Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 203 (2018) 348–356

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Spectral properties and structure of unsymmetrical diarylethenes based on thiazole ring with hydrogen at the reactive carbon

Andrey G. Lvov [a,*], Anna M. Alexeeva [b], Evgeniya A. Lvova [a], Mikhail M. Krayushkin [a], Valerii Z. Shirinian [a]

[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky prosp., 119991 Moscow, Russian Federation
[b] Mendeleev University of Chemical Technology of Russia, Miusskaya Sq., 9, Moscow 125047, Russian Federation

ARTICLE INFO

Article history:
Received 28 March 2018
Received in revised form 20 May 2018
Accepted 27 May 2018
Available online 31 May 2018

Keywords:
Diarylethene
Photocyclization
Photoreaction
Reaction intermediate
Conformation
Thermal stability
Fluorescence

ABSTRACT

Six new photoactive unsymmetrical diarylethenes bearing thiazole ring with hydrogen at the reactive carbon atom have been synthesized. Their structures have been studied by DFT calculations and X-ray crystallography. All compounds undergo irreversible photochemical transformations under irradiation with ultraviolet light, proceeding through the photocyclization stage. It has been found that only some normal (thiophene, imidazole and pyrazole derivatives) and inverse type (oxazole derivative) diarylethenes form colored photoinduced isomers under UV. In polar acetonitrile these intermediates show relatively fast irreversible thermal reaction, while in nonpolar toluene slow cycloreversion to initial diarylethenes is the predominant process of these species.

1. Introduction

The photocyclization of diarylethenes (DAE's) is a well-known transformation, which is of great importance for the development of advanced materials and devices (reversible isomerization, *i.e.* photochromism) [1] and in organic synthesis [2]. In recent years a new direction in photochemistry of DAE's is developing, associated with general cascade process photocyclization/[1,n]-H shift/cycloreversion [3]. A key requirement for such processes is the presence of a hydrogen atom at least at one of the reactive center of the hexatriene system of diarylethene **I** (Scheme 1A). After photocyclization the hydrogen atom is capable of sigmatropic rearrangement accompanied by a rearomatization of one ring. The final step of this cascade process is the cycloreversion of another ring and formation of the functionalized naphthalene or its isoelectronic analog **IV**. The first time the rearrangement was found by Ho and coworkers [4]. Further, related reactions of terarylenes [5], diarylethenes [6] and stilbene analogs [7] were also described. Diversity of substrates and high efficiency of their photoreactions allow us to consider this cascade process as a new method for the synthesis of polyaromatic compounds. On the other hand, this cascade process is closely related to the photochromism of diarylethenes (reversible isomerization of **I** to **II**) and has a significant effect on it. The photochemical rearrangement leads to the degradation of fatigue resistance [8] and, as a consequence, a decrease in the number of cycles of photocyclization/cycloreversion, which was recently demonstrated by Jäschke and coworkers [9].

The mechanistic studies and evaluation of the scope and limitations of this transformation are important issue for the development of novel synthetic methods towards polyaromatic compounds for medicinal and material chemistry [10]. The aim of this work is to clarify the effect the thiazole residue comprising hydrogen atom at the reactive center on the photochemical transformation of unsymmetrical diarylethenes. Recently we have demonstrated that the photorearrangement of hetarylphenylethenes based on the cyclopentenone bridge can proceed with different various heterocycles giving the corresponding naphthalenes (Scheme 1B) [6b]. Kawai et al. reports an efficient photoreaction of terarylenes towards corresponding annulated benzothiazoles (Scheme 1C) [5b]. It should be also mentioned a number of works, where unsubstituted diarylethenes with thiazole moiety as aromatic residue participate in the photochemical transformation leading to tetracycle aromatics by photocyclization/elimination process [11]. In the present work we have synthesized a series of unsymmetrical diarylethenes bearing thiazole ring with hydrogen at α-position and studied their structures and photochemical properties to clarify whether such compounds can participate in the photoinduced rearrangement with the formation of functionalized benzothiazoles.

* Corresponding author.
E-mail address: lvov-andre@yandex.ru (A.G. Lvov).

https://doi.org/10.1016/j.saa.2018.05.097
1386-1425/

2. Experimental

2.1. General Methods

NMR spectra were recorded in deuterated solvents on spectrometers working at 300.13 MHz for ^{1}H and 75.77 MHz for ^{13}C. Both ^{1}H and ^{13}C NMR chemical shifts are referenced relative to the residual solvents signals ($CHCl_3$: δ 7.27 for ^{1}H NMR and δ 77.2 for ^{13}C NMR) and reported in parts per million (ppm) at 293 K. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; m, multiplet; t, triplet; br, broad), coupling constant in hertz (Hz), integration, and assignment. Melting points (mp) were recorded using an apparatus and not corrected. High-resolution mass spectra were obtained from a TOF mass spectrometer with an ESI source. All chemicals and anhydrous solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F_{254} plates.

2.2. Photochemical Studies

UV–Vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed in the presence of air in the solutions of freshly distillated acetonitrile and toluene. The irradiation was carried out by 6W Vilber Lourmat (France) UV-lamps (313 and 365 nm). The fluorescence quantum yields were determined by comparing with 4-nitro-4′-(dimethylamino)stilbene ($\varphi_{fl}^{365} = 0.53$) in toluene [12].

2.3. Calculation Details

All results were obtained using the GAUSSIAN 09 program package [13]. Density functional theory (DFT) calculations were performed using the B3LYP or ωB97xD functionals with the 6-31G(d) or 6-31G(d,p) basis sets. All energies were calculated without zero-point correction. Calculation of vibrational frequencies was performed to prove that the optimized structure corresponds to a true minimum on the potential energy surface.

2.4. X-ray Studies

Single crystals suitable for X-ray structure determination were obtained by the slow evaporation of $CDCl_3$ solution of **3b**. X-ray diffraction data were collected on APEX II DUO CCD diffractometer. Other parameters are collected in the Table S1. Crystal structure was analyzed by OLEX2 program [14].

2.5. Synthesis

2-(2-Phenylthiazol-4-yl)acetic acid **1** (500 mg, 2.28 mmol) was dissolved in DMF (10 ml) and argon was bubbled through this solution for 15 min. To the stirred solution under argon atmosphere K_2CO_3 (472 mg, 3.42 mmol) was added. After 15 min bromoketone **2** (2.28 mmol) was added. The reaction mixture was stirred for 30 min at ambient temperature and for 30 min at 80 °C. The resulting mixture was poured in water (100 ml), extracted with ethyl acetate (3 × 30 ml). The combined organic phases were washed with brine (2 × 50 ml), dried over under $MgSO_4$ and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (4:1).

- **4-(2,5-Dimethylthiophen-3-yl)-3-(2-phenylthiazol-4-yl)furan-2(5*H*)-one (3a)**

Yield 52%, yellow powder, mp 103–105 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 5.06 (s, 3H, CH_3), 6.70 (s, 1H, $H^{thiophene}$), 7.35–7.50 (m, 3H, H^{arom}), 7.75–7.85 (m, 2H, H^{arom}), 8.24 (s, 1H, $H^{thiazole}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.9, 15.1, 71.7, 119.7, 119.9, 125.4, 126.4 (2C), 128.5, 128.9 (2C), 130.1, 133.4, 136.6, 138.4, 146.3, 153.5, 167.0, 172.8.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{19}H_{15}NO_2S_2$ 354.0617, found 354.0607.

- **4-(5-Methyl-1,2-diphenyl-1*H*-imidazol-4-yl)-3-(2-phenylthiazol-4-yl)furan-2(5*H*)-one (3b)**

Yield 27%, yellow crystals, mp 227–229 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79 (s, 3H, CH_3), 5.43 (s, 2H, CH_2), 7.12–7.63 (m, 13H, H^{arom}), 7.77–8.01 (m, 2H, H^{arom}), 8.22 (s, 1H, $H^{thiazole}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 12.2, 71.9, 117.0, 119.9, 126.3 (2C), 127.8 (2C), 128.3 (2C), 128.4 (2C), 128.6, 128.9 (2C), 129.3, 129.7, 129.9 (2C), 130.2, 130.4, 133.2, 133.5, 136.8, 146.9, 147.3, 152.4, 166.6, 173.6.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{29}H_{21}N_3O_2S$ 476.1427, found 476.1414.

- **4-(5-Methyl-1-phenyl-1*H*-pyrazol-4-yl)-3-(2-phenylthiazol-4-yl)furan-2(5*H*)-one (3c)**

Yield 58%, pale brown powder, mp 177–179 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H, CH_3), 5.17 (s, 2H, CH_2), 7.35–7.55 (m, 8H, H^{arom}), 7.80–7.90 (m, 2H, H^{arom}), 8.04 (s, 1H, $H^{pyrazole}$), 8.24 (s, 1H, $H^{thiazole}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 13.0, 71.1, 113.0, 117.7, 120.2, 125.3 (2C), 126.4 (2C), 128.6, 129.1 (2C), 129.3 (2C), 130.3, 133.2, 139.0, 140.2, 146.4, 150.0, 150.3, 167.2, 172.9.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{23}H_{17}N_3O_2S$ 400.1114, found 400.1106.

- **4-(4-Methyl-2-phenylthiazol-5-yl)-3-(2-phenylthiazol-4-yl)furan-2(5*H*)-one (3d)**

Yield 21%, yellow powder, mp 159–161 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, CH_3), 5.19 (s, 2H, CH_2), 7.38–7.4 (m, 3H, H^{arom}), 7.48–7.5 (m, 3H, H^{arom}), 7.83–7.87 (m, 2H, H^{arom}), 7.97–7.99 (m, 2H, H Ar), 8.28 (s, 1H, $H^{thiazole}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 71.8, 120.6, 121.3, 122.0, 126.5 (2C), 126.6 (2C), 129.0 (2C), 129.1 (2C), 130.3, 130.7, 133.0, 133.1, 145.6, 147.8, 155.1, 167.5, 168.8, 172.0.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{23}H_{16}N_2O_2S_2$ 417.0726, found 417.0720.

- **4-(2,4-Dimethyloxazol-5-yl)-3-(2-phenylthiazol-4-yl)furan-2(5*H*)-one (3e)**

Yield 40%, yellow powder, mp 119–121 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.01 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 5.15 (s, 2H, CH_2), 7.41–7.43 (m, 3H, H^{arom}), 7.85–7.87 (m, 2H, H^{arom}), 8.13 (s, 1H, $H^{thiazole}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 14.1, 69.6, 117.4, 121.0, 126.4 (2C), 129.0 (2C), 130.4, 133.1, 139.0, 141.6, 142.9, 145.7, 163.0, 167.2, 172.2.

HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{18}H_{14}N_2O_3S$ 339.0798, found 339.0793.

- **4-(6-Methylimidazo[2,1-*b*]thiazol-5-yl)-3-(2-phenylthiazol-4-yl)furan-2(5*H*)-one (3f)**

Yield 55%, orange powder, mp 171–173 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (3H, s, CH_3), 5.28 (2H, s, CH_2), 6.62 (d, $J = 4.5$ Hz, 1H, $H^{imidazothiazole}$), 6.68 (d, $J = 4.5$ Hz, 1H, $H^{imidazothiazole}$), 7.25–7.40 (m, 5H, H^{arom}), 8.41 (s, 1H, $H^{thiazole}$).