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Stable Triazenes Derived from 2-Alkylaminonaphthalenes and 5-Nitrobenzo[*c*]-1,2-thiazole-3-diazonium Hydrogensulfate

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Dedicated to the memory of Professor Otto Exner

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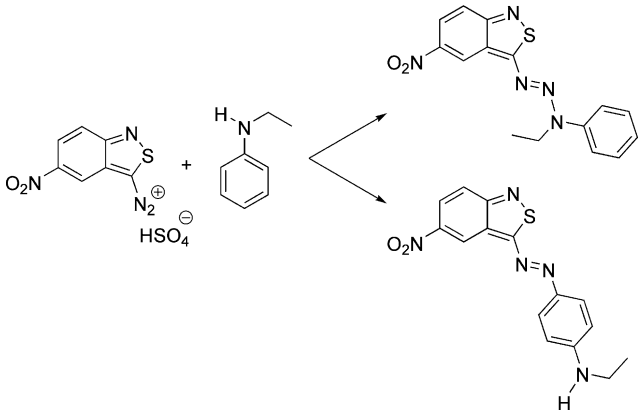
A calculation using the DFT method confirmed that the extraordinary stability of the triazenes formed by an azo coupling reaction of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium with primary or secondary aromatic amines is caused by the fact that these substances are protonated at the heterocyclic nitrogen atom and not at the nitrogen atom of the triazene grouping –N=N–N(R)Ar. Stable triazenes are also formed by reaction of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium with 2-alkylaminonaphthalenes. In the cases of the azo coupling reaction with 2-methylamino- and 2-ethylaminonaphthalene, the content of triazenes is almost 50 % in the product mixture with the isomeric azo compounds. The structures of the triazenes were confirmed by X-ray analysis.

Introduction

In our previous papers we described the formation of extraordinarily stable triazenes by the reaction of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium hydrogensulfate with primary and secondary anilines and their 3-chloro and 3-methyl derivatives.[1–3] We found that the azo coupling reaction of the said anilines with this diazonium salt gives a mixture of triazenes **1** in addition to azo compounds **2** (i.e. the expected isomeric azo dyestuff). Triazenes **1** are formed as the major products in yields reaching up to 95%; for example, see the azo coupling with *N*-ethylaniline (Scheme 1). The proportion of isomeric azo compounds **2** increased up to 50% only in the reactions of the above-mentioned diazonium salt with diphenylamine, 3-methylaniline, and 3-methyl-*N*-alkylanilines (Scheme 1).



Scheme 1.

Triazenes **1** are extraordinarily stable in acid media. Half lives of their decomposition to the diazonium salt and amine in 0.5 mol L^{-1} H_2SO_4 in aqueous acetic acid (1:1 v/v) are in the order of magnitude of hours.[1,3] 1,3-Diaryltriazenes in the benzene series decomposed at a measurable rate in aqueous ethanol (20% v/v) in buffers at room temperature already at pH <7. For example, 1,3-diphenyltriazene decomposes in the medium mentioned at pH 6 with a half life of 7 min.[4]

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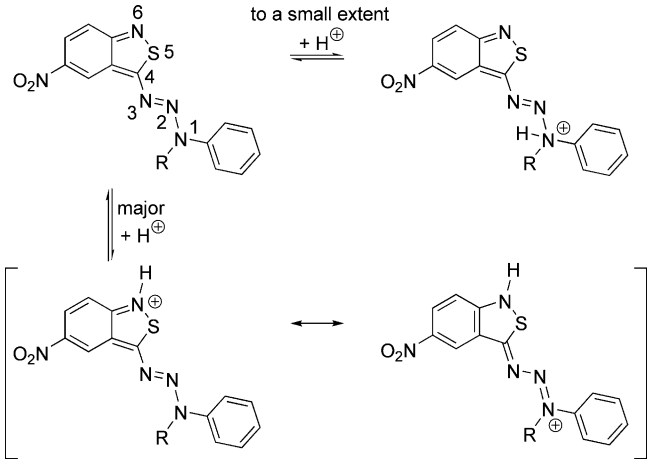
The decomposition of triazenes **1** obtained by azo coupling with *N*-alkylanilines gives the original 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium, whereas the decomposition of triazenes derived from primary anilines produces substituted benzenediazonium salts and 3-amino-5-nitrobenzo[*c*]-1,2-thiazole.[1,3] The reason for the extraordinary stability of triazenes **1** probably lies in the fact that they are protonated at a different site in comparison to the protonation of common 1,3-diaryltriazenes: whereas 1,3-diaryltriazenes are protonated at the nitrogen atom adjacent to the azo group,[4–6] triazenes **1** are presumably protonated mostly at the heterocyclic nitrogen atom,[1–3] which leads to the formation of a structure stabilized by a classic benzene ring (Scheme 2). However, this presumption cannot be confirmed experimentally. Therefore, the aim of this work is to study the structure and stability of triazenes **1** by means of quantum-chemical methods.



Scheme 2.

In the benzene series, triazenes are formed by azo coupling with anilines in neutral to slightly acidic media. According to Zollinger,[6] *N*-alkylnaphthylamines do not give triazenes under such conditions. Štěrba[7] also states that the main reaction of naphthylamines with diazonium salts is C coupling. Bagal[8] presumes that the primary attack of the nitrogen atom of the diazonium group takes place at the nitrogen atom of the naphthylamines, but the triazenes in the naphthalene series are unstable and have been neither isolated nor identified so far. The reluctance of naphthylamines to produce triazenes by the azo coupling reaction is obviously due to the lower aromaticity of naphthalene relative to that of benzene and, hence, also the lower activation energy of the azo coupling reaction in the aromatic ring. Therefore, the reversible azo coupling reaction at the nitrogen atom does not make itself felt. Only Abezgauz et al.[9] reported a diazotization reaction of heptafluoro-2-naphthylamine giving the product of elemental composition $C_{20}HN_3F_{14}$ corresponding to 1,3-bis(heptafluoronaphthalen-2-yl)triazene. In the presence of sodium 2-naphtholate, this compound gives 1-(heptafluoronaphthalen-2-yl)diazenyl-naphthalen-2-ol. Of course, heptafluoro-2-naphthylamine does not possess any C–H group to allow the azo coupling reaction in the aromatic ring. The high inclination of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium to undergo the azo coupling reaction to give stable triazenes allows the possible formation of triazenes in the case of the azo coupling reaction with naphthylamines to also be considered. In order to avoid complications with potential reaction at the 2- and 4-positions in the azo coupling with 1-naphthylamine, we chose 2-(*N*-alkyl)naphthylamines as the substrates. The azo coupling reaction of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium hydrogensulfate with 1-(2-hydroxyethylamino)naphthalene was described by Georgiadou and Tsatsaroni,[10] who did not mention any formation of potential triazene besides the expected azo compound, viz. 3-[4-*N*-(2-hydroxyethylamino)naphthalen-1-yldiazenyl]-5-nitrobenzo[*c*]-1,2-thiazole.

Results and Discussion

Calculations

The stability of triazenes **1** in acid media has been ascribed to a different site of protonation of these substances[1–3] in comparison to common 1,3-diphenyltriazenes. Protonation at the heterocyclic nitrogen atom (Scheme 2) has been proposed. In order to verify this hypothesis, DFT calculations were performed for the model compound 3-methyl-3-phenyl-1-(5-nitrobenzo[*c*]-1,2-thiazol-3-yl)triazene. The calculations were performed by using the hybrid exchange-correlation functional B3LYP[11,12] and valence-triple-ζ basis set with polarization functions (TZVP).[13] The effect of water as the solvent was investigated by using the polarizable continuum model (PCM).[14] Natural bond orbital analysis (NBO, Version 3.1)[15] was used for discussion of atomic charges. Calculations were performed with the Gaussian 03 program suite.[16]

The relative stability of various products of protonation were calculated for 3-methyl-3-phenyl-1-(5-nitrobenzo[*c*]-1,2-thiazol-3-yl)triazene in the gas phase and in aqueous solution (Table 1). The solvent effect does not change the relative stabilities of the individual protonated forms (Table 1). The results of these calculations unambiguously indicate that the protonation preferably takes place at the heterocyclic nitrogen atom (N6, atom-numbering scheme is defined in Scheme 2). Triazene protonated at this site is more stable by 103 kJ mol^{-1} than the same compound pro-

Table 1. Relative energies [kJ mol^{-1}] of 3-methyl-3-phenyl-1-(5-nitrobenzo[*c*]-1,2-thiazol-3-yl)triazene molecule protonated at various positions with respect to the energy of most stable species (protonated at N6); calculation at the B3LYP/TZVP level (for notation see Scheme 2).

Site of protonation	Gas phase	Solution
N6	0.0	0.0
O	62.0	83.7
N1	112.6	103.4
S5	207.7	190.9

tonated at the nitrogen atom of the triazene grouping (N1). In fact, the protonation on N1 is even less likely than protonation at the nitro group oxygen atom (about 20 kJ mol^{-1} difference in stability of triazene protonated at the N1 and O atoms).

Atomic charges at selected atoms calculated for gas-phase and solvated triazene (by using Mulliken, NBO, and ESP analysis) are summarized in Table 2. The electron density on the N1 triazene nitrogen atom is significantly lower than that on the N6 heterocyclic nitrogen atom and that on the O atom of the nitro group (NBO analysis for the solvated triazene). Thus, protonation on the N6 heterocyclic nitrogen atom appears to be the most likely on the basis of orbital population analysis; this is in very good agreement with predictions based on the calculated stabilities of individual protonated forms.

Table 2. Atomic charges at selected atoms of 3-methyl-3-phenyl-1-(5-nitrobenzo[*c*]-1,2-thiazol-3-yl)triazene molecule calculated at the B3LYP/TZVP level (for notation see Scheme 2).

Atom	Mulliken (gas phase)	Mulliken (solution)	NBO (solution)	ESP (solution)
N6	–0.16	–0.16	–0.61	–0.55
O	–0.18	–0.27	–0.41	–0.49
N1	0.02	–0.03	–0.11	0.47
S5	0.37	0.24	0.62	0.14

On the basis of relative energies calculated at the DFT level, triazenes of the 3-methyl-3-phenyl-1-(5-nitrobenzo[*c*]-1,2-thiazol-3-yl)triazene type are protonated in acid media predominantly at the heterocyclic nitrogen atom. The results of NBO analysis of Lewis structures of this protonated form show a double bond between N1–N2 and between N3–C4. The Wiberg bond indices calculated for the N1–N2, N2–N3, and N3–C4 bonds are 1.436, 1.421, and 1.296, respectively.

As a result of its high energy, the form that can decompose to give the diazonium ion is present at only a negligible concentration, which explains the stability of the triazene in acid medium. The results of DFT calculations confirm the previously formulated hypothesis[1–3] about the protonation site and explain the unexpected stability of these triazenes in acid media.

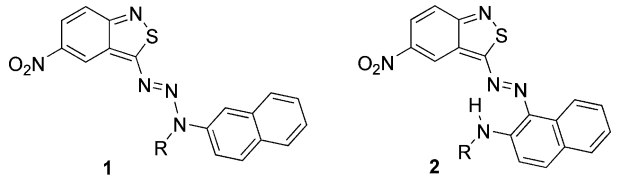
Reaction of 5-Nitrobenzo[*c*]-1,2-thiazole-3-diazonium Hydrogensulfate with 2-Alkylaminonaphthalenes

The reaction of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium hydrogensulfate with 2-(but-1-ylamino)naphthalene gives two products differing on TLC (Silufol; toluene/ethyl acetate, 5:1): an orange substance ($R_F \approx 0.7$) and a blue substance ($R_F \approx 0.6$) (Table 3). The products were separated on preparative scale on the basis of solubility differences in acetone (see Experimental Section). Elemental analysis indicates that they are isomers (Table S1).

Table 3. Electron spectra in chloroform of triazenes **1a**–**d** and azo compounds **2a**–**d**.

Compound	λ_{max} [nm]	ε [L g^{-1} cm^{-1}]	ε [L mol^{-1} cm^{-1}]
1a	478	67.67	24590
1b	481	75.60	28533
1c	483	73.05	29620
1d	480	67.33	26490
2a	628	80.08	29102
2b	629	82.50	31173
2c	632	76.20	30897
2d	631	78.33	30818

The compounds were identified by means of their ^{1}H NMR spectra. On the basis of the presence of an AMX system of the protons of the naphthalene residue {δ = 7.75 (d, 1′-H), 7.78 (dd, 3′-H), 7.91 (d, 4′-H) ppm, ^3J = 8.9 Hz, ^4J = 2.3 Hz, Table S2}, the orange substance was assigned the structure of triazene **1c** (Figure S1). The 3′-H and 4′-H protons of the naphthalene residue of the blue substance form two doublets with δ = 7.05 (d, 3′-H), 7.78 (d 4′-H) ppm, ^3J = 9.4 Hz. This compound was identified as azo compound **2c** (Figure S2). Also, 2-methylaminonaphthalene, 2-ethylaminonaphthalene, and 2-(2-hydroxyethylamino)naphthalene behaved similarly as 2-(but-1-ylamino)naphthalene in their azo coupling reactions with 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium hydrogensulfate (Scheme 3). In all the cases, the reactions produced mixtures of triazenes **1a**,**b**,**d** and azo compounds **2a**,**b**,**d**. The ratios of triazenes to azo compounds in the azo coupling products are presented in Table S1. Because of the very low solubility of both triazenes **1a**–**d** and azo compounds **2a**–**d** in $CDCl_3$ and their near insolubility in [D$_6$]DMSO, high-quality ^{1}H NMR spectra could only be measured for triazenes **1a**,**b**,**c** and azo compounds **2b**,**c**. The ^{13}C NMR spectra were only measured with the above-mentioned triazenes and azo compound **2c**. The values of the δ(^{1}H) and δ(^{13}C) chemical shifts are presented in Table S2.



R = CH_3 (**a**), C_2H_5 (**b**), *n*-C_4H_{10} (**c**), CH_2CH_2OH (**d**)

Scheme 3.

The chemical shifts of the protons of the heterocyclic residue in azo compounds **2b**,**c** differ from those of the same protons in the azo compounds prepared earlier by azo coupling reaction of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium hydrogensulfate with secondary amines of the benzene series.[3] These differences may be due to the existence of intramolecular hydrogen bonds in naphthalene derivatives **2b**,**c** [δ(NH) ≈ 12 ppm] and its absence in the benzene derivatives, or to a different position of the equilibrium for the azo–hydrazone tautomer in the two series of compounds (in connection with different solvent used; $CDCl_3$

vs. [D_6]DMSO). The calculation shows that azo compound **2b** is only present in the form containing an intramolecular hydrogen bond and a *trans* configuration at the azo group (Figure 1). The form without a hydrogen bond and the forms with *cis* arrangement at the azo group were not identified, not even as local minima at the potential energy surface. The carbon atoms of the naphthalene residue in compound **2c** exhibit very similar chemical shifts to those in 2-amino-1-phenyldiazenylnaphthalene[17] and 2-ethylamino-1-(4-nitrophenyldiazenyl)naphthalene (**3**) (Table S2). The ^{1}H NMR spectra of the aromatic protons of triazene **1c** and azo compound **2c** are given in Figures S1 and S2.

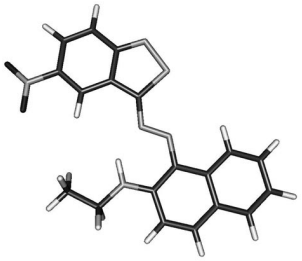


Figure 1. Structure of azo compound **2b** calculated by using the B3LYP/TZVP method.

The structures of triazenes **1b** and **1c** were confirmed by X-ray analysis. Azo compounds **2a**–**d** could not be prepared in the crystalline form that is needed for X-ray analysis. Triazenes **1a**–**d** are brilliant orange-red substances with λ_{max} ≈ 480 nm and high absorptivity, $\varepsilon_{max} \approx 2.8 \times 10^4$ L mol^{-1} cm^{-1}. Absorption spectra (Table 3, Figure S3) were measured in chloroform. The substances are not very soluble in other solvents (methanol, ethanol, acetone, ethyl acetate). Isomeric azo dyestuffs **2a**–**d** exhibit λ_{max} values around 630 nm: they are blue pigments with a strong green hue. The absorptivity $\varepsilon_{max} \approx 3.1 \times 10^4$ L mol^{-1} cm^{-1} is ca. 10% higher than that of the isomeric triazenes.

Solid-State Study

Selected bond lengths and angles are given in Figures 2 and 3. Compound **1b** crystallizes in the monoclinic space group, whereas **1c** crystallizes in an orthorhombic space group with two geometrically independent molecules in the crystal unit. Views of **1b** and **1c** (Figures 2 and 3) show an almost planar arrangement of both molecules where the triazene group adopts the C–N=N–N *trans* configuration. The interplanar dihedral angles in triazene and benzoisothiazole moieties are 4.9(1) (for **1b**) and 7.0(1), 11.8(1)° (for **1c**), whereas those between the triazene and the naphthyl ring are 2.9(1)° and 2.5(1), 2.9(1)° in **1b** and **1c**, respectively. The interplanar angles between both rings are 2.7(1) and 9.4(1), 13.6(1)°. These values are significantly smaller than those found for analogous phenyl derivatives.[1] All these values support the concept of highly extended conjugation between the heterocyclic and triazene moieties. Small values of the dihedral angles between the benzoisothiazole ring and the nitro group [5.7(1) and 4.5(1), 4.7(1)° for **1b** and **1c**, respectively] are additional proof for high resonance contribution to a structure of resonance hybrid. A couple of values of parameters for triazene **1c** belong to two independent molecules in the crystal unit. For numbering of atoms see Figures 2 and 3.

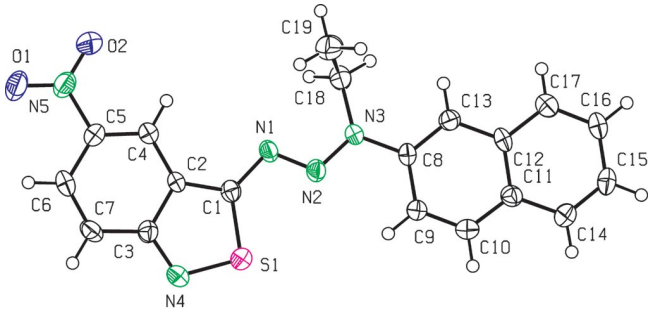


Figure 2. ORTEP view of triazene **1b** showing the thermal ellipsoids at 50% probability; selected bond lengths [Å] and angles [°]: S1–N4 1.646(3), S1–C1 1.707(3), N1–1.279(4), N1–C1 1.379(4), N4–C3 1.338(4), N3–N2 1.323(4), N3–C8 1.412(4), N3–C18 1.483(4), O1–N5 1.214(4), N5–O2 1.224(4), N5–1.457(4); N4–S1–C1 96.50(16), N2–N1–C1 111.0(3), C3–N4–S1 108.9(2), N2–N3–C8 116.0(3), N2–N3–C18 120.0(3), C8–N3–C18 123.8(3), N1–N2–N3 114.4(3), N1–C1–C2 124.1(3), N1–S1–127.8(2), C2–C1–S1 108.1(3), O1–N5–O2 122.8(3), O1–N5–C5 119.0(3), O2–N5–C5 118.2(3), C4–C5–N5 118.6(3), C6–C5–N5 118.3(3), C13–C8–N3 120.2(3), N3–C8–C9 120.1(3), N4–C3–C7 124.5(3), N4–C3–C2 115.9(3), N3–C18–C19 111.9(3).

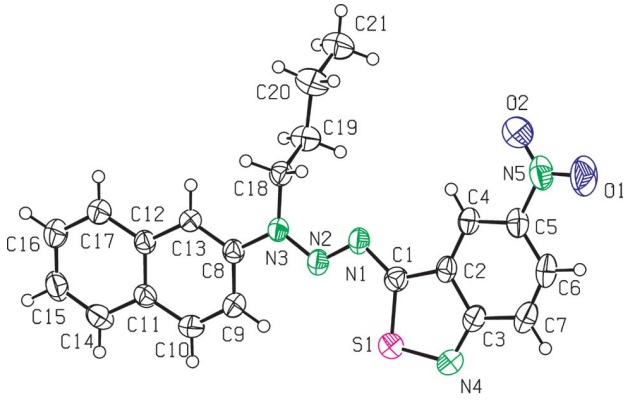


Figure 3. ORTEP view of one of two independent molecules of triazene **1c** showing the thermal ellipsoids at 50% probability; selected bond lengths [Å] and angles [°]: S1–N4 1.651(3), S1–C1 1.706(3), S1′–N4′ 1.644(3), S1′–C1′ 1.708(4), N3–N2 1.314(4), N3–C8 1.419(4), N3–C18 1.480(4), N3′–N2′ 1.320(4), N3′–C8′ 1.429(4), N3′–C18′ 1.473(4), N1–N2 1.295(4), N1–C1 1.372(4), N2′–N1′ 1.284(4), N1′–C1′ 1.363(4), C3–N4 1.325(5), N5–O2 1.200(5), N5–O1 1.213(4), N5–C5 1.473(5), N4′–C3′ 1.336(5), N5′–O2′ 1.212(6), N5′–O1′ 1.230(5), N5′–1.477(6); N4–S1–C1 97.12(16), N4′–S1′–C1′ 96.95(17), N2–N3–C8 116.1(3), N2–N3–C18 121.2(2), C8–N3–C18 122.7(3), N2′–N3′–C8′ 115.7(3), N2′–N3′–C18′ 121.1(3), C8′–N3′–C18′ 123.1(3), N2–N1–C1 109.7(3), N1′–N2′–N3′ 114.3(3), N2′–N1′–C1′ 110.7(3), N1–N2–N3 114.8(3), C13–C8–N3 120.5(3), C9–C8–N3 119.3(3), N4–C3–C7 123.9(3), N4–C3–C2 117.5(3), C3–N4–S1 108.1(2), C13′–C8′–N3′ 120.5(3), C9′–C8′–N3′ 119.7(3), N1′–C2′–124.5(3), N1′–C1′–S1′ 128.3(3), C2′–C1′–S1′ 107.2(3), C20–C19–C18–113.6(3), N3–C18–C19 111.9(3), N3′–C18′–C19′ 112.0(3), O2–N5–O1 124.5(4), O2–N5–C5 118.7(3), O1–N5–C5 116.8(4), N1–C1–C2 124.4(3), N1–C1–S1 127.7(3), C2–C1–S1 107.9(2), C4–C5–N5 118.3(3), C6–C5–N5 118.6(3), C3′–N4′–S1′ 108.8(3), C10′–C9′–C8′ 120.3(3), N4′–C3′–C2′ 116.1(3), N4′–C3′–C7′ 124.6(4), C2′–C7′–119.2(4), O2′–N5′–O1′ 123.7(5), O2′–N5′–C5′ 118.8(4), O1′–N5′–C5′ 117.5(5), C4′–C5′–N5′ 117.6(4), C6′–C5′–N5′ 118.9(4).

The π conjugation through both aromatic rings (benzoisothiazole and naphthyl ones) and the triazene moiety is further supported by delocalization of electron density within the triazene moiety. The lengthening of the N1=N2 bond lengths, at 1.279(4) for **1b** and 1.295(4), 1.284(4) Å for **1c**, relative to the standard N=N distance of 1.24 Å[18] is similar to that found for phenyl derivatives studied previously.[1] Further similarities with structure of previously published compounds were found in the shortening of the N2–N3 distances, at 1.323(4) for **1b** and 1.314(4), 1.320(4) Å for **1c**, relative to the N(sp^2)–N(sp^3) single bond of 1.40 Å,[18] and they are attributable to the resonance inherent in the triazene moiety. All studied and comparative compounds[19–25] display close delocalization within the triazene moieties, and structures **1b** and **1c** display C1–N1 bond lengths of 1.379(4) and 1.372(4), 1.363(5) Å, which are much shorter than the standard C(aryl)–N single bond (1.44 Å[18]).

These data, together with the resonance within the C1=C2–C3=N4 atomic chain, provide evidence that the benzoisothiazole ring takes part significantly in the triazene π conjugation. Furthermore, compounds **1b** and **1c** each display a shortening of the N3–C8 bond [1.412(4) for **1b** and 1.419(4), 1.429(4) Å for **1c**] with respect to the standard N(sp^3)–C(sp^2) distance of 1.44 Å,[18] which is attributable to a small extension of triazene delocalization to the N3–C8 bond, where C8 belonging to the naphthyl group is almost coplanar with the triazene moiety.

Both molecules of **1b** and **1c** display a layered structure without classical H-bonding connections but by π–π stacking or short contacts between the nitro group of one molecule and the methyl fragment of the alkyl group of the other one with interplanar distances of 3.390 and 3.470 Å for **1b** and 3.467 Å for **1c**; supramolecular architectures are shown in Figures S4 and S5. Compound **1c** shows a cavity in area between the alkyl chain and the benzoisothiazole moiety (Figure S6).

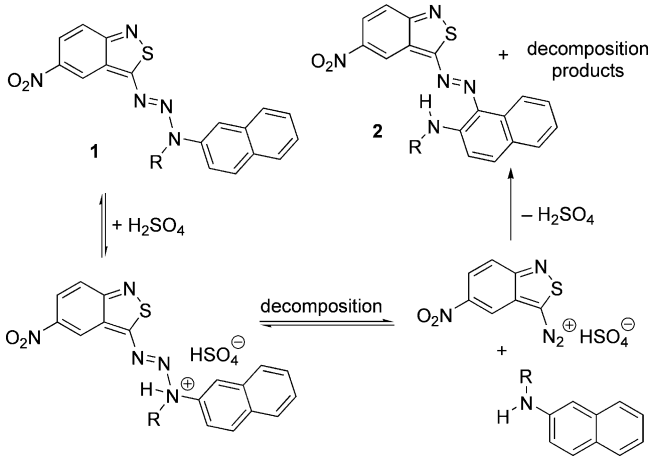
Decomposition of Triazenes 1a–d in Acid Media

Like in the case of the earlier described triazenes obtained by the azo coupling reaction of 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium with *N*-alkylanilines,[1,3] triazenes **1a–d** formed by azo coupling with 2-alkylaminonaphthalenes also exhibit unexpected stability in acid medium. In the solution of 1 mol L^{-1} H_2SO_4 in aqueous acetic acid (1:1 v/v), these compounds decompose with half lives of up to several tens of hours at 25 °C (Table 4). The decomposition half lives of individual triazenes **1a–d** considerably differ, and these differences cannot be explained by polar or steric effects of the *N*-alkyl groups. The differences may be due to the preservation of certain supramolecular structures of compounds containing hydrophobic naphthalene rings in strongly polar media (H_2O, H_2SO_4, CH_3COOH). A certain difference between molecular arrangements of ethyl and butyl derivatives **1b** and **1c** in crystals was confirmed by X-ray analysis, but the ^1H NMR spectra of these compounds measured in less polar $CDCl_3$ did not prove the existence of different structures in solution: both the derivatives have almost identical spectra in the aromatic region. We continue to deal with this problem.

Table 4. Kinetic parameters for the decomposition of triazenes **1** in H_2SO_4 (1 mol L^{-1}) in aqueous CH_3COOH (1:1, v/v) at 25 °C.

Triazene	Rate constant k [h^{-1}]	Half life $t_{1/2}$ [h]
1a	2.005×10^{-2}	34.58
1b	28.190×10^{-2}	2.46
1c	4.937×10^{-2}	14.04
1d	4.889×10^{-2}	14.18

The decomposition of triazenes derived from secondary amines in acid medium produces the original 5-nitrobenzo[*c*]-1,2-thiazole-3-diazonium, which can (to a small extent) undergo the azo coupling reaction in the aromatic ring of the amine formed by the decomposition of triazene (Scheme 4). However, this reaction is of little probability, as the concentration of the amine formed in the solution during kinetic measurements is very low and the amine is in effect present only in its unreactive protonated form.



Scheme 4.

Therefore, the predominant part of the diazonium salt undergoes decomposition. If 4,5-dihydroxynaphthalene-2,7-disulfonate (which is able to react in the sense of azo coupling even in acidic medium) is added to the reaction mixture, it acts as a scavenger for the diazonium salt and produces a new azo compound ($\lambda_{max} \approx 570$ nm). Spectral records of decomposition of triazene **1c** in the presence of 4,5-dihydroxynaphthalene-2,7-disulfonate, in its absence, and the kinetic curve of decomposition of this triazene are presented in Figures S7–S9. The identity of azo compound **2c** formed during decomposition of triazene **1c** in the absence of 4,5-dihydroxynaphthalene-2,7-disulfonate was proved chromatographically.

Conclusions

DFT calculations confirmed the hypothesis that 1-(5-nitrobenzo[*c*]-1,2-thiazol-3-yl)-3-alkyl-3-phenyltriazenes are protonated at the nitrogen atom of the isothiazole ring. The nitrogen atom adjacent to the azo group [–N=N–N(R)Ar]

is protonated very little, which explains the high stability of these triazenes in acidic media. Strong inclination of the 5-nitrobenzo[*c*]-1,2-thiazol-3-diazonium cation to undergo azo coupling reactions with aromatic primary and secondary aromatic amines at the nitrogen atom was also manifested by the fact that triazenes are formed by the reaction of this diazonium cation with 2-alkylaminonaphthalenes. The structure of triazenes of this so far unknown type was confirmed by ^{1}H and ^{13}C NMR spectroscopy and X-ray structure analysis.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance spectrometer at 500.13 (^{1}H) and 125.77 MHz (^{13}C) in $CDCl_3$. ^{1}H and ^{13}C chemical shifts (Table S2) were referenced to TMS. All 2D experiments (gradient-selected gs-COSY, gs-HSQC, gs-HMBC) were performed by using the software of the manufacturer (XWINNMR 3.1). Proton–proton connectivities were found by using gs-COSY. Protonated carbon atoms were assigned by gs-HSQC and quaternary carbon atoms by gs-HMBC spectra.

X-ray data for crystals of compounds **1b** and **1c** (Table 5) were obtained at 150 K by using an Oxford Cryostream low-temperature device with a Nonius Kappa CCD diffractometer and Mo-K_α radiation (λ = 0.71073 Å), a graphite monochromator, and ϕ and the χ scan mode. Date reduction were performed with the Denzo-SMN package.[26] The absorption was corrected by integration methods.[27] Structures were solved by direct methods (SIR92)[28] and refined by full-matrix least-squares based on F^2 (SHELXL-97).[29] Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of 1.5 U_{eq} for the methyl moiety, with C–H = 0.96, 0.97, and 0.93 for the methyl, methylene, and hydrogen atoms in the aromatic ring, respectively. CCDC-632632 for (**1b**) and -610595 (for **1c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The electron spectra were measured with a diode array spectrophotometer Hewlett Packard 8453. The molar absorption coefficients were determined by using ca. 5×10^{-5} mol L^{-1} solutions of the substances in chloroform (Table 3). The stability of the triazenes in acidic media was measured with the use of ca. 3×10^{-5} mol L^{-1} solution of the substance in 1.0 mol L^{-1} H_2SO_4 in aqueous acetic acid (1:1, v/v) at 25 °C. A similar experiment was carried out in the presence of 4,5-dihydroxynaphthalene-2,7-disulfonic acid of 2.5×10^{-3} mol L^{-1} concentration.

The starting 2-alkylaminonaphthalenes were prepared by the Bucherer reaction of 2-naphthol with primary alkylamines in aqueous solution of $NaHSO_3$ under pressure in an autoclave in pressure vessels with Teflon lining of laboratory dyeing apparatus Linitest (Original Hanau Comp.) as in the case of 2-ethylaminonaphthalene. A 250-mL cooled pressure vessel was charged with 2-naphthol (14.4 g, 0.1 mol), $Na_2S_2O_5$ (47.75 g, 0.25 mol), ethylamine (22.5 g, 0.5 mol) and ice (70 g). The closed pressure vessel was agitated in the apparatus at 150 °C for 10 h. The course of conversion was monitored by TLC (Silufol; *n*-heptane/acetone, 5:3, v/v). After 10 h, 2-naphthol completely disappeared from the reaction mixture. The reaction mixture was diluted with water and heated to boiling. The aqueous layer was removed, and the organic phase was repeatedly washed with water. After dilution with dichloromethane, drying, distilling off of volatile components, and vacuum distillation, the product (16.2 g, 95%) was sufficiently pure for subsequent application.

Table 5. Crystallographic data for triazenes **1c** and **1d**.

Compound	**1c**	**1d**
Empirical formula	$C_{19}H_{15}N_5O_2S$	$C_{21}H_{19}N_5O_2S$
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pca*21
a [Å]	7.4000(14)	45.5310(5)
b [Å]	8.3910(12)	4.8850(14)
c [Å]	14.081(3)	17.519(3)
α [°]	94.208(12)	90
β [°]	98.864(15)	90
γ [°]	96.809(12)	90
Z	2	8
V [Å^3]	854.1(3)	3896.6(13)
$D_{calcd.}$ [g cm^{-3}]	1.468	1.382
Crystal size [mm]	0.4 × 0.3 × 0.2	0.57 × 0.128 × 0.067
Crystal form	red block	red needle
μ [mm^{-1}]	0.216	0.195
F (000)	392	1696
h; *k*; *l* range	–9, 9; –10, 10; –18, 18	–58, 56, –5, 6, –22, 21
θ range [°]	2.95; 27.5	3.55; 27.5
Reflns measured	17076	34882
– indep. (R_{int})[a]	3910 (0.1601)	8610 (0.0657)
– obs. [$I > 2\sigma(I)$]	1808	7020
Parameters refined	244	523
Max/min $\Delta\rho$ [e Å^{-3}]	0.353/–0.327	0.271/–0.337
GOF[b]	1.025	1.173
R[c]/wR [c]	0.0693/0.1167	0.0584/0.1305

[a] $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$. [b] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data. [c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for observed data, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

For the preparation of 2-methylaminonaphthalene, a 40% aqueous solution of methylamine was used. *n*-Butylamine and ethanolamine were used as neat liquids. The preparation and diazotization of 3-amino-5-nitrobenzo[*c*]-1,2-thiazole was previously described.[1]

1-(5-Nitrobenzo[*c*]-1,2-thiazol-3-yl)-3-ethyl-3-(naphthalen-2-yl)triazene (1b) and 3-(2-*N*-Ethylaminonaphthalen-1-yldiazenyl)-5-nitrobenzo[*c*]-1,2-thiazole (2b): A solution of 2-ethylaminonaphthalene (9.67 g, 0.0525 mol) and emulsifier (sodium C_{12}–C_{13} alkyltriethoxysulfate, 2 g) in 99% acetic acid (10 mL) was added with stirring to 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 5-nitrobenzo[*c*]-1,2-thiazole-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 the temperature of 60 °C. Yield of crude product 16.2 g (86%). TLC (Silufol; toluene/ethyl acetate, 5:1, v/v) showed that the azo coupling reaction product is a mixture of compounds **1b** and **2b** in a ca. 1:1 ratio. The molar ratio of product **1b**/**2b** 46:54 was then estimated by HPLC. The more soluble triazene **1b** was separated from azo dyestuff **2b** by repeated extraction of the mixture with boiling acetone and subsequent dilution of the extract with aqueous (ca. 5%) ammonia. The separated precipitate of triazene was then purified by repeated recrystallization from chloroform (m.p. 241–242 °C). Azo dyestuff **2b** was obtained from the residue after extraction of triazene by repeated recrystallization from chloroform (m.p. 262–263 °C).

Analogous procedures were used for the preparation of **1a**, **1c**, **1d**, **2a**, **2c**, and **2d**. The electron spectra of compounds **1a**–**d** and **2a**–**d** are described in Table 3; the elemental analyses, melting points, and ratios of components in crude reaction mixture after the azo coupling reaction are presented in Table S1.

Supporting Information (see footnote on the first page of this article): Analytical data, ^{1}H and ^{13}C NMR spectroscopic data, ^{1}H NMR and UV VIS spectra of the compounds **1c**, **2c**; supramolecular architecture of compounds **1b**, **1c** in crystals; spectral records of decomposition of triazene **1c** in acidic media.

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