Structure and Reactivity of 3,3-Disubstituted 1-(5-Nitro-2,1-benzisothiazol-3-yl)triazenes

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The reaction between 5-nitro-2,1-benzisothiazole-3-diazonium species and *N*-substituted anilines produces the 1-(5-nitro-2,1-benzisothiazol-3-yl)-3,3-disubstituted triazenes **1**. These triazenes are highly stable, and even in strongly acidic medium (0.5 molL^{-1} H_2SO_4) they are only slowly decomposed back to the diazonium ion and substituted anilinium ion (for the *N*-ethyl derivative in 0.5 mol·L^{-1} H_2SO_4 at 25 °C, $t_{1/2} \approx 7$ h). A series of six triazenes were characterised by their ^1H and ^{13}C NMR spectra and mass spectra. Two of the triazenes were also identified by X-ray crystallography.
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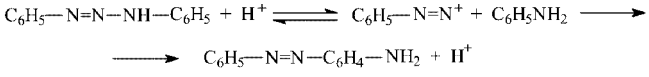
Introduction

1,3-Diaryltriazenes, derivatives of the hypothetical triazene $HN{=}N{-}NH_2$, are formed through substitution of a proton by a diazonium ion in anilines or *N*-substituted anilines. Anilines and *N*-alkylanilines are ambident nucleophiles[1] and can react with the electrophilic diazonium ion at nitrogen or in the aromatic nucleus. The azo coupling reaction at nitrogen takes place in neutral to weakly alkaline media.[2] In acidic media, the azo coupling reaction at nitrogen is reversible, and so the triazenes are not stable in acids. They are protonated by acids at the amino group and decompose back to the aniline and diazonium ion.[2−4] This cleavage may be followed by azo coupling reaction in the nucleus of the aniline formed (Scheme 1).



Scheme 1

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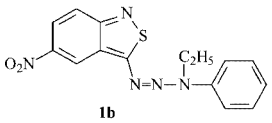
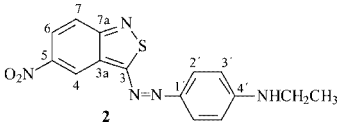
We have found that azo coupling reactions between 5-nitro-2,1-benzisothiazole-3-diazonium species and secondary aliphatic/aromatic amines and diphenylamine in acidic media produces triazenes that are surprisingly stable in such media and are split only very slowly. The structures of these substances are dealt with in this paper. The synthetic applications and mechanistic aspects of the reactions of triazenes are summarised in refs.[5,6]

Results and Discussion

An attempt to prepare 5-nitro-3-(4-ethylaminophenyl)-azo-2,1-benzisothiazole (**2**) through an azo coupling reaction between 5-nitro-2,1-benzisothiazole-3-diazonium ion and *N*-ethylaniline by a procedure analogous to that reported in ref.[7] did not produce the expected blue azo compound **2** but instead a high yield of an isomeric orange substance, identified by ^1H and ^{13}C NMR spectroscopy as 1-(5-nitro-2,1-benzisothiazol-3-yl)-3-ethyl-3-phenyltriazene (**1b**).



1b



2

The expected blue azo dyestuff **2**, the product of an azo coupling reaction in the aromatic nucleus, was only formed in traces and could not be obtained by a direct coupling reaction. We found out that 5-nitro-2,1-benzisothiazole-3-diazonium also reacts similarly with other *N*-alkylanilines and diphenylamine (Table 1).

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Table 1. Yields, melting points and elemental analyses of the prepared 3-substituted 1-(5-nitro-2,1-benzisothiazol-3-yl)-3-phenyltriazenes **1a**−**f** and azo dyestuff **2**

Compound	Yield %	M.p. °C	Empirical formula Mass	Elemental analysis data (calcd./found) % C	% H	% N	% S	% Cl
1a	76	217−218	$C_{14}H_{11}N_5O_2S$	53.32	4.15	22.21	10.17	−
$R^1 = CH_3$, $R^2 = H$			313.33	53.37	3.94	22.35	10.23	−
1b	84	170−171	$C_{15}H_{13}N_5O_2S$	55.04	4.00	21.39	9.79	−
$R^1 = C_2H_5$, $R^2 = H$			327.36	55.09	3.94	21.43	9.92	−
1c	31	181−182	$C_{19}H_{13}N_5O_2S$	60.79	3.49	18.66	8.54	−
$R^1 = Ph$, $R^2 = H$			375.40	60.99	3.53	18.83	8.42	−
1d	66	120−121	$C_{18}H_{19}N_5O_2S$	58.52	5.18	18.96	8.68	−
$R^1 = n$Bu, $R^2 = CH_3$			369.44	58.59	5.11	18.96	8.64	−
1e	52	185−187	$C_{17}H_{14}N_6O_2S$	55.73	3.85	22.94	8.75	−
$R^1 = C_2H_4CN$, $R^2 = CH_3$			366.40	56.18	3.85	23.16	8.33	−
1f	61	191−192	$C_{15}H_{12}ClN_5O_3S$	47.69	3.20	18.54	8.49	9.38
$R^1 = C_2H_4OH$, $R^2 = Cl$			377.81	47.95	3.18	18.68	8.40	9.54
2	84	228−230	$C_{15}H_{13}N_5O_2S$	55.04	4.00	21.39	9.79	−
$R^1 = CH_2CH_3$, $R^2 = H$			327.36	55.04	3.96	21.14	9.87	−

Azo compound **2** was prepared by means of a coupling reaction with the tertiary amine produced by temporary blocking of the NH group in *N*-ethylaniline with the labile CH_2SO_3Na group and subsequent removal of this group after the completed azo coupling reaction.

The prepared triazenes **1** are characterised by their stabilities in acid medium, which is unusual for triazene derivatives.[8] They are cleaved only very slowly in acid media. Thus, in 0.5 mol·L^{-1} H_2SO_4 in aqueous acetic acid (1:1, v/v; this mixture was used because of the complete insolubility of triazene **1b** in aqueous sulfuric acid) at 25 °C, it was possible to observe only a very slow decrease in the absorbance of the absorption band at $\lambda_{max.}$ = 477 nm. In order to verify that the decrease in the absorbance of the triazene is due to its reverse decomposition to the diazonium ion and *N*-ethylanilinium, the same experiment was carried out in the presence of 4,5-dihydroxynaphthalene-2,7-disulfonic acid at a concentration 80 times that of the triazene. 4,5-Dihydroxynaphthalene-2,7-disulfonic acid can act as a scavenger for the diazonium ion even in very strongly acidic solution, in which it does not react as a naphtholate but as a non-dissociated naphthol. We have found that the decrease in absorbance at the triazene $\lambda_{max.}$ (477 nm) is accompanied by an increase in absorbance at 579 nm, the spectra intersecting at an isosbestic point (Figure 1). The solution of azo coupling product prepared from 5-nitro-2,1-benzisothiazole-3-diazonium and 4,5-dihydroxynaphthalene-2,7-disulfonic acid in 0.5 mol·L^{-1} H_2SO_4 in aqueous acetic acid (1:1, v/v) shows the same spectral characteristics as observed after the decomposition of triazene towards the end of the reaction (Figure 1, spectrum 9). The decomposition of 3-ethyl-1-(5-nitro-2,1-benzisothiazol-3-yl)-3-phenyltriazene (**1b**) in 0.5 mol·L^{-1} H_2SO_4 in aqueous acetic acid (1:1, v/v) obeys first order kinetics (Figure 1), the reaction half-life determined from the decrease in the triazene absorbance being $t_{1/2}$ = 417 min. A very slow decomposition of triazene **1b** was also observed in a solution of the triazene in trifluoroacetic acid. In this case, however, only a small amount of azo compound **2** is formed,

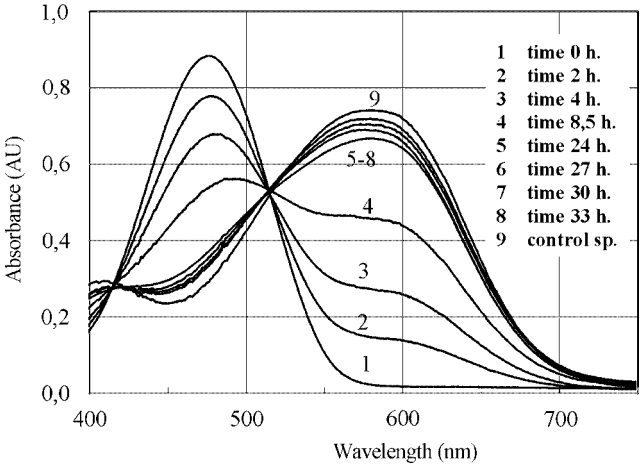

Figure 1. Spectral record of the decomposition of triazene **1b** in 0.5 mol·L^{-1} H_2SO_4 in aqueous acetic acid 1:1 (v/v) in the presence of 4,5-dihydroxynaphthalene-2,7-disulfonic acid (2.5×10^{-3} mol·L^{-1}) at 25 °C; the spectral recordings No. 1−8 were obtained at time intervals of 0, 2, 4, 8.5, 24, 27, 30 and 33 h from the moment of mixing of the solutions. Absorbance-time dependence $X(t) = [A(0) - A(\infty)]\cdot[1 - \exp(-k\cdot t)]$ at 477 nm; the parameters found for the initial absorbance $A(0) = 0.8836$ by non-linear regression are as follows: $A(\infty) = 0.28311$, rate constant $k = 1.66 \times 10^{-3}$ min^{-1} (decomposition half-life $t_{1/2} = \ln 2\cdot k^{-1} = 417$ min); spectrum No. 9 is of the azo coupling product obtained from 5-nitro-2,1-benzisothiazole-3-diazonium and 4,5-dihydroxynaphthalene-2,7-disulfonic acid in the same medium

since the coupling component is present at a very low concentration and, moreover, in its non-reactive protonated form.

The behaviour of 5-nitro-2,1-benzisothiazole-3-diazonium in its azo coupling reaction with *N*-ethylaniline in acid medium is consistent with the general mechanism of azo coupling reactions of anilines;[1] that is, the primary reversible attack of nitrogen by the electrophile is followed by an irreversible coupling reaction in the aromatic nucleus (Scheme 1). In the case of triazene **1b**, the acid-catalysed splitting is very slow, and the *N*-ethylanilinium formed does not undergo coupling in the strongly acid medium. How-

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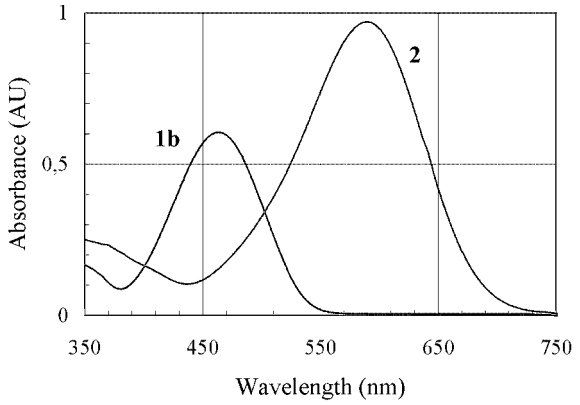
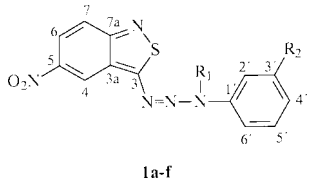


Figure 2. Electron spectra of triazene **1b** and azo compound **2** in methanol at concentrations of 2.45×10^{-5} mol·L^{-1}

ever, the formation of diazonium ion was established by its coupling reaction with 4,5-dihydroxynaphthalene-2,7-disulfonic acid.

The low cleavage rates of 3-alkyl-1-(5-nitro-2,1-benzisothiazol-3-yl)-3-phenyltriazenes **1** in acidic media can be explained by a difference in the protonation site, as compared with common triazenes. Triazenes are usually protonated at the nitrogen atom adjacent to the azo group, and then split off the diazonium ion (Scheme 1). In the case of 3-alkyl-1-(5-nitro-2,1-benzisothiazol-3-yl)-3-phenyltriazenes **1**, the basicity of the nitrogen atom in the NRPh group is lowered by conjugation with the nitrobenzisothiazole residue, while on the other hand the protonation at the heterocyclic nitrogen is facilitated by the formation of the energetically favourable benzene system. The protonation at the heterocyclic nitrogen atom, however, does not allow the diazonium ion to split off (Scheme 2).

It was impossible to determine the pK_a values of the conjugated acids formed by protonation at the heterocyclic and the *tert*-amine nitrogen atoms experimentally, but the increase in the basicity of the heterocyclic nitrogen N(1) is indicated by the formation of an intermolecular N···H−O hydrogen bond, which was verified by X-ray analysis of compound **1f**.



1a-f

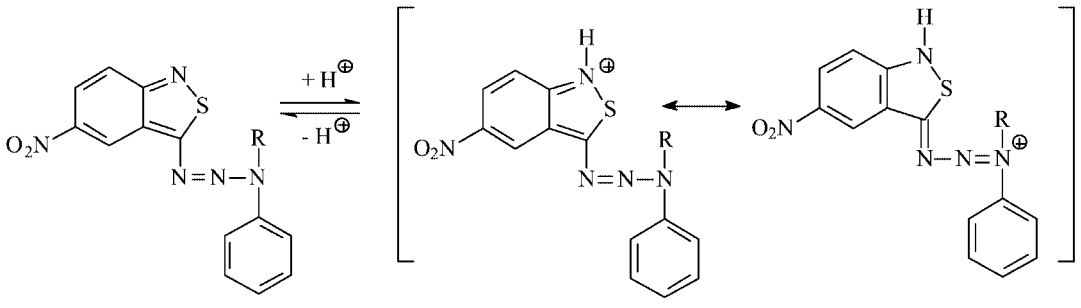
The $\lambda_{max.}$ and $\varepsilon_{max.}$ values of the prepared triazenes **1** (Table 1) in the visible region and the same parameters of azo dyestuff **2** are given in Table 2, together with APCI mass spectra. The electronic spectra of compounds **1b** and **2** measured in methanol are presented in Figure 2. Triazenes **1** exhibit absorption maxima at the wavelengths 457−468 nm with absorption coefficients 23000 to 25500 L/mol·cm, which makes them efficient chromophores. Although their colour strength does not reach that of azo chromophores, it is nevertheless higher than that of anthraquinone chromophores.

Azo compound **2**, a constitutional isomer of triazene **1b**, is a brilliant blue with the absorption maximum bathochromically shifted to 590 nm and a more intense colour strength, with $\varepsilon_{max.} \approx 70\%$ higher than that of triazenes **1**.

NMR Spectroscopy

Protons C(4)-H, C(6)-H and C(7)-H of compounds **1** resonate at the highest frequencies, due to the presence of a nitro group in the vicinity, giving a typical splitting pattern: proton C(4)-H is split into a doublet with $^4J_{H,H} \approx 2$ Hz, C(7)-H into a doublet with $^3J_{H,H} \approx 10$ Hz, and C(6)-H is split into a doublet of doublets with $J_{H,H} \approx 2$ and 10 Hz. A typical splitting pattern was also observed for the monosubstituted benzene ring. Proton−proton connectivities in compounds **1d**−**f**, possessing phenyl groups substituted by methyl or chlorine in position 3′, were determined by gs-COSY.

Proton-bearing carbon atoms were assigned unambiguously from gs-HSQC spectra and quaternary carbon atoms by analysis of data from gs-HMBC spectra. In the latter type of NMR spectra, the signal resonating at the highest frequency correlates with C(4)-H and so is C(3), the signal at $\delta \approx 161$ ppm gave appropriate cross-peaks with protons C(4)-H and C(6)-H and so belongs to C(7a), the *ipso* carbon of the phenyl group C(1′) correlates with the protons



Scheme 2

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Table 2. Electron spectra in methanol and APCI mass spectra of triazenes **1a**−**f** and azo dyestuff **2**

Compound	Electron spectra $\lambda_{max.}$ (nm)	$10^{-4}\cdot\varepsilon_{max.}$ (L/mol·cm)	APCI mass spectra Positive ion	Negative ion
1a $C_{14}H_{11}N_5O_2S$ *Mw* = 313	461	2.36	$[M + H]^+$ (*m/z* = 314, 100%) $[M + H - NO]^+$ (284) $[M + H - NO - N_2]^+$ (256)	$M\cdot^-$ (*m/z* = 313, 43%) $[M - CH_3]^-$ (298) $[M - CH_3 - N_2]^-$ (270) $[C_7H_3O_2N_2S]^-$ (179,100%)
1b $C_{15}H_{13}N_5O_2S$ *Mw* = 327	463	2.48	$[M + H]^+$ (*m/z* = 328, 100%) $[M + H - NO]^+$ (298) $[M + H - NO - N_2]^+$ (270)	$M\cdot^-$ (*m/z* = 327, 50%) $[M - CH_3CH_2]^-$ (298) $[M - CH_3CH_2 - N_2]^-$ (270) $[C_7H_3O_2N_2S]^-$ (179, 100%)
1c $C_{19}H_{13}N_5O_2S$ *Mw* = 375	467	2.50	$[M + H]^+$ (*m/z* = 376, 100%) $[M + H - N_2]^+$ (348) $[M + H - NO_2]^+$ (330) $[M + H - N_2 - NO]^+$ (318)	$M\cdot^-$ (*m/z* = 375, 1%) $[M - N_2]^-$ (347) $[C_7H_3O_2N_2S]^-$ (179, 100%)
1d $C_{18}H_{19}N_5O_2S$ *Mw* = 369	468	2.35	$[M + H]^+$ (*m/z* = 370, 100%) $[M + H - NO]^+$ (340) $[M + H - NO - N_2]^+$ (312)	$M\cdot^-$ (*m/z* = 369, 95%) $[M - CH_3CH_2CH_2CH_2]^-$ (312) $[M - CH_3CH_2CH_2CH_2 - N_2]^-$ (284) $[C_7H_3O_2N_2S]^-$ (179, 100%)
1e $C_{17}H_{14}N_6O_2S$ *Mw* = 366	457	2.55	$[M + H]^+$ (*m/z* = 367, 100%) $[M + H - NO]^+$ (337) $[M + H - NO - N_2]^+$ (309)	$M\cdot^-$ (*m/z* = 366, 37%) $[M - CH_2CH_2CN]^-$ (312) $[M - CH_2CH_2CN - N_2]^-$ (284) $[C_7H_3O_2N_2S]^-$ (179, 100%)
1f $C_{15}H_{12}N_5O_3SCl$ *Mw* = 377	458	2.30	$[M + H]^+$ (*m/z* = 378, 100%) $[M + H - NO]^+$ (348) $[M + H - NO - N_2]^+$ (320)	$M\cdot^-$ (*m/z* = 377, 39%) $[M - N_2]\cdot^-$ (349) $[M - CH_2CH_2OH]^-$ (332) $[M - CH_2CH_2OH - N_2]^-$ (304) $[C_7H_3O_2N_2S]^-$ (179, 100%)
2 $C_{15}H_{13}N_5O_2S$ *Mw* = 327	590	3.96	$[M + H]^+$ (*m/z* = 328)	$M\cdot^-$ (*m/z* = 327)

of the R^1 group, etc. Both the ^1H and the ^{13}C signals of two phenyl groups in compound **1c** are broadened, probably by restricted rotation. The NMR spectroscopic data are collected in Table 3.

The subspectra of the heterocyclic systems in both the ^1H and the ^{13}C NMR spectra of triazenes **1** and azo compound **2** are almost identical and all the proton and carbon signals are sharp. The phenyl group protons in triazenes **1** give broadened signals. This broadening can probably be explained by partially hindered rotation around the N(2)−N(3) bond, the magnitude of which is increased by a contribution of the polar resonance structure to the resonance hybrid of the molecule. Simultaneously, the bond order of azo group N(1)=N(2) is lowered (Scheme 3).

The same effect is also manifested in the ^{13}C NMR spectrum of azo compound **2**. While the carbon atoms of the heterocyclic skeleton and carbon atoms C(1′) and C(4′) give sharp signals at room temp., the signals of carbon atoms C(3′), C(5′) and particularly C(2′) and C(6′) are so broad that they only could be identified in the spectrum after very long accumulation (δ_C = 113 ppm and 128 ppm). In the molecule of azobenzene in the solid phase, the rotation of the phenyl group around the N−C bond is hindered. The anisotropy of the azo group makes itself felt, which causes considerable anisochronism of the chemical shifts of the carbon atoms in the *ortho* positions {for azobenzene: δ_C = 130.7 ppm [C(2′), C(3′) and C(5′)] and δ_C = 117.9 ppm [C(6′)], $\Delta\delta(^{13}C)$ = 12.8 ppm, ref.[9]} It is presumed that the N−N bond order in the molecule of azo compound **2** is lowered due to the resonance (Scheme 4), and that, on the other hand, the N−C(Ar) bond order is increased. This also produces a partial hindrance to rotation around the N−C(Ar) bond, although the restriction of rotation is not as strong as it is in the solid phase, and only makes itself felt in a broadening of the signals of the C(3′) and C(5′) carbon atoms and a large broadening of the signals of the C(2′) and C(6′) carbon atoms. The ^{13}C NMR spectrum of azo compound **2** at 330 K, unlike that determined at room temp., shows a distinct narrowing of the originally broad signals, greater narrowing being observed with the signals of carbon atoms C(3′)and C(5′) (δ_C = 112.8 ppm) than with those of C(2′) and C(6′) (δ_C = 128.2 ppm). This means that even room temp. is higher than the coalescence temperature T_c.

Atmospheric Pressure Chemical Ionization Mass Spectrometry

The positive-ion APCI mass spectra (Table 2) enabled unambiguous molecular weight determination due to the presence of protonated molecules $[M + H]^+$, which are the base peaks of the spectra for all compounds studied. Furthermore, the presence of the nitro group is characterized by low-abundance loss of neutral NO molecules typical of compounds containing nitro groups. The neutral loss of NO

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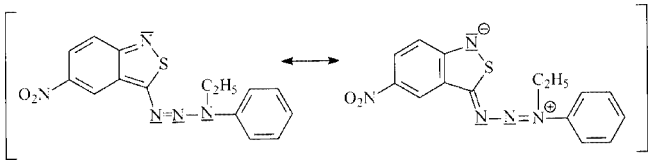
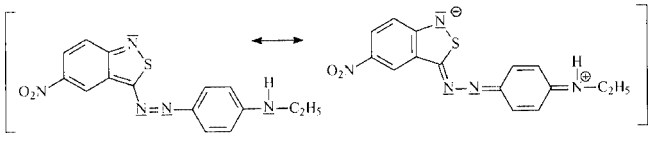
Table 3. ^1H and ^{13}C shifts of compounds **1a**−**f** in [D_6]DMSO

Pos.	**1a**		**1b**		**1c**		**1d**		**1e**		**1f**	
No.	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
3	–	178.62	–	178.68	–	177.53	–	178.56	–	177.49	–	177.64
3a	–	124.84	–	124.82	–	125.15	–	124.71	–	125.19	–	124.99
4	8.97	119.48	8.91	119.39	8.36	119.10	8.86	119.51	9.01	119.71	8.86	119.10
5	–	143.20	–	143.16	–	143.48	–	143.17	–	143.53	–	143.34
6	8.21	122.79	8.19	122.77	8.16	122.90	8.17	122.72	8.18	122.90	8.17	122.67
7	7.84	122.92	7.82	122.90	7.82	122.90	–	178.56	–	177.49	–	177.64
7a	–	161.55	–	161.54	–	161.44	–	124.71	–	125.19	–	124.99
1′	–	143.20	–	142.05	–	[a]	8.86	119.51	9.01	119.71	8.86	119.10
2′	7.72	119.20	7.71	118.99	[a]	[a]	–	143.17	–	143.53	–	143.34
3′	7.61	129.75	7.60	129.91	[a]	[a]	8.17	122.72	8.18	122.90	8.17	122.67
4′	7.43	126.86	7.42	126.82	[a]	[a]	7.79	122.85	7.81	122.75	7.80	122.75
5′	7.61	129.75	7.60	129.91	[a]	[a]	–	161.49	–	161.50	–	161.35
6′	7.72	119.20	7.71	118.99	[a]	[a]	–	142.28	–	142.08	–	144.46
R^2	–	–	–	–	–	–	7.51	119.29	7.55	119.63	7.79	119.10
$R^{1[b]}$	4.01	35.61	4.65	42.56	[a]	[a]	–	139.51	–	139.47	–	133.87
			1.42	11.12	[a]	[a]	7.23	127.56	7.24	127.60	7.41	126.02
					[a]	[a]	7.44	129.66	7.47	129.62	7.58	131.00
					[a]	[a]	7.49	116.33	7.52	116.41	7.70	117.94
							2.45	21.24	2.46	21.22	–	–
							4.60	46.76	4.87	42.81	4.66	50.51
							1.80	27.65	3.22	14.60	3.91	56.44
							1.47	19.84	–	118.77	5.20(OH)	–
							1.02	13.65				

[a] Phenyl groups are not equivalent and provide a complicated pattern both in ^1H and ^{13}C NMR spectra. [b] Arranged according to the increasing distance from nitrogen atom.



Scheme 3



Scheme 4

is followed by the loss of N_2 from the azo group. Surprisingly enough, the negative-ion APCI mass spectra of all compounds exhibit the radical anion $M^{\cdot -}$ instead of the usual deprotonated molecule $[M - H]^-$. The observed fragmentation paths can easily be correlated with the structure and permits the identification of functionality on the tertiary nitrogen atom (see Exp. Sect.). The typical feature of negative-ion APCI mass spectra is the stabilization of cyclic fragment ion $[O_2NC_6H_3NSC]^-$, producing the base peaks of all the spectra.

X-ray Structure Determinations

ORTEP[10] views of compounds **1c** and **1f** are shown in Figures 3 and 4, respectively. In both compounds the triazene group adopts the C−N=N−N *trans* configuration and is almost coplanar both with the 5-nitro-2,1-benzisothiazol-3-yl moiety and with the C8−C13 phenyl ring (for numbering see Figures 3 and 4). The interplanar dihedral angles in triazene and benzothiazole derivative are 8.6(1)° and 6.3(1)°, while those between the triazene and the C8−C13 phenyl ring are 12.0(1)° and 15.6(1)° in **1c** and **1f**, respectively. This arrangement allows an extended conjugation within both molecules, with a significant contribution of the polar resonance structure, shown in Scheme 3, to the fundamental molecular state. The lengthening of the N3=N4 double bond lengths, at 1.282(2) and 1.286(3) Å, relative to the standard N=N distance of 1.24 Å (ref.[11]), and the shortening of the N4−N5 distances, at 1.331(2) and 1.326(3) Å, relative to the N(sp^2)−N(sp^3) single bond of 1.40 Å (ref.[11]), are attributable to the resonance inherent in the triazene moiety. Table 4 shows a comparison of bond lengths in the current compounds and those in other structures of 1,3-diaryltriazenes and 1-aryl-3,3-dimethyltriazenes.[12−18] All compounds display close delocalizations within the triazene moieties, and structures **1c** and **1f** display C1−N3 bond lengths of 1.379(2) and 1.390(3) Å, much shorter than the standard C(aryl)−N single bond (1.44 Å, ref.[11]). These data, together with the resonance within the C1=C2−C7=N1 atomic chain, provide

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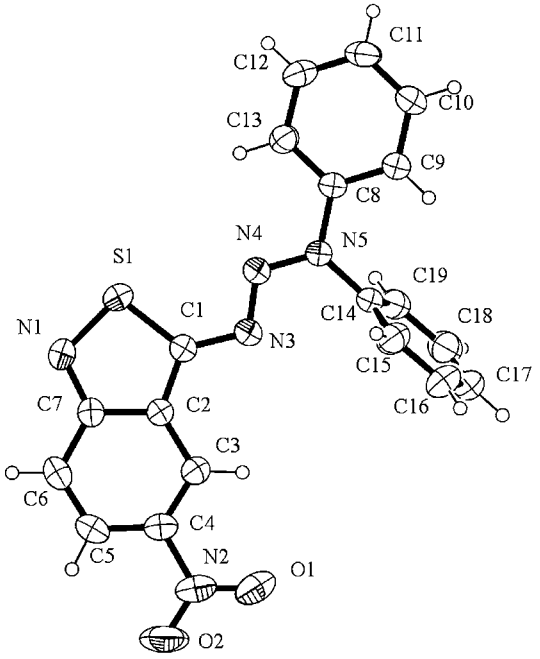


Figure 3. ORTEP view of compound **1c** showing the thermal ellipsoids at 40% probability; selected bond lengths (Å) and angles (°): S1−N1 1.643(2), S1−C1 1.705(2), N1−C7 1.338(2), C1−N3 1.379(2), C1−C2 1.397(2), C2−C3 1.407(2), C2−C7 1.427(2), C3−C4 1.358(2), C4−C5 1.410(3), C5−C6 1.352(3), C6−C7 1.425(3), N3−N4 1.282(2), N4−N5 1.331(2), N5−C8 1.426(2), N5−C14 1.448(2); N1−S1−C1 96.7(1), S1−N1−C7 108.8(1), S1−C1−C2 108.2(1), S1−C1−N3 128.3(1), N3−C1−C2 123.5(1), C1−C2−C7 109.9(1), N1−C7−C2 116.4(2), C1−N3−N4 111.5(1), N3−N4−N5 113.3(1), N4−N5−C8 117.1(1), N4−N5−C14 121.7(1), C8−N5−C14 120.9(1)

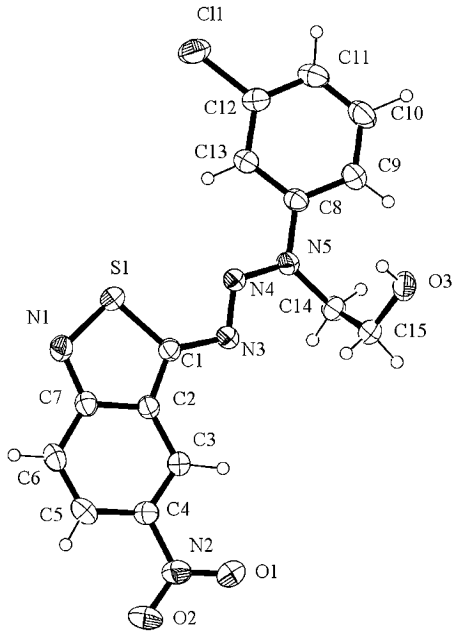
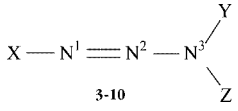


Figure 4. ORTEP view of compound **1f** showing the thermal ellipsoids at 40% probability; selected bond lengths (Å) and angles (°): S1−N1 1.651(2), S1−C1 1.706(2), N1−C7 1.345(3), C1−N3 1.390(3), C1−C2 1.395(3), C2−C3 1.415(3), C2−C7 1.434(3), C3−C4 1.354(4), C4−C5 1.423(4), C5−C6 1.349(4), C6−C7 1.424(4), N3−N4 1.286(3), N4−N5 1.326(3), N5−C8 1.421(3), N5−C14 1.472(3); N1−S1−C1 96.1(1), S1−N1−C7 109.2(2), S1−C1−C2 108.9(2). S1−C1−N3 126.5(2), N3−C1−C2 124.6(2), C1−C2−C7 109.8(2), N1−C7−C2 115.9(2), C1−N3−N4 109.9(2), N3−N4−N5 114.6(2), N4−N5−C8 115.4(2), N4−N5−C14 121.6(2), C8−N5−C14 123.0(2)

evidence that the benzothiazole ring takes part significantly in the triazene π-conjugation. Furthermore, compounds **1c** and **1f** each display a shortening of the N5−C8 bond (1.426(2) and 1.421(3) Å), with respect to the standard $N(sp^3)-C(sp^2)$ distance of 1.44 Å (ref.[11]), attributable to a small extension of triazene delocalization to the N5−C8 bond, where C8 belongs to the phenyl group almost coplanar with triazene moiety. Accordingly, the analogue N5−C14 bond length of 1.448(2) Å in **1c** is significantly longer, because C14 belongs to the C14−C19 phenyl ring rotated by 78.34(5)° with respect to the triazene plane. In 1,3-diaryltriazenes **3**−**7**, these N−C(aryl) distances, in the 1.39−1.40 Å range (Table 4), indicate greater involvement of the 3-phenyl ring in the triazene π-conjugation.

The molecules of **1f** form dimers linked by O3−H···N1 hydrogen bonds around centres of symmetry, as shown in Figure 5.

Table 4. Comparison of bond lengths in compounds **1c** and **1f** with those in 1,3-diaryltriazenes (compounds **3**−**7**: X = Ar, Y = Ar, Z = H) and 1-aryl-3,3-dimethyltriazenes (compounds **8**−**10**: X = Ar, Y = Me, Z = Me)



3-10

Compound	N^1-X	$N^1=N^2$	N^2-N^3	N^3-Y	N^3-Z
1c	1.379(2)	1.282(2)	1.331(2)	1.426(2)	1.448(2)
1f	1.390(3)	1.286(3)	1.326(3)	1.421(3)	1.472(3)
3, see ref.[12]	1.415(4)	1.267(4)	1.329(3)	1.389(4)	
4, see ref.[12]	1.420(8)	1.260(10)	1.339(7)	1.397(11)	
5, see ref.[13]	1.426(2)	1.261(2)	1.326(2)	1.393(2)	
6, see ref.[14]	1.422(7)	1.267(7)	1.332(7)	1.388(8)	
7, see ref.[15]	1.422(4)	1.274(3)	1.338(3)	1.391(4)	
8, see ref.[16]	1.415(2)	1.282(2)	1.307(2)	1.438(2)	1.454(2)
9, see ref.[17]	1.433(8)	1.282(8)	1.312(8)	1.470(9)	1.466(8)
10, see ref.[18]	1.418(1)	1.270(1)	1.316(1)	1.445(2)	1.446(2)

Experimental Section

3-Amino-5-nitro-2,1-benzisothiazole: Technical grade (Synthesia, a.s. Pardubice), was freed of traces of 2-amino-5-nitrobenzonitrile and 2-cyano-5-nitrobenzamide by heating in 85% sulfuric acid at 110 °C for 30 min. The solution was then diluted with water and alkalised to pH 10 by addition of aqueous ammonia. The obtained suspension was heated to boiling, hot filtered, washed on the filter with hot 3% ammonia, then with hot water until neutral, and dried at 105 °C. HPLC of the product did not reveal any side products. The substance does not melt up to 300 °C and decomposes above 300 °C, in accordance with ref.[19] ^{1}H NMR (500.13 MHz, [D$_6$]DMSO, 298 K): δ = 9.11 [d, $^4J_{H,H}$ = 2.2 Hz, 1 H, C(4)-H], 7.96 [dd, $^3J_{H,H}$ = 9.7 Hz, and $^4J_{H,H}$ = 2.2 Hz, 1 H, C(6)-H], 7.32 [d, $^3J_{H,H}$ = 9.7 Hz, 1 H, C(7)-H], 8.79 (broad s, 2 H, NH_2) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 178.85 [C(3)], 117.61

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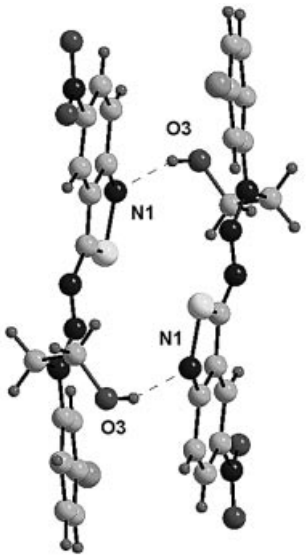

Figure 5. A perspective view of a dimer formed by the molecules of compound **1f** linked by O3−H···N1 hydrogen bonds. Hydrogen bond lengths (Å) and angles (°): O3−H 0.90(5), H···N1 2.08(5), O3···N1 (1 − *x*, −*y*, 1 − *z*) 2.927(3), O3−H···N1 158(4)

[C(3a)], 121.90 [C(4)], 138.27 [C(5)], 122.56 [C(6)], 120.68 [C(7)], 160.50 [C(7a)] ppm.

***N*-Substituted Anilines:** These coupling components were commercial products (Lachema, Fluka, or Sigma−Aldrich).

Preparation of Compound 1b

Diazotization of 3-Amino-5-nitro-2,1-benzisothiazole in Nitrosylsulfuric Acid: Sulfuric acid (96%, 25 mL, 0.45 mol) was cooled and stirred, and $NaNO_2$ (3.48 g, 0.05 mol) was added in small portions at such a rate as to avoid evolution of nitrous gases. The solution was stirred and slowly heated to 70 °C until complete dissolution of the salts. The solution of nitrosylsulfuric acid thus obtained was stirred and cooled to 25−30 °C, and 3-amino-5-nitro-2,1-benzisothiazole (9.77 g, 0.05 mol) was added, after which the reaction mixture was stirred at 25−30 °C for 3 h.

Azo Coupling Reaction of 5-Nitro-2,1-benzisothiazole-3-diazonium with *N*-Ethylaniline: *N*-Ethylaniline (6.36 g, 0.0525 mol) was dissolved in aqueous HCl (concd. 1 mol·L^{-1}, 60 mL, 0.06 mol). The solution was treated with charcoal (0.25 g) and Kieselguhr (0.25 g), and after 10 min stirring the solution was filtered. The filtrate, *N*-ethylanilinium chloride solution, was treated with emulsifier − sodium C_{12}-C_{13} alkyltriethoxysulfate (2 g) and $CH_3COONa·3H_2O$ (68 g, 0.5 mol) − with stirring. The obtained emulsion of *N*-ethylaniline was mixed with finely crushed ice (450 g), and the diazonium salt solution (0.05 mol) was then added with stirring. The reaction mixture was stirred for 3 h, after which the separated orange-brown precipitate of triazene **1b** was collected by suction. The filter cake was washed with distilled water (500 mL) and dried at 80 °C. Yield of raw product (12.4 g, 76% th.). The crude product was purified by repeated (3 ×) recrystallisation from acetone; m.p. 170−171 °C.

The other triazenes 1, except for triazene **1c**, were prepared in the same way. The yields, melting points and elemental analyses are given in Table 1.

Preparation of Compound 1c: Diphenylamine (8.88 g, 0.0525 mol) was dissolved in glacial acetic acid (25 mL, 0.43 mol); emulsifier − sodium C_{12}-C_{13} alkyltriethoxysulfate (4 g) − was added, and the solution was poured into a stirred mixture of $CH_3COONa·3H_2O$ (127 g, 0.94 mol), water (100 mL) and ice (500 g). The obtained emulsion of diphenylamine was treated with the diazonium salt solution (0.05 mol) (see above).

Preparation of Compound 2: Compound **2** was prepared by an azo coupling reaction between 5-nitro-2,1-benzisothiazole-3-diazonium and sodium *N*-ethyl-*N*-phenylaminomethanesulfonate and subsequent hydrolysis of the CH_2SO_3Na group. The sodium *N*-ethyl-*N*-phenylaminomethanesulfonate was prepared by treatment of *N*-ethylaniline with formaldehyde and sodium hydrogensulfite by a procedure analogous to that used in the preparation of other sodium α-aminoalkanesulfonates:[20,21] a solution of disodium disulfite (96 g, 0.505 mol) in water (350 mL) was stirred at room temp. and treated with aqueous formaldehyde (36%, 75 mL, 0.97 mol). The reaction mixture was kept at 65−70 °C for 1 h, the pH value of 7−8 being maintained by small additions of sodium carbonate or dilute sulfuric acid. With stirring, distilled *N*-ethylaniline (113 g, 0.93 mol) was gradually added, the pH value being maintained at 6−8.

The reaction mixture was stirred at 65−70 °C for 3 h, then heated to 95 °C, and treated at this temperature with NaCl (60 g) (salting out of product). The reaction mixture was then left to cool to room temp. and stirred overnight (15 h). The separated sodium *N*-ethyl-*N*-phenylaminomethanesulfonate was collected by suction. The obtained product paste was mixed with ethanol (300 mL) on filter, vacuum filtered, again washed with ethanol (150 mL) and again vacuum filtered to remove the unchanged *N*-ethylaniline, and the filter cake was dried at 40 °C. Yield 148.5 g product containing 78.7% sodium *N*-ethyl-*N*-phenylaminomethanesulfonate (nitrosation titration), i.e. yield 52.8% th. calculated on *N*-ethylaniline.

The diazonium salt solution was prepared in the way described above. Dry sodium *N*-ethyl-*N*-phenylaminomethanesulfonate (16 g, 0.053 mol) was dissolved in water (70 mL) and treated with stirring with $CH_3COONa·3H_2O$ (68 g, 0.5 mol) and ice (450 g). The diazonium salt solution (0.05 mol) was then added drop by drop, and the reaction mixture was stirred at room temp. for 3 h. After addition of HCl (36%, 100 mL, 1.16 mol) the reaction mixture was heated to 85−90 °C and stirred for ca 90 min. The hydrolysis course was monitored chromatographically (TLC: Alufol, *n*-hexane/acetone, 5:3). After completion of hydrolysis, the reaction mixture was allowed to cool to room temp., diluted with water (500 mL), and partially neutralised by addition of $NaHCO_3$ (110 g, 1.3 mol). The precipitated azo dyestuff **2** was collected by suction, and the filter cake was washed with water (500 mL) and dried. The yield of crude product **2** was (15.6 g, 95% th.). After repeated recrystallisation (3 ×) from ethanol m.p. 228−230 °C. ^{1}H NMR (500.13 MHz, [D$_6$]DMSO, 298 K): δ = 9.01 [d, $^4J_{H,H}$ = 2.4 Hz, 1 H, C(4)-H], 8.20 [dd, $^3J_{H,H}$ = 9.8 Hz, and $^4J_{H,H}$ = 2.4 Hz, 1 H, C(6)-H], 7.83 [d, $^3J_{H,H}$ = 9.8 Hz, 1 H, C(7)-H], 8.79 (triplet, $^3J_{H,H}$ = 5.5 Hz, 1 H, NH), 7.92 [part of AA′BB′ system of 1,4-disubstituted benzene, 2 H, C(2′)-H, C(6′)-H], 6.82 [part of AA′BB′ system of 1,4-disubstituted benzene, 2 H, C(3′)-H, C(5′)-H], 3.34 [doublet of quadruplet $J_{H,H}$ = 5.5 Hz and 7.2 Hz, 2 H, NCH_2], 1.28 (triplet, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO, 298 K): δ = 181.06 [C(3)], 126.36 [C(3a)), 119.39 [C(4)], 143.65 [C(5)], 122.87 [C(6)], 122.92 [C(7)], 161.98 [C(7a)), 143.37 [C(1′)], 128 [very broad signal, C(2′), C(6′)], 113 [broad signal, C(3′), C(5′)], 155.39 [C(4′)], 37.46 (NCH_2), 14.11 (CH_3) ppm.

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The electronic spectra were measured with a Hewlett−Packard 8453 diode array spectrophotometer. The molar absorption coefficients were determined on ca 5×10^{-5} mol·L^{-1} solutions of the substances in methanol (Table 2). The stability of triazene **1b** in acid medium was measured by use of a ca 3×10^{-5} mol·L^{-1} solution of the substance in 0.5 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 ^{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 [D$_6$]DMSO. The ^{1}H and ^{13}C chemical shifts (Table 3) were referenced to the central peaks of solvent (δ = 2.55 and 39.60 ppm, respectively). All 2D experiments (gradient-selected gs-COSY, gs-HSQC, gs-HMBC) were performed with the aid of the manufacturer's software (XWIN NMR 3.1). Proton−proton connectivities were found by gs-COSY. Protonated carbon atoms were assigned by gs-HSQC and quaternary carbon atoms by gs-HMBC spectra.

Atmospheric pressure chemical ionization (APCI) mass spectrometry (Table 2): individual samples were dissolved in 80% aqueous acetonitrile and injected into the same liquid and analysed on a quadrupole mass spectrometer Platform (Micromass, Manchester, UK) by use of both positive-ion and negative-ion atmospheric pressure chemical ionization (APCI) mass spectrometry under the following conditions: the ion source temperature was 100 °C, the APCI probe temperature was 300 °C, the cone voltage was 10 V for positive-ion APCI and 20 V for negative-ion APCI measurements.

Table 5. Crystal data

Structure	**1c**	**1f**
Empirical formula	$C_{19}H_{13}N_5O_2S$	$C_{15}H_{12}ClN_3O_3S$
Molecular mass	375.40	377.81
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/ Å	6.9659(2)	7.0275(3)
b/ Å	8.2357(2)	9.9995(5)
c/ Å	16.2357(6)	11.4618(6)
α /°	91.835(1)	88.700(2)
β /°	92.671(1)	88.866(2)
γ /°	108.590(1)	89.026(3)
V /Å^3	880.98(5)	804.96(7)
Z	2	2
$D_{calcd.}$ /g cm^{-3}	1.415	1.559
F(000)	388	388
μ /cm^{-1}	2.092	3.939
Temperature /K	295	295
Crystal form, colour	prism, red	plate, red
Crystal size /mm	0.07 × 0.24 × 0.36	0.03 × 0.12 × 0.35
$\theta_{min.}-\theta_{max.}$	3.0−27.5	2.9−27.5
Measured reflections	6677	5964
Range of *h,k,l*	−9,9; −10,10; −20,20	−9,9; −12,12; −14,14
Unique reflections	3956	3535
R_{int}	0.026	0.031
Obsd. reflections [$F^2>2\sigma(F^2)$]	3087	2898
$R(F^2)$ (obsd. reflections)	0.0441	0.0483
$wR(F^2)$ all reflections	0.1254	0.1296
No. parameters	296	274
GOF	1.069	1.126
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$	0.23; −0.22	0.34, −0.42

X-ray structure determinations: X-ray diffraction data for **1c** and **1f** were collected with a Nonius−Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). Data sets were integrated by use of the Denzo-SMN package.[22] The structures were solved by direct methods (SIR97)[23] and refined (SHELXL-97)[24] by full-matrix, least-squares with anisotropic non-H and isotropic hydrogen atoms. All other calculations were performed by use of PARST.[25] Crystal data are given in Table 5; selected bond lengths and angles are given in Figure 3−5.

CCDC-207356 and -207357 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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