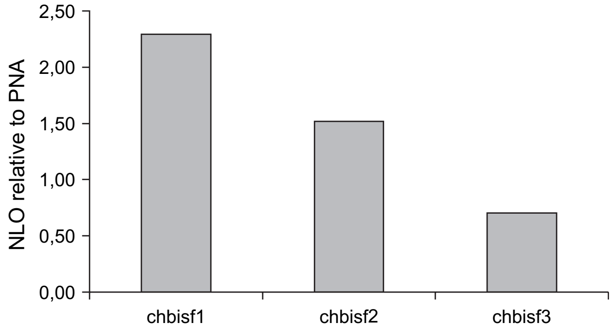

Fig. 2. First-order hyperpolarizability values in relation to *p*-nitroaniline.

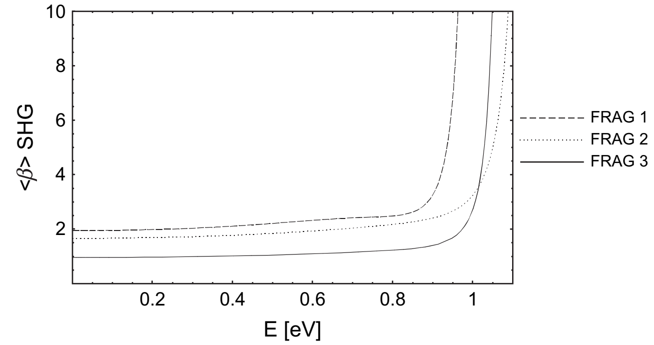

Fig. 4. Frequency dependent Kerr effect for polymer fragments.

As was expected the calculated first- and second-order hyperpolarizability values are larger for compounds with azo bond in comparison with compounds with azomethine bonds [8]. First-order hyperpolarizability (β_0) values for monomers described here lie in range from 5.41×10^{-30} to 1.77×10^{-29} and seem to be superior in comparison with the same values for *p*-nitroaniline (Fig. 2).

Exceptionally interesting seems to be monomer CHBISF **1**, which contains nitro group in position 5 of thiazole ring ($\beta_0 = 1.77 \times 10^{-29}$) and monomer CHBISF **2** ($\beta_0 = 1.17 \times 10^{-29}$), which contains benzothiazole ring with methyl group in position 5 of benzene ring. Data in Table 1 indicate that the presence of $-CH_3$ group increases first- and second-order hyperpolarizabilities. However, in both cases (CHBISF **1** and CHBISF **2**) values of first-order hyperpolarizability are lower than in case of CHBISF **3**, which include $-NO_2$ group. It should be expected that in case of copolyarylates, properties of obtained polymers may be exceptionally gainful. They are products of chlorobisphenole, special monomers, and izo- and terephthalic acid chlorides copolycondensation with interfacial catalysis, where double bonds conjugated system is ensured due to chlorobisphenole structure. The basic theory of non-linear-optical properties of Π-conjugated organic materials emphasizes that the conjugation length can enhance the electron delocalization in molecules, which are needed for large second hyperpolarizabilities γ [9].

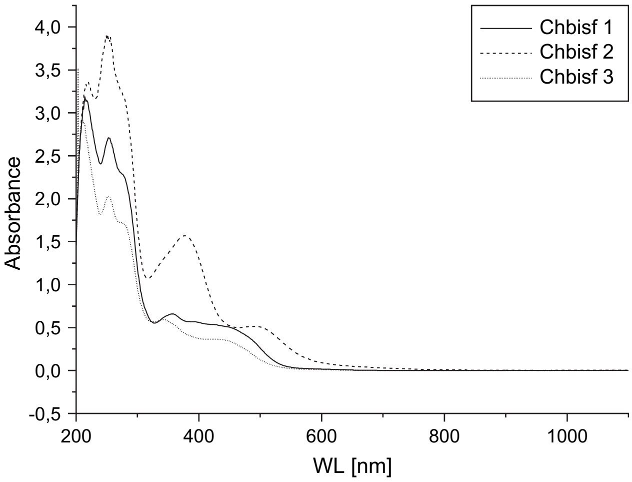

Fig. 5. The UV–vis spectra of chromophores.

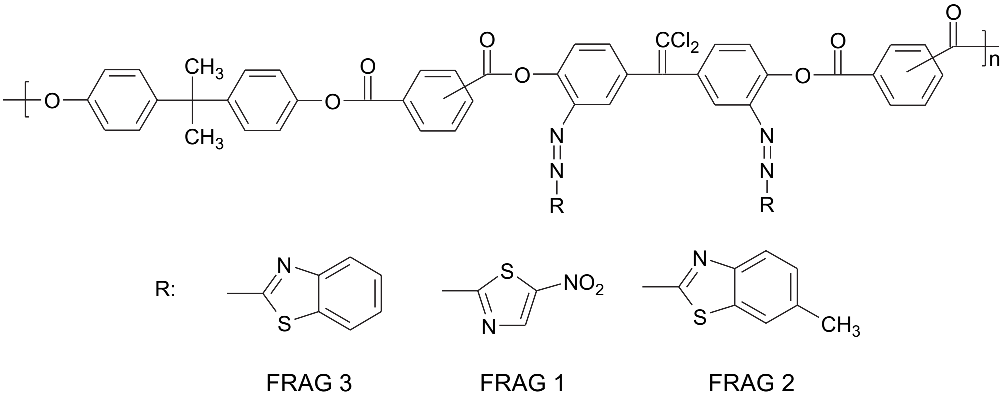

Fig. 3. The structure of designed polymers.

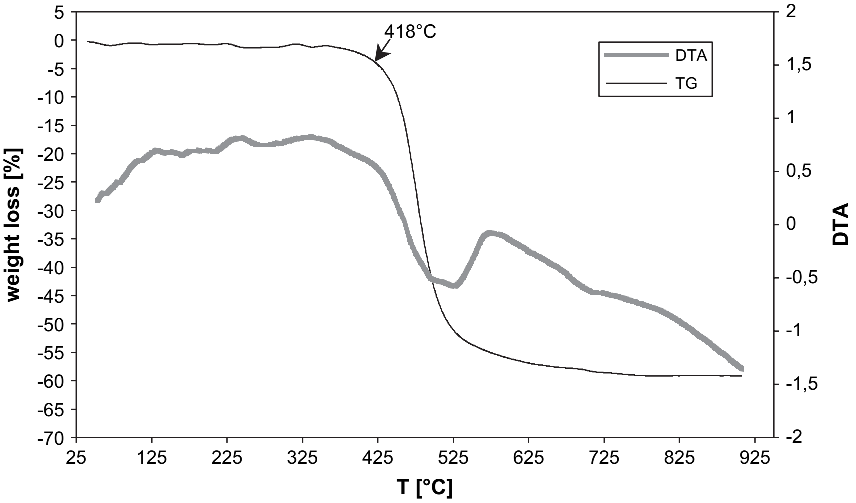

Fig. 6. Derivatogram of polymer containing CHBISF **2** as a special monomer.

This is confirmed by our calculations for polyarylates fragments containing chromophores.

The hyperpolarizability calculations for polymers' fragments, the structure of which is shown in Fig. 3, were performed in MOPAC93 package, using PM3 method. They indicate that all polymers' fragments which contain thiazolyloazo monomers have higher β_0 values than 4-nitroaniline. The best result was obtained for compounds with side-chain azo group having 5-nitrothiazole and benzothiazole ring. The polyarylates with 5-methylbenzothiazole have lower value of hyperpolarizability (Fig. 4). Change of the field has no significant influence on the value of hyperpolarizability.

Westmoreland and co-workers in their papers [5] studied inter alia thermostability and incombustibility of polyarylates based on chlorobisphenole. They show that the aromatic polyester has highest thermostability in comparison with others polymers due to the presence of chlorobisphenole in polymer chain. This motivates our interest in this monomer and its chemical modification, which ensures excellent physico-chemical, mechanical and optical properties. The structure of polymers we designed is shown in Fig. 3.

Thermal analysis of polymers which contain azo chromophores (CHBISF **1**, CHBISF **2** and CHBISF **3**) was done. The obtained results show that the investigated compounds decompose at the temperature above 400 °C (Fig. 6).

The chromophores can be dissolved in chlorinated solvents, alcohols and aliphatic ketones. The UV–vis spectra of chromophores are shown in Fig. 5. All chromophores exhibit a strong absorption in visible range. Values of $\lambda_{\max}$ are in proximity for all monomers and no significant changes in absorption maxima were observed for different substituents. Utilizing obtained data it is possible to determine optimal working wavelength for the materials based on these chromophores.

5. Conclusions

Three novel NLO chromophores, whose structures are shown in Fig. 1, have been synthesized and characterized. Heterocyclic rings of substituted thiazole are conjugated through azo bonds with the chlorobisphenole structure. They exhibit fairly good first- and second-order hyperpolarizabilities. Physico-chemical data indicate that they are perfect candidates to synthesize thermostable and incombustible polymers, which would display nonlinear-optical properties.

Acknowledgments

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