Dyes and Pigments 80 (2009) 136–140

Contents lists available at ScienceDirect

Dyes and Pigments

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

Acid-catalyzed decomposition of stable 1-(2,1-benzisothiazol-3-yl)-3-phenyltriazenes

Jiří Hanusek [a,*], Hana Bělohlavová [b], Josef Přikryl [b,1], Vladimír Macháček [a]

[a] University of Pardubice, Institute of Organic Chemistry and Technology, Nám. Čs. legií 565, CZ-532 10 Pardubice, Czech Republic
[b] University of Pardubice, Institute of Polymeric Materials, Nám. Čs. legií 565, CZ-532 10 Pardubice, Czech Republic

ARTICLE INFO

Article history:
Received 1 April 2008
Received in revised form 30 May 2008
Accepted 4 June 2008
Available online 13 June 2008

Keywords:
1-(2,1-Benzisothiazol-3-yl)-3-phenyltriazenes
Acid-catalyzed decomposition
Tautomerism
Mechanism
Kinetics

ABSTRACT

The acid-catalyzed decomposition of unusually stable 1-(2,1-benzisothiazol-3-yl)-3-phenyltriazenes in either aqueous perchloric acid or an aqueous mixture of perchloric and acetic acid was studied under pseudo-first order reaction conditions at 25 °C. Different products were obtained according to substitution on nitrogen *N*-3. For a triazene carrying hydrogen, the corresponding 3-amino-2,1-benzisothiazole and benzenediazonium salts were formed whereas in the case of substitution by an alkyl group (methyl and *n*-butyl) the 2,1-benzisothiazole-3-diazonium salt and *N*-alkylaniline were obtained. The observed rate constant (k_{obs}) of the acid-catalyzed decomposition increased, initially, nonlinearly with increasing concentration of acid. Subsequently, k_{obs} decreased slightly and at high acid concentration, increased steeply once again. An A-S_E2 mechanism in which protonation of the triazene nitrogen proceeds simultaneously with cleavage of the N–N bond is proposed. Tautomerism of 1-(2,1-benzisothiazol-3-yl)-3-phenyltriazene was investigated using ^{1}H NMR spectroscopy.

1. Introduction

Triazenes are a very useful and diverse class of compounds whose synthetic applications were recently reviewed [1]. They have also been studied for their anticancer potential [2,3], and used as protecting groups in natural product synthesis [4] or as ligands in organometallic chemistry [5]. Triazenes are easily synthesized from readily available anilines and diazonium salts (aromatic triazenes) or from alkyl azides and appropriate Grignard or alkyl lithium reagents (aliphatic triazenes) [6]. However, anilines and *N*-alkylanilines are ambident nucleophiles [7] and can react with the electrophilic diazonium ion on nitrogen or in the aromatic nucleus. The azo coupling reaction on nitrogen takes place in neutral to weakly alkaline media [8]. In acidic media, the azo coupling reaction on nitrogen is reversible, and so the triazenes are not stable in acids. They are protonated by acids and decompose back to the aniline and diazonium ion [8–10]. This cleavage may be followed by azo coupling reaction in the nucleus of the aniline formed (acid-catalyzed rearrangement of aromatic triazenes into azo compounds).

In our previous papers [11,12] we have found that azo coupling reactions between 5-nitro-2,1-benzisothiazole-3-diazonium species and secondary aliphatic/aromatic amines and diphenylamine in acidic media produces mainly triazenes that are surprisingly stable in such media and are split only very slowly. Similar triazene is undesirable by-product in the production of the azo dyestuff C.I. Disperse Blue 148 which is produced by azo coupling of 5-nitro-2,1-benzisothiazole-3-diazonium hydrogensulphate with methyl-3-(*N*-ethyl-*N*-phenyl)aminopropanoate.

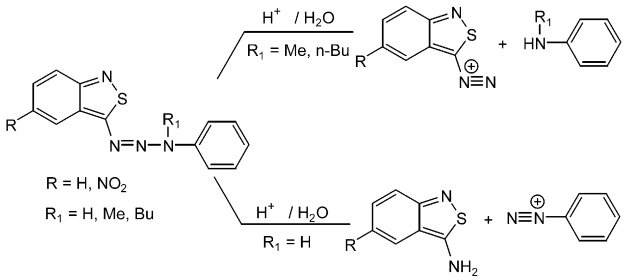
Previously [11,12] we have found that hydrolysis affords different products according to substitution (R^1) on nitrogen *N*-3. If $R^1 = H$ then corresponding 3-amino-2,1-benzisothiazoles and benzenediazonium salt are formed whereas in the case of substitution on nitrogen *N*-3 by an alkyl group (R^1 = Me, *n*-Bu) the 2,1-benzisothiazole-3-diazonium salt and *N*-alkylanilines are formed exclusively (Scheme 1). In the present paper we have focused on the reaction mechanism of decomposition of 3-substituted-3-phenyl-1-(2,1-benzisothiazol-3-yl)triazenes and 3-substituted-3-phenyl-1-(5-nitro-2,1-benzisothiazol-3-yl)triazenes in strong acid medium.

2. Results and discussions

The newly prepared compounds **1a–c** were synthesized by an azo coupling reaction of 2,1-benzoisothiazol-3-diazonium cation with aniline, *N*-ethylaniline, and *N*-butylaniline, respectively. After the azo coupling reaction, the reaction mixture always contained the required triazene **1a–c** along with the product of azo coupling

* Corresponding author. Tel.: +420 466 037 015; fax: +420 466 037 068.
E-mail address: jiri.hanusek@upce.cz (J. Hanusek).
[1] Dr. J. Přikryl passed away in September 2007.

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.06.003



	1a	1b	1c	1d	1e	1f	1g
R	H	H	H	NO_2	NO_2	NO_2	NO_2
R^1	H	Et	Bu	H	Me	Et	Bu

Scheme 1.

reaction in aromatic nucleus, i.e. the respective azo compound, which was separated chromatographically. The formation of a mixture of triazene and azo compound was observed earlier, when we prepared and characterized compounds **1d**–**g** [12].

Compounds **1a**–**c** were identified on the basis of their ^{1}H and ^{13}C NMR spectra and elemental analyses. In the case of the spectrum of compound **1a** in DMSO-d_6, the signals of protons were broadened, and the extent of signal broadening changed with the concentration of solution. In the ^{13}C NMR spectrum of this substance (DMSO-d_6), there were only three sharp signals corresponding to the CH groups of monosubstituted benzene nucleus (δ 129.7, 128.2, and 121.0). The signals of the other carbon atoms were very broad and virtually disappeared in the noise. The addition of a strong acid should suppress dissociation of triazene and thus rate of chemical exchange which should lead to ^{13}C NMR signal sharpening. After adding a drop of CF_3COOH into the solution of compound **1a** in DMSO-d_6 and immediate measurement, the obtained ^{1}H NMR spectrum was identical with that measured without CF_3COOH. The ^{13}C NMR spectrum measured subsequently within a period of ca. 12 h (because of the very low solubility of compound **1a**) showed only unidentified triazene decomposition products (probably diazonium salt decomposition products).

The situation is simpler in the case of compounds **1b** and **1c**, due to bond fixation and the absence of prototropy resulting from the *N*-alkyl group. The signals in both ^{1}H and ^{13}C NMR spectra of **1b** and **1c** are sharp, and the chemical shifts of the corresponding atoms are very similar (see Section 3). The observed small dependence of δ (^{1}H) upon concentration ($\Delta\delta$ is max. $\pm$0.03 ppm) is obviously due to the association of the molecules in solution. The chemical shift of proton H-4, which is the nearest to the potential tautomeric centre, in compound **1a** differs by 0.4 ppm from the shifts of the same protons in compounds **1b** and **1c**, which indicates that compound **1a** is present in a tautomeric form (or rapidly equilibrating mixture of forms) different from those fixed in compounds **1b** and **1c**.

Quite analogous behavior was observed [12] in the case of triazenes formed by azo coupling reaction from 5-nitro-2,1-benzoisothiazol-3-diazonium cation. The triazenes obtained by the reaction with *N*-alkylanilines have the chemical shifts of proton H-4 in the δ region of 8.86–9.01, but the triazenes derived from primary amines (aniline, 3-methylaniline, 3-chloraniline) have δ(H-4) = 9.48. Due to the chemical exchange, it was impossible to measure the ^{13}C NMR spectra of the triazenes formed by azo coupling reaction from primary aromatic amines.

Kinetics of the acid-catalyzed decomposition of triazenes in weak acid or weak base medium (pH $\approx$ 3.5–10) has been studied by several authors. First, Hughes and Ingold [13] suggested the A2 mechanism for the decomposition whose first step involves fast protonation of the triazene which is followed by the attack of nucleophile to give Ar–N=N–Nu and corresponding amine. However, further investigations [14,15] disproved participation of a nucleophile species in the course of mechanism. Later [16,17] it was found that acid-catalyzed triazene decomposition involves proton transfer in the rate-limiting step, i.e. general acid catalysis makes itself felt. The magnitude of the primary kinetic isotope effect ($k_H/k_D > 1$) also supported such conclusions [18]. Therefore the most probable mechanism is A–S_E2 in which the protonation of the triazene nitrogen proceeds simultaneously with the cleavage of N–N bond. The structure of the transition state varies with the strength of catalyzing acid and the pK_a of the liberated amine. For example for primary 3-alkyl-1-aryltriazenes the proton is essentially transferred from the weak acid catalyst to nitrogen and a little breakage of the N–N bond has occurred [16].

Acid-catalyzed decomposition of triazenes **1a**–**c** was followed in aqueous solutions of perchloric acid whereas decomposition of **1d**–**g** was followed in aqueous solutions of perchloric acid containing 50% of acetic acid due to their very low solubility.

The kinetics of the acid-catalyzed decomposition was determined by monitoring the decrease in concentration of **1a**–**g** spectrophotometrically at 470 nm in the presence of excess acid, i.e. under pseudo-first order conditions. The absorbance decreased exponentially with time from which a pseudo-first order rate constant (k_{obs}) was obtained. Pseudo-first order rate constants varied nonlinearly with the concentration of the acid. Fig. 1 presents k_{obs} vs. $c(HClO_4)$ dependences for **1a**–**c**. Similarly shaped dependences were obtained for triazenes **1d**–**g** in aqueous $HClO_4$/AcOH solutions. However, it was possible to determine rate constants only up to 5 mol l^{-1} for derivatives **1d**–**g** (Table 1).

From Fig. 1 and Table 1 it is seen that the observed rate constant (k_{obs}) at low acid concentrations increases with increasing acid concentration but from the concentration ca. 1–2 mol l^{-1} a slight decrease occurs. From the concentration ca. 6.5 mol l^{-1} further steep increase in k_{obs} was observed for derivatives **1a**–**c**. The effect of the acid concentration (and hence also acidity of medium) on the rate of transformation of the protonated substrate into products predominantly depends on the role played by water in the rate-limiting step. If water only acts as the reaction medium (i.e. only by its solvation effect), then the rate constant value of the rate-limiting

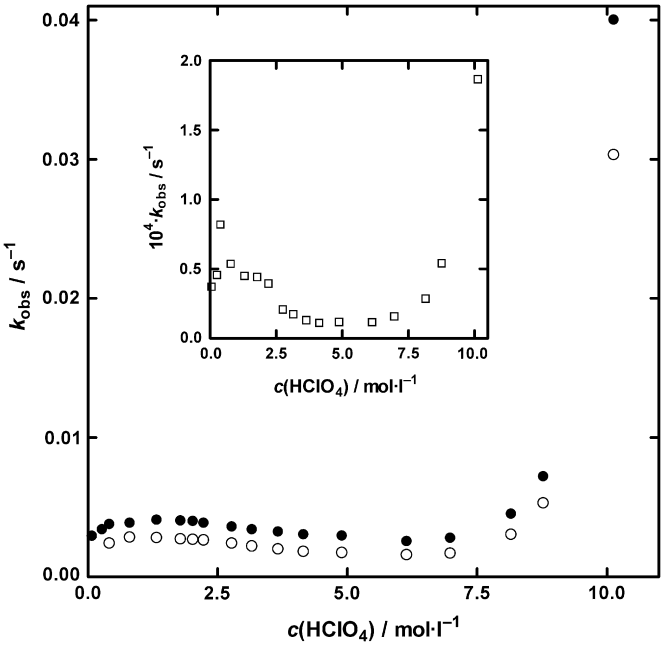


Fig. 1. Dependence of the observed rate constant (k_{obs}) of acid-catalyzed decomposition of **1a** (□ – inset), **1b** (●) and **1c** (○) on the concentration of perchloric acid.

Table 1
Dependence of the observed rate constant (k_{obs}) of acid-catalyzed decomposition of **1d–g** measured in solutions of $HClO_4$ in 50% aqueous AcOH

$c(HClO_4)$ mol l^{-1}	k_{obs} (**1d**) $\times 10^5$ (s^{-1})	k_{obs} (**1e**) $\times 10^5$ (s^{-1})	k_{obs} (**1f**) $\times 10^5$ (s^{-1})	k_{obs} (**1g**) $\times 10^5$ (s^{-1})
0	2.90	–	–	–
0.10	10.7	–	–	–
0.25	17.1	0.706	2.08	1.43
0.50	15.4	2.24	6.12	4.58
1.0	11.6	5.50	13.4	10.0
2.0	10.9	7.89	23.7	16.4
3.5	9.09	6.64	18.6	11.7
5.0	9.23	4.89	12.0	6.93

step usually increases with increasing concentration of acid. If water reacts in the rate-limiting step as a nucleophile and/or proton is transferred on water as a base, then this rate constant rapidly decreases [19].

In order to elucidate whether the k_{obs} decrease in the concentration range of 1–6.5 mol l^{-1} corresponds to the situation of water acting as a nucleophile, we studied the effect of concentration of nucleophilic chloride anion. This effect is shown in Table 2.

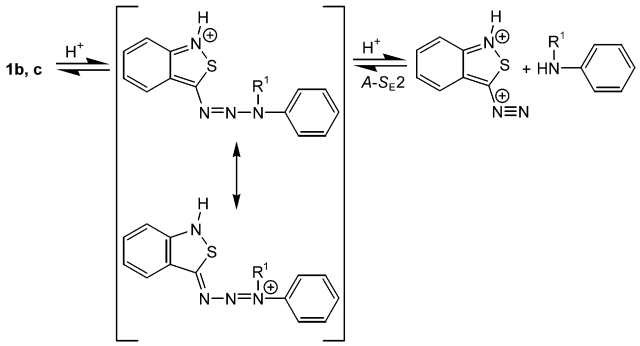
Table 2 shows that the rate of solvolysis is not substantially affected by the concentration of external nucleophile. Hence water, which is a weaker nucleophile than Cl^-, does not directly participate in the reaction. The mild decrease in decomposition rate within the concentration interval of 1–6.5 mol l^{-1} can be explained by protonation of nitrogen in the isothiazole skeleton (Scheme 2). This protonation is more favorable than the protonation of triazene nitrogen atom, which follows from results of the quantum-chemical calculation (B3LYP, TZVP-base, PCM) carried out for compound **1e**. According to these results, the protonation on the isothiazole nitrogen is much more favorable ($\Delta G = 24.6$ kcal mol^{-1}) than that on the nitrogen atom of the triazene grouping (Table 3).

The resonance structures of the cation formed by protonation of compound **1b** on isothiazole nitrogen atom indicate that the N(2)–N(3) bond order is higher than 1, which negatively affects the rate of cleavage of *N*-ethylaniline. Above the concentration of ca. 6.5 mol l^{-1}, diprotonation is probably taking place, which strongly facilitates the cleavage of *N*-ethylaniline, and the observed rate constant of decomposition of the triazene considerably increases.

The 100-fold lower reactivity of unsubstituted triazene **1a**, as compared with the *N*-alkyl substituted triazenes **1b–c**, is caused by the inductive effect of the alkyl group on nitrogen which facilitates protonation and also by the N=N bond fixation. In the case of compounds **1b–c** prototropic tautomerism is absent and thus only an *N*-alkylaniline unit can be split off. In the case of compound **1a** there exist two tautomeric forms Ph–NH–N=N–Ar (**I**) and Ph–N=N–NH–Ar (**II**) (where Ar is 2,1-benzisothiazol-3-yl). From the ^{1}H NMR spectrum of compound **1a** in DMSO-d_6 it clearly follows that the preferred tautomeric form is form **II**, which after protonation decomposes into benzenediazonium ion and 3-amino-2,1-benzisothiazole. If we presume operation of the A–S_E2 mechanism, in which the protonation of the triazene nitrogen proceeds simultaneously with the cleavage of N–N bond (Scheme 3), then not only the acid strength but also the nucleofugality of the leaving amine is

Table 2
Dependence of the observed rate constant (k_{obs}) of acid-catalyzed decomposition of **1b** in 2 mol l^{-1} $HClO_4$ and in 4 mol l^{-1} $HClO_4$ with addition of NaCl

2 mol l^{-1} $HClO_4$				4 mol l^{-1} $HClO_4$	
c_{NaCl} (mol l^{-1})	$k_{obs} \times 10^3$ (s^{-1})	c_{NaCl} (mol l^{-1})	$k_{obs} \times 10^3$ (s^{-1})	c_{NaCl} (mol l^{-1})	$k_{obs} \times 10^3$ (s^{-1})
0	3.96	2.0	4.35	0.5	3.17
0.5	3.80	2.5	4.29	1.0	3.05
1.0	4.11	3.0	3.88	2.0	3.09
1.5	4.44	3.5	3.90		



Scheme 2.

a decisive factor. Given the validity of Brønsted relation and $\beta_{lg} \approx 1$, the difference in the rates of cleavage of the amine corresponds to the difference between pK_a (aniline) and pK_a (3-amino-2,l-benzisothiazole). Hence 3-amino-2,l-benzisothiazole (p$K_a = 3.8$) [20] is approximately six times better leaving group than aniline (p$K_a = 4.6$) [21], which explains why compounds **1a** and **1d** preferably decompose into 3-amino-2,l-benzisothiazole and benzenediazonium cation and not into aniline and 2,1-benzisothiazol-3-diazonium cation.

The approximately 16- to 17-fold reactivity difference of derivatives **1b** and **1f** or **1c** and **1g** can be explained by the electron-withdrawing effect of a nitro group in the nucleus potentiated by the lowered polarity of medium when going from water to the mixture of water and acetic acid. The similar course of the dependence of k_{obs} vs. concentration of acid allows the conclusion that the same reaction mechanism A–S_E2 also operates in the case of derivatives **1d–g**.

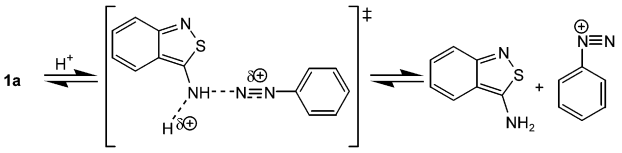
3. Experimental

The ^{1}H and ^{13}C NMR spectra were recorded with Bruker AVANCE 500 spectrometer at 500.13 (^{1}H) and 125.77 MHz (^{13}C) in DMSO-d_6 at 25 °C. The ^{1}H and ^{13}C chemical shifts were referenced to the central peaks of solvent (δ (^{1}H) 2.55 and δ (^{13}C) 39.6 ppm, respectively). ^{13}C NMR spectra were measured in a standard way and by means of the APT (Attached Proton Test) pulse sequence to distinguish CH, CH_3 and CH_2, C_{quart}. Proton–proton connectivities were found by gs-COSY. Protonated carbon atoms were assigned by gs-HSQC and quaternary carbon atoms by gs-HMBC spectra. All NMR experiments were performed with the aid of the manufacturer's software.

The kinetic measurements were carried out on an HP UV/VIS 8453 Diode Array apparatus in 1 cm closable cells at 25 °C under pseudo-first order conditions (large excess of an acid). Suitable wavelength (470 nm) was chosen for the kinetic measurements. The cell was always charged with 2 ml acid solution and after attaining 25 °C, 10 μl methanolic solution of the substrate **1a–e** was

Table 3
Atomic charges at selected atoms of 3-methyl-3-phenyl-1-(5-nitrobenzo[*c*]-1,2-thiazol-3-yl)triazene molecule calculated at B3LYP/TZVP level and ΔG of protonation related to the most basic isothiazole nitrogen

Site of protonation	Mulliken NBO charges		ΔG (kcal mol^{-1})		
	Gas phase	Aqueous solution	Gas phase	Aqueous solution	Solvation
N (isothiazole)	−0.16	−0.16	0	0	−61.9
O in NO_2	−0.18	−0.27	14.8	20.0	−56.7
NCH_3 (triazene)	0.02	−0.03	26.9	24.6	−64.1
S (isothiazole)	0.37	0.24	49.6	45.6	−65.9



Scheme 3.

added so that the resulting substrate concentration would be about 5×10^{-4} mol l^{-1}. The observed pseudo-first order rate constants k_{obs} were calculated from the measured time dependences of absorbance with help of an optimization program.

Quantum chemical computations were carried out with the Gaussian 03 program [22] employing the hybrid density functional B3LYP [23]. Full geometry optimizations were performed by using the TZVP basis set [24]. The nature of the stationary points was verified by analytical computations of harmonic vibrational frequencies. Solvation effects were included using the polarizable continuum model (PCM) [25]. A Natural Bond Orbital (NBO) analysis [26] was invoked using the population keyword in Gaussian 03.

3.1. Diazotization of 3-amino-2,1-benzisothiazole in nitrosylsulfuric acid

Solid $NaNO_2$ (3.48 g; 0.05 mol) was added in small portions to 25 ml 96% sulfuric acid (0.45 mol) with stirring and cooling at such a rate as to prevent the formation of nitrous gases. The solution was stirred and slowly heated to 70 °C until complete dissolution of the present salts. Then it was cooled with stirring to 25–30 °C, and 7.5 g (0.05 mol) of 3-amino-2,1-benzisothiazole was gradually added, whereupon the reaction mixture was stirred at 25–30 °C for another 3 h.

3.1.1. 1-(2,1-Benzisothiazol-3-yl)-3-ethyl-3-phenyltriazene (**1b**)

A solution of *N*-ethylaniline (6.36 g, 0.0525 mol) and emulsifier (sodium C_{12}–C_{13} alkyltriethoxysulfate, 1 g) in 99% acetic acid (10 mL) was added with stirring into a mixture of $CH_3COONa \cdot 3H_2O$ (68 g, 0.5 mol) in water (50 mL) and finely crushed ice (450 g). The emulsion obtained was stirred and treated with a solution of 2,1-benzisothiazol-3-diazonium hydrogensulfate in 96% sulfuric acid (0.05 mol) added drop by drop. The reaction mixture was stirred for another 3 h, whereupon the precipitated brown solid was collected by suction. The filter cake was washed with distilled water (500 mL) and dried at 60 °C. Yield of crude product 13.4 g (95%). TLC (Silufol; toluene/ethyl acetate, 5:1, v/v) showed that the azo coupling reaction product is a mixture of compounds **1b** and isomeric azo compound at a ratio of about 1:1. Mixture of triazene **1b** and azo compound was chromatographed on a column (SiO_2/toluene) and crystallized from cyclohexane. Triazene **1c** was prepared in the same way. Crude product (14.5 g, 94%) containing approximately 50% of triazene was chromatographed on a column (SiO_2/toluene) and crystallized from cyclohexane.

In the case of **1a** resulting crude mixture of triazene and azo (12.7 g; ratio 20:1) compound was extracted by ammonia/acetone (conjugated base of triazene **1a** is well soluble), diluted by water, neutralized by acetic acid and crystallized from acetone. Identity and purity of **1a**–**c** was checked by melting point, microanalysis and NMR spectroscopy.

Compound **1a**: yield: 6 g (47%), m.p. 154–157 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6, 298 K): $\delta = 8.41$ [d, $^3J = 8.6$ Hz, 1H, H-4], 7.84 [m, 1H, H-2′], 7.68 [d, $^3J = 8.8$ Hz, 1H, H-7], 7.58–7.59 [m, 2H, H-6, H-3′], 7.44 [m, 1H, H-4′], 7.30 [m, 1H, H-5], 14-15 [vbs, 1H, NH]. ^{13}C NMR (125.77 MHz, DMSO-d_6, 298 K): $\delta = 121.0$ (C-2′), 128.2 (C-4′), 129.7 (C-3′). Other signals are very broad. Anal. Calcd for $C_{13}H_{10}N_4S$: 61.40 (C), 3.96 (H), 22.03 (N), 12.61 (S). Found: 61.68 (C), 3.76 (H), 22.03 (N), 12.55 (S).

Compound **1b**: yield: 3.4 g (24%), m.p. 119–121 °C (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6, 298 K): $\delta = 8.01$ [d, $^3J = 8.6$ Hz, 1H, H-4], 7.67 [d, $^3J = 9.1$ Hz, 1H, H-7], 7.64 [m, 1H, H-2′], 7.56 [m, 1H, H-3′], 7.51 [m, 1H, H-6], 7.35 [m, 1H, H-4′], 7.28 [m, 1H, H-5], 4.56 [q, $^3J = 7.1$ Hz, 2H, CH_2], 1.37 [t, $^3J = 7.1$ Hz, 3H, CH_3]. ^{13}C NMR (125.77 MHz, DMSO-d_6, 298 K): $\delta = 11.0$ (CH_3), 41.5 (CH_2), 118.2 (C-2′), 121.0 (C-4), 121.8 (C-7), 123.8 (C-5), 125.7 (C-4′), 127.0 (C-3a), 129.8 (C-6), 129.8 (C-3′), 142.4 (C-1′), 161.7 (C-7a), 172.1 (C-3). Anal. Calcd for $C_{15}H_{14}N_4S$: 63.81 (C), 5.00 (H), 19.84 (N), 11.35 (S). Found: 63.54 (C), 4.95 (H), 19.89 (N), 11.35 (S).

Compound **1c**: yield: 3.3 g (21%), m.p. 64–66 °C. ^{1}H NMR (500.13 MHz, DMSO-d_6, 298 K): $\delta = 7.93$ [d, $^3J = 8.5$ Hz, 1H, H-4], 7.64 [d, $^3J = 8.9$ Hz, 1H, H-7], 7.58 [m, 1H, H-2′], 7.52 [m, 1H, H-3′], 7.47 [m, 1H, H-6], 7.30 [m, 1H, H-4′], 7.24 [m, 1H, H-5], 4.44 [t, $^3J = 7.4$ Hz, 2H, CH_2], 1.72 [sp, $^3J = 7.4$ Hz, 2H, CH_2], 1.42 [sx, $^3J = 7.4$ Hz, 2H, CH_2], 0.96 [t, $^3J = 7.4$ Hz, 3H, CH_3]. ^{13}C NMR (125.77 MHz, DMSO-d_6, 298 K): $\delta = 13.7$ (CH_3), 19.8 (CH_2), 27.5 (CH_2), 45.7 (CH_2), 118.1 (C-2′), 120.8 (C-4), 121.7 (C-7), 123.7 (C-5), 125.6 (C-4′), 127.0 (C-3a), 129.7 (C-6), 129.7 (C-3′), 142.6 (C-1′), 161.7 (C-7a), 171.9 (C-3). Anal. Calcd for $C_{17}H_{18}N_4S$: 65.78 (C), 5.84 (H), 18.05 (N), 10.33 (S). Found: 65.68 (C), 5.66 (H), 18.22 (N), 10.42 (S).

Commercially available 3-amino-2,l-benzisothiazole (Synthesia a.s., Czech Republic) was crystallized from toluene, m.p. 176–178 °C (Ref. [20] gives m.p. 178–179 °C) a its purity was checked by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR (500.13 MHz, DMSO-d_6, 298 K): $\delta = 7.80$ [dd, $^3J = 8.6$ Hz, $^4J = 0.7$ Hz, 1H, H-4], 7.30 [dd, $^3J = 8.9$ Hz, $^4J = 0.6$ Hz, 1H, H-7], 7.25 [ddd, $^3J = 8.9$, 6.2 Hz, $^4J = 1.2$ Hz, 1H, H-6], 6.83 [ddd, $^3J = 8.6$, 6.2 Hz, $^4J = 1.0$ Hz, 1H, H-5], 7.77 [b, 2H, NH_2]. Chemical shifts of all protons are slightly concentration dependent. ^{13}C NMR (125.77 MHz, DMSO-d_6, 298 K): $\delta = 173.2$ (C3), 160.8 (C7a), 129.3 (C6), 121.6 (C4), 120.6 (C7), 119.4 (C3a), 117.9 (C5) in accordance with Ref. [27].

Acknowledgment

The authors thank to Petr Jansa (UOCHB Prague) for computational calculations and the Ministry of Education, Youth and Sports of the Czech Republic (Project No. MSM 002 162 7501) for financial support.

References

[1] Kimball DB, Haley MM. Angew Chem Int Ed 2002;41:3338–51.
[2] Rouzer CA, Sabourin M, Skinner TL, Thompson EJ, Wood TO, Chmurny GN, et al. Chem Res Toxicol 1996;9:172–8.
[3] Connors TA, Goddard PM, Merai K, Ross WCJ, Wilman DEV. Biochem Pharmacol 1976;25:241–6.
[4] Nicolaou KC, Boddy CNC, Li H, Koumbis AE, Hughes R, Natarajan S, et al. Chem—Eur J 1999;5:2602–21.
[5] Ang HG, Koh LL, Yang GY. J Chem Soc Dalton Trans 1996:1573–81.
[6] Kirmse W, Seipp U. Chem Ber 1974;107:745–58.
[7] Zollinger H. Diazo chemistry I. Aromatic and heteroaromatic compounds. Weinheim: Wiley VCH; 1994 [chapter 13.2] p. 391–444.
[8] Clusius K, Weisser HR. Helv Chim Acta 1952;35:1524–7.
[9] Shine HJ. In: Zollinger H, editor. MTP International Reviews of Science. Organic chemistry, series one, vol. 3. London: Butterworth; 1973. p. 83.
[10] Saunders KH, Allen RML. Aromatic diazo compounds. 3rd ed. London: Arnold; 1985.
[11] Přikryl J, Lyčka A, Bertolasi V, Holčapek M, Macháček V. Eur J Org Chem 2003: 4413–21.
[12] Přikryl J, Černý M, Bělohlavová H, Macháček V, Lyčka A. Dyes Pigments 2007; 72:392–402.
[13] Hughes ED, Ingold CK. Quart Rev Chem Soc 1952;6:34.
[14] Beneš J, Beránek V, Zimprich J, Vetešník P. Collect Czech Chem Commun 1977; 42:702–10.
[15] Svoboda P, Pytela O, Večeřa M. Collect Czech Chem Commun 1986;51:553–63.
[16] Jones CC, Kelly MA, Sinnott ML, Smith PJ, Tzotzos GT. J Chem Soc Perkin Trans II 1982:1655–64.

[17] Pytela O, Svoboda P, Večeřa M. Collect Czech Chem Commun 1987;52:2492–9.
[18] Isaacs NS, Rannala E. J Chem Soc Perkin Trans II 1974:899–902.
[19] McClelland RA, Modro TA, Goldman MF, Yates K. J Am Chem Soc 1975;97:5223–31.
[20] Meyer RF, Cummings BL, Bass P, Collier HOJ. J Med Chem 1965;8:515–9.
[21] Perrin DD. Dissociation constants of organic bases in aqueous solution. London: Butterworths; 1965. p. 58–59.
[22] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 03 (revision B.4). Pittsburgh, PA: Gaussian, Inc.; 2003.
[23] (a) Becke AD. Phys Rev A 1988;38:3098–100;
(b) Lee C, Yang W, Parr RG. Phys Rev B 1988;37:785–9;
(c) Becke AD. J Chem Phys 1993;98:5648–52.
[24] Schafer A, Horn H, Ahlrichs R. J Chem Phys 1992;97:2571–7.
[25] (a) Miertus S, Scrocco E, Tomasi J. Chem Phys 1981;55:117–29;
(b) Cossi M, Scalmani G, Rega N, Barone V. J Chem Phys 2002;117:43–54.
[26] Reed AE, Curtis LA, Weinhold F. Chem Rev 1988;88:899–926.
[27] Gorelik MV, Lomzakova VI, Khamidova EA, Kuznetsova MG. Zh Org Khim 1996;32:1734–41.