Dyes and Pigments 124 (2016) 258–267

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Photo- and PH-switchable fluorescent diarylethenes based on 2,3-diarylcyclopent-2-en-1-ones with dialkylamino groups

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ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form
12 August 2015
Accepted 17 September 2015
Available online 3 October 2015

Keywords:
Photochromic diarylethenes
Fluorescence
Diarylcyclopent-2-en-1-one
Spectral properties
Thermal stability
Synthesis

ABSTRACT

New dialkylamino groups-comprising diarylethenes of 2,3-diarylcyclopent-2-en-1-one (DCP) series have been synthesized and its photochromic, fluorescent as well as acidochromic features have been investigated. It was shown that photochromic properties of the substances depend strong on their structures; the non-symmetry of the photochromic molecule is a powerful tool to properly control and tune the parameters of diarylethenes. It has been found that the most promising of DCPs synthesized are those containing dialkylamino groups in ethene “bridge” (rather than in aryl moieties) because they possess photo- and pH-switchable emission along with thermal stability. It has been established that the introduction at the second position of the cyclopentenone ring the benzene residue leads to the disappearance of the photochromic properties.

1. Introduction

Design and synthesis of functional organic and hybrid materials has a high priority in the development of new technologies and smart devices [1–3]. Among them photochromic materials have been the focus of much attention because of their potential technological applications in display, high-density memory devices and other high technology fields [4–6]. One of promising classes of photochromic organic dyes are diarylethenes due to excellent thermal stability of its ring-open and ring-closed isomers, high fatigue resistance, rapid response, and photochromism in crystals [7–10].

The possible applications of diarylethenes are connected with design of photonic devices (optical memories and molecular photoswitches) [5,7], chemosensors [11–14], write-by-light/erase-by-heat recording systems [15,16], cell markers for biochemistry and medicine [17], smart devices and materials, *etc* [18,19]. To gain compounds with properties appropriate for definite purposes it is necessary first of all to study the correlations between chemical structures of compounds and their spectral properties, which, in turn, require the synthesis and modification of the structures.

One of interesting modifications of diarylethenes structures seems to be introduction into the molecules of electron donating dialkylamino groups including those forming merocyanine systems (conjugation between donating and withdrawing atoms – push-pull-system). To the best of authors' knowledge, a few of similar substances and systems have been synthesized as multi-chromophoric fluorescent switches [20–23] (including pH-sensitive ones [24–27]) and systems switching between P- and T-types [26]. In most cases dialkylamino-substituents, merocyanine dye [20] or spiropyran moieties [21] were attached to aryl groups (covalently or by hydrogen bonds [13]); there is also the only example of diarylethene with dimethylamino group in thiazole ethene “bridge” [25].

To extend the number of known diarylethenes with dialkylamino-substituents (essentially in ethene “bridge”, which actually has not been described) and to study thoroughly their properties and “structure-property” relationships it was proposed to synthesize the compounds based on photochromic 2,3-diarylcyclopent-2-en-1-ones (DCPs). DCPs have been reported earlier [28,29] to be promising class of photochromic diarylethenes with easily modifiable ethene “bridge” [30–34].

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http://dx.doi.org/10.1016/j.dyepig.2015.09.027

Here, we have performed the design of three types of photoswitchable compounds with dialkylamino-groups. It was prepared new photochromic and fluorescent substances **4** and **6** (Scheme 1) comprising various electron donating dialkylamino groups both in aryl moieties (compounds **4**) and in cyclopentenone “bridge” (compounds **6**).

It is important to note that the introduction in diarylethene molecule of an additional conjugated π-system along with hexatriene is an effective way to design high-efficiency multifunctional photosensitive substances (materials). DCPs **4a**–**d** and **6a**–**e** include merocyanine system (conjugation between donating nitrogen atom and withdrawing oxygen atom) along with hexatriene system responsible to photochromic reaction. While in compounds **6a**–**e** merocyanine and hexatriene systems are separated from each other, in diarylethenes **4a**–**d** two systems intersect, whereas in DCPs **4e**,**f** merocyanine system is absent at all. The differences are certain to influence on photochromic and fluorescent characteristics of diarylethenes; the properties of dialkylamino groups-containing DCPs as well as their switching parameters have been investigated and are discussed below.

2. Experimental

2.1. Materials and methods

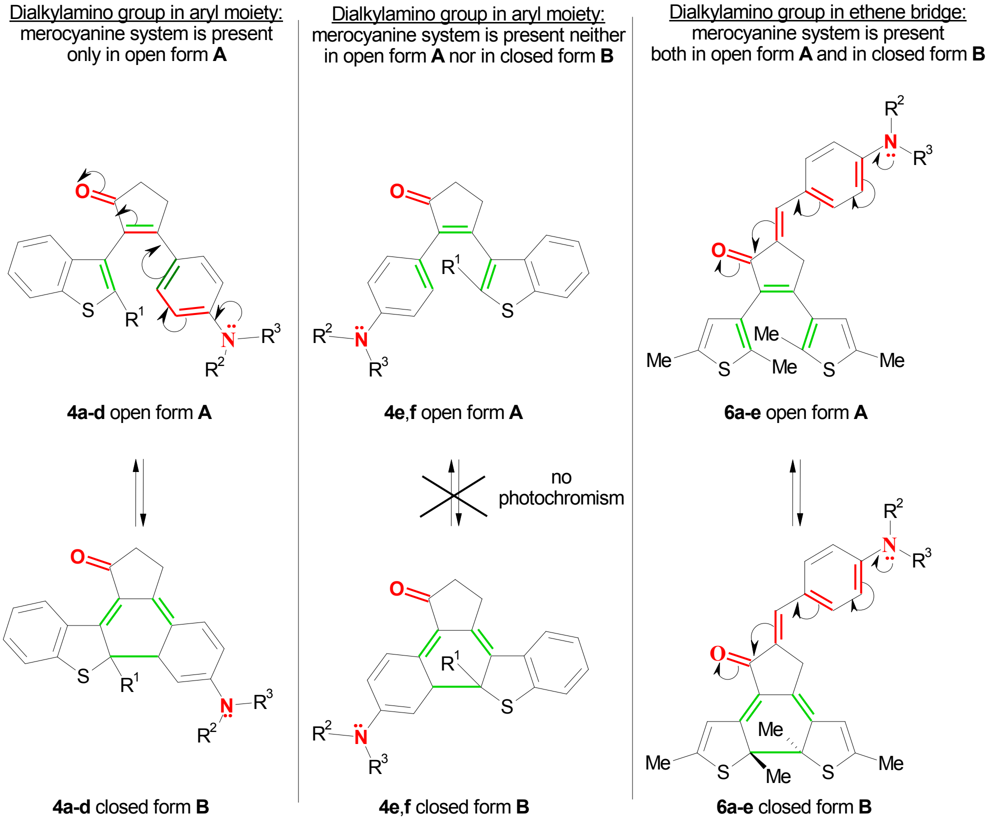
^{1}H and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker AM-300 spectrometer working at 300 MHz for ^{1}H, 75 MHz for ^{13}C. Mass spectra were obtained on a Kratos mass spectrometer (70 eV) with direct sample injection into the ion source. Melting points were measured on a Boetius hot stage and were not corrected. IR spectra were obtained on a Specord M80 or M82 spectrometer in KBr pellets. High resolution mass spectra were obtained from a TOF mass Bruker maXis spectrometer with an ESI source. Microanalyses were obtained using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

Electronic absorption spectra were recorded on a LOMO SF-56 spectrophotometer. Fluorescence spectra were measured using a Fluorat®-02-Panorama spectrofluorometer. The experiments were performed in acetonitrile solutions ($C = 2 \cdot 10^{-5}$ mol L^{-1} for absorption spectra and $C = 2 \cdot 10^{-6}$ mol L^{-1} for emission ones) at 293 K in the air presence. Photocoloration was carried out using 6W Vilber Lourmat (France) UV-lamp model VL-6.LC (365 nm light); the emission was induced at maxima of excitation spectra. Quantum yields of ring-closure ($\varphi_{A \to B}$) and ring-opening ($\varphi_{B \to A}$) processes were calculated by previously reported technique [28,35]. The fluorescence quantum yields were determined by using as references the solutions of 4-dimethylamino-4′-nitrostilbene in benzene ($\varphi_f = 0.53$) [36] (for compounds **6b**,**e**), quinine in 0.1 N sulfuric acid ($\varphi_f = 0.55$) [37] (for compounds **4b**,**c**,**g**), naphthalene in methylcyclohexane ($\varphi_f = 0.23$) [38] (for compounds **4e**,**f**), coumarin-1 in ethanol ($\varphi_f = 0.73$) [39] (for compounds **4a**,**d**) or coumarin-30 in acetonitrile ($\varphi_f = 0.67$) [39] (for compounds **6a**,**c**,**d**).

Commercially available reagents and solvents were used. Column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F$_{254}$ plates.

2.2. Synthesis

1-Arylethanones **1** based on 2-methyl-1-benzothiophen and 2-heptyl-1-benzothiophen were obtained by their successive 3-acetylation [40]. 1-[4-(Dialkylamino)phenyl]ethanones were synthesized from commercial fluorobenzene by its 4-acetylation [41]



Scheme 1. DCPs containing dialkylamino groups in ethene “bridge” or in aryl moieties.