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The synthesis and properties of triazine-stilbene fluorescent brighteners containing the phenolic antioxidant

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Abstract

Disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives (**11a–h**) which were substituted with 4-amino-2,6-di-*tert*-butylphenol (**3**) or 4-(2-amino-ethyl)-2,6-di-*tert*-butylphenol (**6**) as an antioxidant on triazine moiety were prepared. The obtained compounds were characterized by the analysis of the proton NMR spectrum and confirmed by UV spectrum. The physical properties of the new compounds (**11a–h**) were performed by fastness test and whiteness measurement, compared with those of **CI86** and **CI90**.

Keywords: Antioxidant; Triazine-stilbene FBs; Whiteness; Fastness; 4-Amino-2,6-di-*tert*-butylphenol; 4-(2-Aminoethyl)-2,6-di-*tert*-butylphenol

1. Introduction

Disodium 4,4′-bis(triazinylamino)stilbene-2,2′-disulfonate derivatives are most widely used as fluorescent brighteners for the whitening of both cotton and wool [1–3]. They increased the whiteness by a process of absorption of the light in ultraviolet region (330–380 nm) and emission of the visible blue light (400–450 nm) [4]. It is necessary for the fluorescent brighteners to show the high fluorescence activity a planar molecular structure with conjugated double bonds and electron-donating groups [5]. Fluorescent brighteners, furthermore, should present a high quality of whiteness and fastness.

In some cases, if the matter which was treated with a fluorescent brightener is exposed outside, a free radical could be produced due to the solar light. As a result, the chemical skeleton of the fluorescent brightener is destroyed and the whiteness is decreased rapidly. Recently, our research interests are focused on the development of the fluorescent brightener that could be capable of being exposed under the sun for a long time.

In this study, disodium 4,4′-bis(1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate derivatives which were substituted with the phenol derivatives on triazine moiety were prepared as the antioxidant fluorescent brighteners. The newly synthesized compounds (**11a–h**) were characterized by analysis of the proton NMR spectrum and confirmed by UV spectrum. The physical properties of the new compounds (**11a–h**) were performed by fastness test and whiteness measurement, compared with those of **CI86** and **CI90**.

2. Result and discussion

2.1. Synthesis of phenolic antioxidant derivatives

Oxygen is an essential element for life, but it also has the possibility of forming a toxic substance called oxygen free radical. Antioxidants could decrease the

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energy of free radical or stop forming it at the first place. Also it interrupts the oxidation chain-reaction in order to minimize free radical's inhibition reaction [6,7].

Phenolic antioxidants form the stable low-energy free radical by the stable resonance hybrids to prevent further oxidation (Fig. 1).

Also if alkyl group is substituted in phenolic compound, phenoxy free radical would be more stable because of the electron donating character of alkyl group. BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) are representative models for phenolic antioxidant compound (Fig. 2) [8].

4-Amino-2,6-di-*tert*-butylphenol (**3**) [9–12] and 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol (**6**) [13,14] were selected as the analogous compounds of BHT and prepared as shown in Scheme 1.

4-Amino-2,6-di-*tert*-butylphenol (**3**) was prepared from the nitrosation of 2,6-di-*tert*-butylphenol (**1**) followed by reduction with sodium hydrosulfite. Compound (**3**) was easily oxidized in air, so it had to be used for the next step without further purification.

The reaction of 2,6-di-*tert*-butylphenol (**1**) with paraformaldehyde in the presence of concentrated hydrochloric acid provided 4-chloromethyl-2,6-di-*tert*-butylphenol (**4**) which was converted to 4-cyanomethyl-2,6-di-*tert*-butylphenol (**5**) by the treatment with potassium cyanide. The reduction of 4-cyanomethyl group of the compound (**5**) with lithium aluminum hydride afforded 4-aminoethyl-2,6-di-*tert*-butylphenol (**6**).

2.2. Synthesis of triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives

The triazine-stilbene fluorescent brighteners are widely used in industrial application as whitening agents [15] and their synthetic procedures are well known. The syntheses of the triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives were started from the reaction of disodium 4,4′-diaminostilbene-2,2′-disulfonate (**7**) with 2,4,6-trichloro-1,3,5-triazine (**8**). Three chloro groups of compound (**8**) showed different chemical reactivities with the nucleophiles depending on the reaction temperature (Fig. 3) [16,17].

After stirring disodium 4,4′-diaminostilbene-2,2′-disulfonate (**7**) with 2 equivalents of 2,4,6-trichloro-1,3,5-triazine (**8**) at 0–5 °C, the resulting disodium 4,4′-bis(2,4-dichloro-1,3,5-triazin-6-yl)diaminostilbene-2,2′-disulfonate (**9**) was treated with aniline derivatives

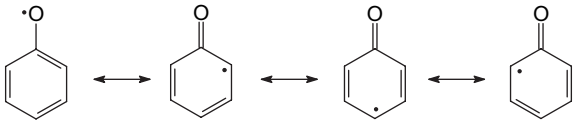

Fig. 1. The resonance structures of the phenoxy free radical.

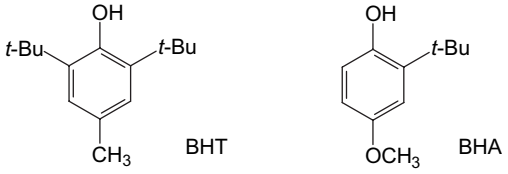

Fig. 2. The structures of BHT and BHA.

(aniline, sodium *o*-aminobenzenesulfonate, *p*-aminobenzenesulfonate, and *m*-aminobenzenesulfonate) at 30 °C without separation. While the substitution of *o*-aminobenzenesulfonate with the chloro group of the intermediate (**9**) took at least 13 h, the substitution of the other aniline derivatives was established within 3–4 h. It is assumed that the *ortho* positioned sulfonate group *o*-aminobenzenesulfonate caused the steric hindrance to prevent the nucleophilic substitution of amino group.

Finally, 4-amino-2,6-di-*tert*-butylphenol (**3**) or 4-(2-aminoethyl)-2,6-di-*tert*-butylphenol (**6**) was added in situ to the reaction mixture. The third substitution reaction occurred when a temperature of 80 °C was reached.

The synthetic procedures of triazine-stilbene fluorescent brighteners containing the phenolic antioxidant derivatives are summarized in Scheme 2 and relevant data are given in Table 1.

2.3. Color assessment and various fastness

Characteristics of the compounds (**11a–h**) are compared with those of **CI86** and **CI90** which are used for commercial purpose. The structures of **CI86** and **CI90** are shown in Fig. 4.

The compounds (**11a–h**) were applied at concentrations of 0.05%, 0.1%, 0.3%, 0.5%, and 1% relative to the weight of cotton fiber. The degree of the whiteness and the CIE $L^*a^*b^*$ coordinates were determined. The data obtained are presented in Table 2. It is apparent that the compounds (**11a–h**) showed lower degree of whiteness than **CI86** and **CI90**. The compounds (**11a–h**) gave the range of the attractive color shade from bluish white to white. The compounds **11a**, **11b**, **11d**, and **11f** presented good resistance to light, but the compound **11c** showed lower light fastness than **CI86** and **CI90**. While the compounds (**11a–h**) afforded low fastness in the chlorinated water, they provided better rubbing fastness than **CI86** and **CI90** as shown in Table 3.

Washing fastness data are given in Table 4. The results of the washing fastness test showed that all the compounds (**11a–h**) preserved excellent fastness, especially superior for cotton.

3. Conclusion

Triazine-stilbene derivatives containing the phenolic antioxidant derivatives (**11a–h**) were prepared as