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Syntheses of azulen-1-yl-benzothiazol-2-yl diazenes

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Abstract

Azulen-1-yl-benzothiazol-2-yl diazenes substituted at thiazole and/or at azulene moiety have been prepared by diazotization of the corresponding benzothiazol-2-ylamines in inorganic acid mixtures or dichloroacetic acid followed by diazonium salts' coupling with azulenes. The nitrosyl sulfate was also used for the synthesis of diazonium salts. The systematic substitution of pattern structure enabled us to study the interdependence between the polarity of different obtained chromophores and their physical characteristics such as the electronic and NMR spectra. Because the NLO response of chromophores is related to the compound solvatochromism, this property of diazenes was also taken into account.

Keywords: Azulene; Diazene; Azo; Benzothiazole; Dyes

1. Introduction

In the recent years, we have studied some azulenic diazenes in order to find materials with valuable technical properties. The electron donor properties of azulene moiety offer the possibility to build a push–pull azo system if an effective electron acceptor substitutes the second position of N=N. As electron acceptors, we have investigated pyridines and their *N*-alkylated salts [1] or *N*-oxides [2] and recently, thiazole and derivatives [3] were also used in azo push–pull systems together with azulenes. Some encouraging results about the optical properties were already obtained in the azulen-1-yl-pyridin-4-yl diazene series [4] and the researches were extended to other azulenic diazenes. According to the theoretical studies about the NLO phenomenon [5], both the bathochromic and solvatochromic effects arise when the electron acceptor five-membered rings such as thiophene, furan, pyrrole or thiazole replaces phenyl group in diazenes, suggesting an increase in their molecular hyperpolarizability. Therefore, the azoic dyes obtained when these groups are associated with azulene moiety could be tested for optical or electrical properties as well as liquid crystals. The high solvatochromic effect obtained for azulen-1-yl-thiazol-2-yl diazenes [3] enables us to suppose good NLO properties for these materials. However, their low stability with time does not allow their use in technical purposes. Some increase in the stability of products is obtained when the 4-position in thiazole moiety is substituted by phenyl and we believe that the same effect could be produced by benzo-annelation of thiazole as in benzothiazole structure.

The good push–pull properties of azulen-1-yl-quinolin-5-yl diazenes [4b] and the similar electronic requirements for quinoline and benzothiazole systems also encouraged us to investigate the azulen-1-yl-benzothiazol-2-yl diazenes. It is forecast theoretically and demonstrated experimentally that the replacement of the phenyl group with 2-benzothiazole in a diazene enhances the β values significantly [6,7], especially when an efficient electron withdrawing group (e.g. nitro) is present in the 6-position [8] (Scheme 1, Table 1).

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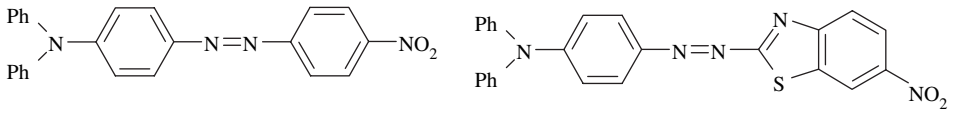


a **b**

Scheme 1.

2. Results and discussion

2.1. Synthesis of azulen-1-yl-benzothiazol-2-yl diazenes

Due to the known very low solubility of the weak base, benzothiazol-2-ylamine, it cannot be diazotized as usual in dilute mineral acids [7,9]. It was, however, diazotized in concentrated sulfuric or phosphoric acid; strong organic acids were also used. On the other hand, azulene, a relatively weak nucleophile, cannot be easily coupled in the strong acidic media used in the solubilization and diazotization of benzothiazol-2-ylamine. Therefore, we considered the procedure could be successfully used for the generation of azulene-1-azo-thiazoles, namely, the diazotization in a mixture of phosphoric and nitric acids and the diazonium salt coupling with azulene in a buffered medium (Scheme 2).

This method worked properly only for pattern amine and for 6-substituted benzothiazol-2-ylamine with poor electron donor or withdrawing groups (Table 1). The mixture of phosphoric and nitric acids reacted with 6-methoxy-benzothiazol-2-ylamine, yielding the desired diazonium salt, together with a mixture of 4-, 5- and 7-nitrated derivatives, **6a–c** (Scheme 3) [10].

However, because of the enhanced basicity of this amine, it could be diazotized using phosphoric acid only followed by buffered coupling with azulene derivative (with 83% conversion of azulene and 80% yield in diazene) (Table 2).

The increase in electron withdrawing capacity of the moiety to which a nitro group is attached in a favorable position suggested us to study the syntheses and the properties of azulen-1-yl-(6-nitro-benzothiazol-2-yl) diazenes. Because of the reversibility of nitrosation step, when nitro-benzothiazolamine was diazotized, the nitrosation of azulene took place extensively. Due to the low stability of nitroso-azulene, only 4% of diazene was obtained together with a high amount of tar. However, if the nitrosyl sulfate is used as the diazotization reagent and both the sulfate and amine are in excess towards azulene, despite the equilibrium of nitrosation, enough diazonium ions are formed to react with azulene. In dichloroacetic–acetic acid, using Sokolowska protocol [11], the coupling occurred quantitatively; however, the yield in diazenes depended largely on the excess of amine and nitrosyl sulfate: for 10, 100, and 200% excess, the reported yields for **3e** (based on azulene) were 26, 48, and 84%, respectively; the rest consisted of tar obtained by the polymerization of niroso-azulenes after the neutralization of the reaction mixture. If instead of acetic acid, an acetate buffer was used as the coupling medium, only tar would be obtained.

Table 1
Electrical moment, hyperpolarizability, absorption maxima and decomposition temperature [6–8] of diazenes represented in Scheme 1

Compound in Scheme 1	μ (D)	B (10^{-30} cm^5 esu^{-1})	λ_{max} (nm)	$\mu\lambda_{max}$	T_d (°C)
a	5.87	54.3	4.86	788	393
b	7.21	71.8	5.50	1390	356

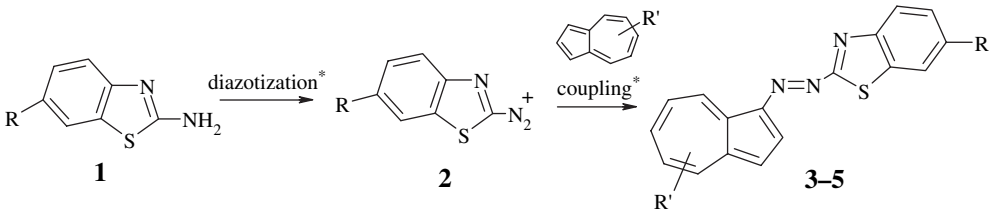
For increasing the donating power of azulene moiety and therefore its effect on the pull–push structure, some alkyl substituted azulene was also coupled with the diazotized benzothiazol-2-ylamine and with its 6-nitroderivative (Table 2). This substitution at both the aromatic systems allows the preparation of blue azo derivatives **4e** and **5e** (in organic solutions), a very rare color for this class of dyes.

2.2. Relationship between diazene structure and NMR spectra

Due to the similar electronic distribution in azulen-1-yl-thiazol-2-yl diazene, **7**, and in its corresponding 4-phenylated or benzoannulene derivative, **8** or **3**, respectively, the values for protons' chemical shifts of azulene moiety do not differ as indeed results from Table 3 (Scheme 4).

More interesting seems to be the comparison between the influence on the azulenic protons at the substitution of C-5′ in diazene **7** and C-6′ in diazene **3c** (Table 3). The difference between the δ values for diazene **3c** and its derivatives substituted at C-6′ with electron releasing or donating groups, **3b**, **3a** and **3d**, is insignificant. The same behavior presents the diazene **7** versus its chloro derivative. Another situation was encountered when C-6′ is substituted with the electron withdrawing NO_2 group, diazene **3e**. As shown in Table 4, the azulene protons, particularly the seven-membered ring protons, of the last compound are strongly deshielded when compared to the unsubstituted diazene **3c**. It is interesting to note that the deshielding values observed between these diazenes are similar to those observed when the C-5′ of compound **7** is substituted with NO_2. Therefore, the benzo-annelation seems to have a little importance in the electron distribution in molecule and the push–pull effect is conserved almost unchanged.

Here, two observations must be made in connection with the NLO properties. Regarding the resonance structures (Scheme 5), the distance between the charges in **3e** being longer as for **7**(NO_2), the electric moment of the first diazene must be higher, increasing the value of molecular hyperpolarizability. At the same time, the energy for transition **3e** (A) → **3e** (B), with the loss of benzene aromaticity, could be higher comparing the same transition for **7**(NO_2), counter-balancing the first effect on the hyperpolarizability. The importance of



*For reaction conditions see Table 1

	R = MeO,	Me,	H,	Cl,	NO_2
R' = H	**3a**	**3b**	**3c**	**3d**	**3e**
R'= 4,6,8-trimethyl			**4c**		**4e**
R'= 3,8-dimethyl-5-isopropyl			**5c**		**5e**

Scheme 2.

'closed' resonance structures as **3e** (C and D), with the participation of the non-bonding electrons of sulfur and nitrogen, is small because of their higher energy resulted by the loss of two aromatic moieties, benzene and azulene.

Results from Table 4 show that the protons at the benzo group are influenced mainly by the substituents at C-6′. Even when three methyl groups are substituted at the azulene moiety, as in diazene **4c**, the δ values of the benzo group protons remain almost unchanged.

From the results shown in Section 4, it can be seen that the ^{13}C chemical shifts for the synthesized diazenes generally obey the same rules as discussed for protons.

2.3. Optical properties of diazenes

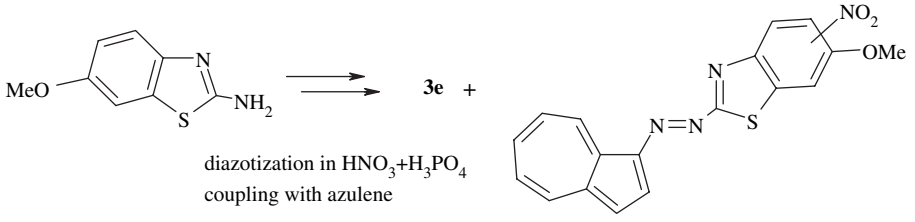
The UV–vis spectra recorded for azulen-1-yl-thiazol-5-yl diazene and for its 5-phenyl substituted and benzo derivative (Table 5) show a bathochromic shift in this series with $\Delta\lambda_{max} = 14$ and 24 nm, respectively, for the main visible band.

Since the main purpose of this paper was to obtain and study new chromophores with azulen-1-yl-benzothiazol-2-yl diazene structure possessing high push–pull properties, we have supposed that valuable information could be obtained by a systematic substitution at C-6′ with different electron demanding groups. As already shown, this position allows the best electronic conjugation over the whole molecule.

For the withdrawing or donating substituents, the values for all recording bands of different diazenes are similar; the slight bathochromic effect exerted by MeO is also encountered for other chromophores. As expected from the behavior of other diazenes studied by us, the nitro group produces a bathochromic shift. However, the value of $\Delta\lambda_{max}$ for the diazene tandem **3c–3e** (~18 nm, MeOH) is smaller than that observed for the benzothiazole diazene derived from *N*,*N*-disubstituted anilines (represented in Scheme 1 (~30 nm, EtOH)) [12] and even more smaller when compared with tandem **7–7**(NO_2) (~78 nm, MeOH) [3]. This difference confirms the above postulated supposition on the more reduced contribution of the resonance structure **3e** (B) (Scheme 5) compared to the similar structures for the two last mentioned nitro diazenes.

A higher bathochromic effect is generated by the azulene substitution with alkyl groups. A slight bathochromic shift due to the substitution with alkyl group is already reported for other azulene derivatives. For the chromophores studied, this substitution produces a more intense bathochromic effect due to the stabilization of the tropylium resonance structure for azulene moiety. For the unsubstituted benzothiazole moiety, limited bathochromic $\Delta\lambda_{max}$ values are observed: for tandem **3c–4c** and **3c–5c** the values are 2 and 23 nm, respectively. A highly dramatic increase in the bathochromic shift can be observed due to the nitration of C-6′. Thus, for tandem **4c–4e** and **5c–5e**, the values for $\Delta\lambda_{max}$ are 34 and 43 nm, respectively, surpassing the value for **3c–3e**. Why this difference? The plausible explanation consists in the higher contribution of the tropylium resonance structure in the nitrated diazenes when compared to the structures without substituents at benzothiazole moiety; for the nitrated diazenes, the influence of alkyl groups is, therefore more important, stabilizing the positive tropylium charge.

The charge distribution that creates the differences in the bathochromic shift of studied diazenes is also responsible for the observed differences in their solvatochromism. Therefore, a parallel can be made between the intensity of bathochromic effect and the solvatochromic properties of



6a : 4-NO_2; **6b** : 5-NO_2; **6c** : 7-NO_2

Scheme 3.

Table 2
Diazotization of benzothiazol-2-ylamines + coupling with azulenes

Compound	**3a**[a]	**3b**[a]	**3c**[a]	**3d**[a]	**3e**	**4c**[b]	**4e**[b]	**5c**[b]	**5e**[b]
Conversion[c]	82	74	64	64	60	100	79	100	100
Yield[c]	–	72	83	75	4[d]	82	33	75	46

[a] Diazotization in HNO_3–H_3PO_4, coupling in methanol with AcOK as buffer.
[b] Diazotization with nitrosyl sulfate in dichloroacetic acid–acetic acid and coupling in the same solvent.
[c] Calculated based on azulene.
[d] When coupling occurred in dichloroacetic acid the yield increased to 84%.

diazenes. Thus, while the substitution at C-6′ of diazene **3c** has a little effect on the compound's solvatochromism, even when nitro group is used, the alkyl substitution of azulene moiety generated an intense solvatochromic shift: the $\Delta\lambda_{max}$ values were 21 and 15 nm, respectively, for **4c** and **5c** in toluene and DMF (Table 6). The highest solvatochromic effect produces the nitro substitution at C-6′ together with the presence of alkyl at azulene: the $\Delta\lambda_{max}$ values were 37 and 33 nm, respectively, for **4e** and **5e** in toluene and DMF. The value of this effect surpasses the reported values for **7**(NO_2) of 16 nm.

3. Conclusions

The synthesis of compounds belonging to a new class, azulen-1-yl-benzothiazol-2-yl diazene, is reported. The structure and some physical characteristics of the obtained compounds are compared with those of corresponding diazenes without benzo-annelation. As a result of the study, a slight bathochromic shift is generated by this annelation. The values of solvatochromic effect, generally, are similar to those for non-annelated compounds or even are placed under these values excepting the azulen-1-yl-benzothiazol-2-yl diazenes, both substituted with alkyls at azulene and nitro group at 6-position in benzothiazole moiety. The purpose of our research was to obtain new materials able to develop NLO properties. From this point of view, the progress obtained by benzo-annelation of thiazole in the compounds with structure **7** is reduced or, even, non-existent. However, as we have mentioned at the beginning, the low stability of the compounds **7** made them useless in technical purposes. The high stability of the benzo diazenes **3**–**5** and the valuable optical properties allow us to think that this class of compounds could have a good technical future.

Table 3
The chemical shifts (δ in ppm) of azulene protons for azulen-1-yl-thiazol-2-yl diazene and the phenylated and benzo-annelated derivatives

Compound	H2	H3	H4	H5	H6	H7	H8
7	8.36	7.41	8.31	7.40	7.78	7.52	9.19
7(Cl)	8.35	7.46	8.36	7.48	7.85	7.60	9.19
7(5-NO_2)	8.38	7.55	8.47	7.70	8.02	7.83	9.30
3c	8.31	7.36	8.24	7.38	7.74	7.52	9.15
3d	8.35	7.44	8.34	7.50	7.85	7.63	9.22
3e	8.44	7.55	8.47	7.66	7.99	7.81	9.35
3a	8.38	7.48	8.36	7.55	7.84	7.68	9.27
3b	8.33	7.39	8.28	7.38	7.70	7.54	9.18
8	8.46	7.47	8.38	7.48	7.84	7.60	9.27

4. Experimental

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV spectra: Beckman DK-2A, UV 5240. IR spectra UR-20 C, Zeiss Jena spectrophotometer, KBr. ^1H and ^{13}C NMR spectra in $CDCl_3$ or DMSO-d_6: Bruker WM 300, AC 300, ARX 300 and Gemini 300 (^1H: 300 MHz, ^{13}C: 75.47 MHz), *J* values are given in Hz, TMS was used as internal standard (for $CDCl_3$); when necessary, unequivocal signal assignment was confirmed by the analysis of the corresponding COSY and HETCOR spectra. Mass spectra: Finnigan MAT 311-A/100 MS. Me=CH_3. Column chromatography: silica gel. All eluted solutions were filtered before concentration. The dichloromethane (DCM) was distilled over calcium hydride and ethyl acetate over anhydrous sodium carbonate, the chloroform was filtered on a basic alumina column.

4.1. General procedure for azocoupling

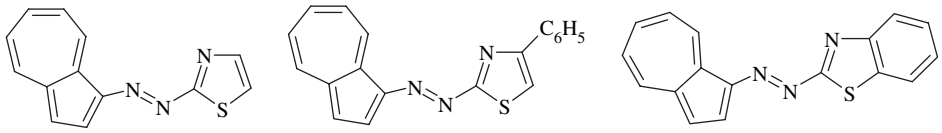
4.1.1. The diazotization in $HNO_3 + H_3PO_4$ mixture; buffered coupling

Benzothiazol-2-ylamine (1.0 mmol), was cooled to 0 °C and phosphoric acid (85%), 0.60 ml, and nitric acid (62%), 0.4 ml, were added. When the mixture reached room temperature, it was stirred for complete solubilization. The solution was again cooled to 0 °C and $NaNO_2$ (crystals), 70 mg (1.0 mmol), was added in 2 min. The suspension was stirred with a glass rod until a deep yellow precipitate was formed (5–10 min). To this suspension, ice, ca. 10 mg, was added in small pieces and the mixture was poured into a suspension of azulene (128 mg, 1.0 mmol), and potassium acetate, ca. 3 g, in methanol, 30 ml, at 0 °C. The color changed in few minutes from blue to red. After 15 min of stirring, aqueous sodium carbonate (20%), 50 ml, was added at 0 °C and the solution was let to warm at room temperature and then extracted three times with DCM (3×50 ml). The combined organic layers were washed with water, dried over sodium sulfate and the solvent was evaporated in vacuum. The residue was chromatographed on silica gel (column, $h = 15 \times d = 2$ cm), for unreacted azulenes eluent *n*-pentane and for diazenes DCM–ethyl acetate.

The nitrosation of 6-methoxy-benzothiazol-2-ylamine in the presence of nitric and phosphoric acids was realized as quickly as possible (in several seconds) in order to reduce the nitration of aromatic moiety. When no nitric acid was used, a little excess of phosphoric acid was used and the diazotization time was prolonged to 15 min.

4.1.2. Diazotization with nitrosyl sulfate in dichloroacetic and acetic acid

6-Nitro-benzothiazol-2-ylamine (214 mg, 1.1 mmol) was dissolved at 50 °C in dichloroacetic acid (3.6 g, 2.3 ml, 28 mmol) and diluted with water (0.7 ml) and acetic acid (0.52 g, 0.5 ml, 8.6 mmol). To this reaction mixture cooled



7 **8** **3c**

Scheme 4.

at 0 °C, a solution of nitrosyl sulfate, obtained from sodium nitrite (76 mg, 1.1 mmol) and sulfuric acid (0.6 ml), was added during 1–2 min with magnetic stirring. The stirring was continued for 30 min at the same temperature and the solution was poured into a solution of azulene (128 mg, 1 mmol) in cooled methanol or acetic acid (0.5 ml). The reaction mixture was stirred for 1 h and the color turned red. Then, potassium acetate (2.0 g, 20.4 mmol) was added and the reaction mixture was kept under stirring, at room temperature overnight. The product was extracted repeatedly with DCM (~400 ml due to its low solubility). The red organic solution was washed with water and was filtered. The solvent was removed and the product was eluted with DCM from a silica gel chromatography column. Due to the low solubility of the nitro-substituted diazenes, their purification on columns was difficult, requiring a large amount of solvent to avoid the precipitation of compounds on the column. Using a mixture of DCM–ethyl acetate, a second polymeric red fraction was eluted smoothly. The yield of the product can be increased if an excess of diazonium salt was used.

4.2. Product characterization

4.2.1. Azulen-1-yl-benzothiazol-2-yl-diazene, **3c**

Dark red-brown crystals, m.p. 204 °C. UV–vis (methanol): λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 226 (4.37), 290 (4.06), 346 (3.78), 494 (4.36). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$ (dt, $^3J = 7.6$ Hz, $^4J = 0.8$ Hz, 1H, 6′-H), 7.36 (d, $^3J = 4.4$ Hz, 1H, 3H), 7.38 (t, $^3J = 9.6$ Hz, 1H, 5H), 7.44 (t, $^3J = 7.6$ Hz, $^4J = 1.2$ Hz, 1H, 5′-H), 7.52 (t, $^3J = 9.6$ Hz, 1H, 7H), 7.74 (t, $^3J = 9.8$ Hz, 1H, 6H), 7.80 (d, $^3J = 7.6$ Hz, 1H, 7′-H), 8.05 (d, $^3J = 8.0$ Hz, 1H, 4′-H), 8.24 (d, $^3J = 9.2$ Hz, 1H, 4H), 8.31 (d, $^3J = 4.4$ Hz, 1H, 2H), 9.15 (d, $^3J = 9.6$ Hz, 1H, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 121.9$ (C-7′), 122.7 (C-3), 123.8 (C-4′), 125.9 (C-6′), 126.1 (C-5′), 126.9 (C-2), 129.6 (C-5), 129.7 (C-7), 134.0 (C-3a′), 136.0 (C-8), 139.2 (C-4), 140.5 (C-6), 141.6 (C-8a), 144.1 (C-3a), 146.6 (C-1), 153.0 (C-7a′), 178.4 (C-2′). IR (KBr) ν (cm^{-1}) = 695 (m), 722 (m), 740 (m), 750 (m), 770 (m), 785 (m), 832 (m), 1025 (m), 1070 (m), 1170 (s), 1232 (s), 1265 (m), 1315 (m), 1323 (m), 1420 (m), 1435 (m), 1450 (m), 1485 (m), 1570 (m). GC–MS (70 eV), *m/z* (%): 289 [M$^+$, 8], 261 (92, M – N_2), 259 (94, M – N_2 – H_2), 126 (100, Az). $C_{17}H_{11}N_3S$: calcd C 70.57, H 3.83, N 14.52, S 11.08; found C 70.62, H 3.88, N 14.61, S 10.89.

Table 4
The chemical shifts (δ in ppm) of benzo moiety protons for azulen-1-yl-benzothiazol-2-yl-diazenes

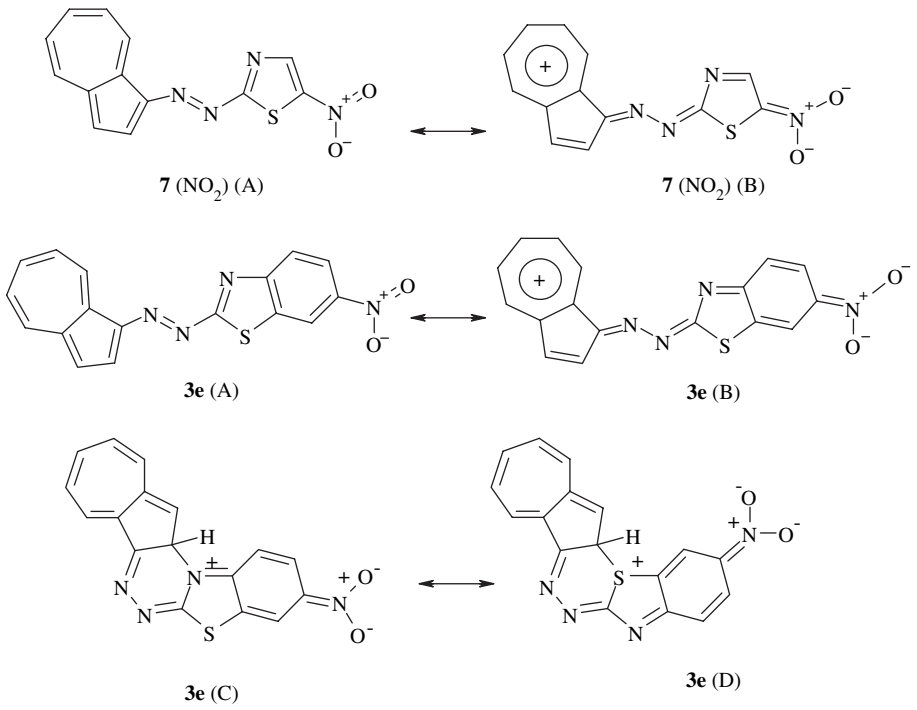
Compound	H4′	H5′	H6′	H7′
3a	7.95	7.06	–	7.29
3b	7.94	7.25	–	7.59
3c	8.05	7.44	7.34	7.80
3d	7.93	7.38	–	7.76
3e	8.12	8.34	–	8.77
4c	8.03	7.44	7.34	7.78

4.2.2. Azulen-1-yl-(6-chloro-benzothiazol-2-yl)-diazene, **3d**

Dark red-brown crystals, m.p. 213 °C. UV–vis (methanol): λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 226 (4.37), 293 (4.09), 347 (3.80), 494 (4.39). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.38$ (dd, $^3J = 8.8$ Hz, $^4J = 2.0$ Hz, 1H, 5′-H), 7.44 (d, $^3J = 4.8$ Hz, 1H, 3H), 7.50 (t, $^3J = 9.6$ Hz, 1H, 5H), 7.63 (t, $^3J = 9.8$ Hz, 1H, 7H), 7.76 (d, $^4J = 2.0$ Hz, 1H, 7′-H), 7.85 (t, $^3J = 9.8$ Hz, 1H, 6H), 7.93 (d, $^3J = 8.8$ Hz, 1H, 4′-H), 8.34 (d, $^3J = 9.2$ Hz, 1H, 4H), 8.35 (d, $^3J = 4.4$ Hz, 1H, 2H), 9.22 (d, $^3J = 9.6$ Hz, 1H, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 121.5$ (C-7′), 123.0 (C-3), 124.5 (C-4′), 131.7 (C-6′), 126.9 (C-5′), 126.9 (C-2), 129.9 (C-5), 130.1 (C-7), 135.3 (C-3a′), 136.2 (C-8), 139.3 (C-4), 140.7 (C-6), 142.4 (C-8a), 144.3 (C-3a), 147.0 (C-1), 151.6 (C-7a′), 178.8 (C-2′). IR (KBr) ν (cm^{-1}) = 702 (m), 741 (m), 772 (m), 785 (m), 810 (m), 833 (m), 850 (m), 1025 (m), 1055 (m), 1160 (s), 1180 (m), 1268 (s), 1318 (m), 1333 (m), 1405 (m), 1433 (m), 1485 (m), 1500 (m), 1590 (m). GC–MS (70 eV), *m/z* (%): 325 (2), 323 [M$^+$, 8], 295 (38, M – N_2), 293 (48, M – N_2 – H_2), 126 (100, Az). $C_{17}H_{10}ClN_3S$: calcd C 62.86, H 3.41, N 12.94, S 9.87, Cl 10.92; found C 62.77, H 3.45, N 12.85, S 9.89, Cl 11.04.

4.2.3. Azulen-1-yl-(6-methyl-benzothiazol-2-yl)-diazene, **3b**

Dark red-brown crystals, m.p. 211 °C. UV–vis (methanol): λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 226 (4.36), 288 (4.07), 347 (3.80), 492 (4.40). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.47$ (s, 3H, Me), 7.25 (d, $^3J = 8.8$ Hz, 1H, 5′-H), 7.38 (t, $^3J = 9.6$ Hz, 1H, 5H), 7.39 (d, $^3J = 4.8$ Hz, 1H, 3H), 7.54 (t, $^3J = 9.6$ Hz, 1H, 7H), 7.59 (s, 1H, 7′-H), 7.70 (t, $^3J = 9.8$ Hz, 1H, 6H), 7.94 (d, $^3J = 8.4$ Hz, 1H, 4′-H), 8.28 (d, $^3J = 9.6$ Hz, 1H, 4H), 8.33 (d, $^3J = 4.8$ Hz, 1H, 2H), 9.18 (d, $^3J = 9.6$ Hz, 1H, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.76$ (Me), 121.7 (C-7′), 122.5 (C-3), 123.4 (C-4′), 136.4 (C-6′), 127.7 (C-5′), 126.9 (C-2), 129.3 (C-5), 129.5 (C-7), 134.2 (C-3a′), 136.0 (C-8), 139.1 (C-4), 140.4 (C-6), 141.3 (C-8a), 144.2 (C-3a), 146.4 (C-1), 151.2 (C-7a′), 177.5 (C-2′). IR (KBr) ν (cm^{-1}) = 670 (m), 690 (m), 710 (m), 740 (m), 762 (m), 785 (m), 812 (m), 837 (m), 1025



Scheme 5.

(m), 1060 (m), 1170 (s), 1205 (m), 1232 (m), 1270 (m), 1320 (m), 1410 (m), 1435 (m), 1450 (m), 1485 (m), 1490 (m), 1570 (m), 1595 (m). GC–MS (70 eV), *m/z* (%): 303 [M^+, 5], 275 (92, $M - N_2$), 273 (65, $M - N_2 - H_2$), 271 (100, $M - N_2 - H_4$), 127 (35, Az). $C_{18}H_{13}N_3S$: calcd C 71.26, H 4.32, N 13.85, S 10.57; found C 71.16, H 4.45, N 13.79, S 10.60.

4.2.4. Azulen-1-yl-(6-methoxy-benzothiazol-2-yl)-diazene, ***3a***

Dark red-brown crystals, m.p. 244 °C. UV–vis (methanol): λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 226 (4.36), 296 (4.06), 347 (3.77), 500 (4.36). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.92$ (s, 3H, Me), 7.08 (dd, $^3J = 9.0$ Hz, $^4J = 2.6$ Hz, 1H, 5′-H), 7.31 (d, $^4J = 2.4$ Hz, 1H, 7′-H), 7.49 (d, $^3J = 4.8$ Hz, 1H, 3H), 7.53 (t, $^3J = 9.2$ Hz, 1H, 5H), 7.88 (t, $^3J = 9.8$ Hz, 1H, 7H), 7.88 (t, $^3J = 9.8$ Hz, 1H, 6H), 7.99 (d, $^3J = 8.8$ Hz, 1H, 4′-H), 8.39 (d, $^3J = 9.8$ Hz, 1H, 4H), 8.41 (d, $^3J = 4.8$ Hz, 1H, 2H), 9.33 (d, $^3J = 9.2$ Hz, 1H, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 55.75$ (Me), 104.6 (C-7′), 122.3 (C-3), 124.6 (C-4′), 158.5 (C-6′), 115.3 (C-5′), 126.7 (C-2), 129.0 (C-5), 129.2 (C-7), 135.7 (C-3a′), 135.9 (C-8), 139.0 (C-4), 140.3 (C-6), 140.9 (C-8a), 144.1 (C-3a), 146.2 (C-1), 147.7 (C-7a′), 176.2 (C-2′). IR (KBr) ν (cm^{-1}) = 737 (m), 780 (m), 820 (m), 830 (m), 1020 (m), 1060 (m), 1160 (s), 1210 (m), 1230 (m), 1263 (m), 1320 (m), 1355 (m), 1410 (m), 1430 (m), 1450 (m), 1480 (m), 1490 (m), 1560 (m), 1593 (m). GCMS (70 eV), *m/z* (%): 319 [M^+, 8], 317 (11, $M - H_2$), 291 (60, $M - N_2$), 289 (35, $M - N_2 - H_2$), 288 (60, $M - N_2 - H_3$), 276 (13, $M - N_2 -$ Me), 274 (13, $M - N_2 - H_2 -$ Me), 248 (11, $M - N_2 -$ Me – CO), 245 ($M - N_2 -$ Me – CO – H_3),

Table 5
The UV–vis spectra of azulen-1-yl-benzothiazol-2-yl diazenes in methanol

Compound	λ_{max} (nm)/log ε (dm^3 mol^{-1} cm^{-1})			
	L1	L2	L3	L4
3b	226(4.36)	288(4.07)	347(3.80)	492(4.40)
3c	226(4.37)	290(4.06)	346(3.78)	494(4.36)
3d	226(4.37)	293(4.09)	347(3.80)	494(4.39)
3a	226(4.36)	296(4.06)	347(3.77)	500(4.36)
3e	226(4.37)	291(4.11)	345(3.79)	512(4.39)
4c	226(4.34)sh	244(4.37), 261(4.19)	344(3.90)	496(4.29)
5c	233(4.34)	260(4.17), 307(3.87)	357(3.70)	517(4.33)
4e	230(4.34)	247(4.23), 257(4.14)	346(3.80)	539(4.35)
5e	230(4.36)	259(4.26), 309(4.07)	373(3.79)	551(4.36)
7	250(4.24)	291(4.18)	342(3.73)	472(4.36)
8	238(4.33), 247(4.33)	296(4.24)	336(3.87)	486(4.45)

Table 6
The solvent effect on λ_{max} (nm)/log ε (dm^3 mol^{-1} cm^{-1}) for main visible band of azulen-1-yl-benzothiazol-2-yl diazenes

Compound	Toluene	Acetone	CH_3CN	CH_2Cl_2	Methanol	DMF
3c	481	481	484	488	488	490
3b	486	484	486	488	492	492
3d	488	488	488	496	498	496
3a	492	492	496	500	504	504
3e	498	500	504	510	512	512
4c	481	486	488	494	496	502
5c	506	508	512	514	517	521
4e	512	517	527	541	541	549
5e	530	541	548	551	551	563

127 (100, Az). $C_{18}H_{13}N_3SO$: calcd C 67.69, H 4.10, N 13.16, S 10.04; found C 67.59, H 4.15, N 13.20, S 10.06.

4.2.5. Azulen-1-yl-(6-methoxy-4-nitro-benzothiazol-2-yl)-diazene, ***6a***

Dark red-brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.97$ (s, 3H, Me), 7.52 (d, $^3J = 4.8$ Hz, 1H, 3H), 7.57 (d, $^4J = 2.4$ Hz, 1H, 7′-H), 7.59 (t, $^3J = 9.2$ Hz, 1H, 5H), 7.72 (t, $^3J = 9.8$ Hz, 1H, 7H), 7.76 (d, $^4J = 2.4$ Hz, 1H, 5′-H), 7.93 (t, $^3J = 9.2$ Hz, 1H, 6H), 8.42 (d, $^3J = 9.2$ Hz, 1H, 4H), 8.42 (d, $^3J = 4.8$ Hz, 1H, 2H), 9.29 (d, $^3J = 9.2$ Hz, 1H, 8H).

4.2.6. Azulen-1-yl-(6-methoxy-5-nitro-benzothiazol-2-yl)-diazene, ***6b***

Dark red-brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.06$ (s, 3H, Me), 7.47 (s, 1H, 7′-H), 7.53 (d, $^3J = 4.8$ Hz, 1H, 3H), 7.61 (t, $^3J = 9.2$ Hz, 1H, 5H), 7.76 (t, $^3J = 9.8$ Hz, 1H, 7H), 7.95 (t, $^3J = 9.2$ Hz, 1H, 6H), 8.42 (d, $^3J = 4.8$ Hz, 1H, 2H), 8.45 (d, $^3J = 9.2$ Hz, 1H, 4H), 8.49 (s, 1H, 4′-H), 9.33 (d, $^3J = 9.2$ Hz, 1H, 8H).

4.2.7. Azulen-1-yl-(6-methoxy-7-nitro-benzothiazol-2-yl)-diazene, ***6c***

Dark red-brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.10$ (s, 3H, Me), 7.23 (d, $^3J = 9.0$ Hz, 1H, 5′-H), 7.54 (d, $^3J = 4.8$ Hz, 1H, 3H), 7.61 (t, $^3J = 9.2$ Hz, 1H, 5H), 7.73 (t, $^3J = 9.8$ Hz, 1H, 7H), 7.91 (t, $^3J = 9.8$ Hz, 1H, 6H), 8.20 (d, $^3J = 8.8$ Hz, 1H, 4′-H), 8.40 (d, $^3J = 9.8$ Hz, 1H, 4H), 8.42 (d, $^3J = 4.8$ Hz, 1H, 2H), 9.34 (d, $^3J = 9.2$ Hz, 1H, 8H).

4.2.8. Azulen-1-yl-(6-nitro-benzothiazol-2-yl)-diazene, ***3e***

Dark red-brown crystals, m.p. >260 °C. UV (methanol): λ_{max} (log ε): 226 (4.37), 291 (4.11), 345 (3.79), 512 (4.39). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (d, $^3J = 4.8$ Hz, 1H, 3H), 7.66 (t, $^3J = 9.6$ Hz, 1H, 5H), 7.81 (t, $^3J = 9.8$ Hz, 1H, 7H), 7.81 (t, $^3J = 9.8$ Hz, 1H, 6H), 8.12 (d, $^3J = 8.8$ Hz, 1H, 4′-H), 8.34 (dd, $^3J = 8.8$ Hz, $^4J = 2.0$ Hz, 1H, 5′-H), 8.44 (d, $^3J = 4.4$ Hz, 1H, 2H), 8.47 (d, $^3J = 9.2$ Hz, 1H, 4H), 8.77 (d, $^4J = 2.0$ Hz, 1H, 7′-H), 9.35 (d, $^3J = 9.6$ Hz, 1H, 8H). IR (KBr) ν (cm^{-1}) = 747 (m), 772 (m), 785 (m), 837 (m), 852 (m), 1010 (m), 1045 (m), 1120 (s), 1162 (m), 1187 (m), 1267 (m), 1330 (m), 1395 (m), 1428 (m), 1450 (m), 1515 (m), 1560 (m), 1593 (m). $C_{17}H_{10}N_4SO_2$: calcd C 61.07, H 3.01, N 16.76, S 9.59, O 9.57; found C 61.06, H 3.05, N 16.66, S 9.55.

4.2.9. Benzothiazol-2-yl-(4,6,8-trimethyl-azulen-1-yl)-diazene, ***4c***

Dark brown crystals, m.p. 212 °C. UV–vis (methanol): λ_{max}/nm (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 226 (4.34)sh, 244 (4.37), 261 (4.19), 344 (3.90), 496 (4.29). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.64$ (s, 3H, Me_4), 2.84 (s, 3H, Me_8), 3.28 (s, 3H, Me_6) 7.31 (s, 1H, 5H), 7.34 (dt, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, 6′-H), 7.36 (d, $^3J = 4.8$ Hz, 1H, 3H), 7.44 (t, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, 5′-H), 7.46 (s, 1H, 7H), 7.78 (dd, $^3J = 7.8$ Hz, $^4J = 0.6$ Hz, 1H, 7′-H), 8.03 (dd, $^3J = 8.0$ Hz, $^4J = 0.4$ Hz, 1H, 4′-H), 8.23 (d, $^3J = 5.2$ Hz, 1H, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.49$ (Me_4), 28.59 (Me_8), 29.73 (Me_6), 120.9 (C-3), 123.6 (C-4′), 121.8 (C-7′), 123.8 (C-2), 125.5 (C-6′), 125.9 (C-5′), 134.1 (C-5), 136.5 (C-7), 136.9 (C-3a′), 141.7 (C-8a), 144.3 (C-3a), 147.9 (C-1), 148.3 (C-8), 149.3 (C-4), 151.0 (C-6), 153.3 (C-7a′), 177.9 (C-2′). IR (KBr) ν (cm^{-1}) = 725 (m), 757 (m), 790 (m), 833 (m), 865 (m), 888 (m), 1075 (m), 1120 (m), 1150 (m), 1170 (m), 1202 (m), 1225 (m), 1283 (m), 1350 (m), 1363 (m), 1452 (m), 1495 (m), 1575 (m). MS (ESI): 332 [$M^+ + 1$, 100]. $C_{20}H_{17}N_3S$: calcd C 72.48, H 5.17, N 12.68, S 9.67; found C 72.42, H 5.28, N 12.61, S 9.69.

4.2.10. Benzothiazol-2-yl-(5-isopropyl-3,8-dimethyl-azulen-1-yl)-diazene, ***5c***

Dark crystals, m.p. 162–163 °C. UV–vis (methanol): λ_{max}/nm (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 222 (4.31), 233 (4.34), 260 (4.17), 307 (3.87), 357 (3.70), 517 (4.33). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.38$ (d, $^3J = 7.2$ Hz, 6H, Me_2C), 2.55 (s, 3H, Me_3), 3.12 (sept. $^3J = 7.2$ Hz, 1H, $CHMe_2$), 3.27 (s, 3H, Me_8), 7.31 (dt, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, 6′-H), 7.42 (dt, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, 5′-H), 7.49 (d, $^3J = 10.0$ Hz, 1H, 7H), 7.56 (dd, $^3J = 10.0$ Hz, $^4J = 2.0$ Hz, 1H, 6H), 7.77 (dd, $^3J = 7.8$ Hz, $^4J = 0.6$ Hz, 1H, 7′-H), 8.01 (dd, $^3J = 8.0$ Hz, $^4J = 0.6$ Hz, 1H, 4′-H), 8.14 (d, $^3J = 2.0$ Hz, 1H, 4H), 8.17 (s, 1H, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.17$ (Me_3), 24.28 (*Me*CH), 38.29 (*C*HMe2), 28.62 (Me_8), 131.7 (C-3), 123.3 (C-4′), 121.7 (C-7′), 126.8 (C-2), 125.2 (C-6′), 125.8 (C-5′), 149.9 (C-5), 135.6 (C-7), 134.0 (C-3a′), 139.0 (C-8a), 145.7 (C-3a), 146.4 (C-1), 150.1 (C-8), 135.4 (C-4), 137.0 (C-6), 153.4 (C-7a′), 179.2 (C-2′). IR (KBr) ν (cm^{-1}) = 720 (m), 748 (m), 819 (m), 846 (m), 970 (m), 1043 (m), 1105 (m), 1170 (m), 1225 (m), 1242 (m), 1270 (m), 1292 (m), 1357 (m), 1410 (m), 1435 (m), 1455 (m), 1525 (m), 1550 (m). MS (ESI): 360 [$M^+ + 1$, 100]. $C_{22}H_{21}N_3S$: calcd C 73.50, H 5.89, N 11.69, S 8.92; found C 73.45, H 5.92, N 11.65, S 8.98.

4.2.11. (5-Isopropyl-3,8-dimethyl-azulen-1-yl)-(6-nitro-benzothiazol-2-yl)-diazene, ***5e***

Dark crystals, m.p. >260 °C. UV–vis (methanol): λ_{max}/nm (log ε/$dm^3\,mol^{-1}\,cm^{-1}$): 230 (4.36), 259 (4.26), 309 (4.07), 373 (3.79), 551 (4.36). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.44$ (d, $^3J = 6.8$ Hz, 6H, Me_2C), 2.58 (s, 3H, Me_3), 3.22 (sept. $^3J = 6.8$ Hz, 1H, $CHMe_2$), 3.33 (s, 3H, Me_8), 7.97 (d, $^3J = 8.8$ Hz, 1H, 4′-H), 7.71 (s, 2H, 6H, 7H), 8.22 (d, $^4J = 2.0$ Hz, 1H, 5′-H), 8.24 (s, 1H, 4H), 8.20 (s, 1H, 2H), 8.64 (dd, $^3J = 8.8$ Hz, $^4J = 2.0$ Hz, 1H, 7′-H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.28$ (Me_3), 24.29 (*Me*CH), 28.77 (Me_8), 38.60 (*C*HMe2), 118.1 (C-7′), 121.5 (C-5′), 122.6 (C-4′), 127.3 (C-2), 133.7 (C-3), 135.9 (C-4), 137.8 (C-7), 137.9 (C-6), 141.2 (C-8a), 141.5 (C-3a′), 144.0 (C-1), 144.8 (C-6′), 148.7 (C-3a), 151.2 (C-8), 153.7 (C-5), 153.8 (C-7a′), 179.2 (C-2′). IR (KBr) ν (cm^{-1}) = 718 (m), 750 (m), 825 (m), 856 (m), 972 (m), 1043 (m), 1105 (m), 1125 (m), 1175 (m), 1253 (m), 1263 (m), 1288 (m), 1323 (m), 1400 (m), 1408 (m), 1452 (m), 1510 (m), 1516 (m), 1550 (m), 1700 (m), 2922 (m), 2965 (m). MS (ESI): 405 [$M^+ + 1$, 100].

$C_{22}H_{20}N_4OS$: calcd C 68.02, H 5.19, N 14.42, S 8.25; found C 68.00, H 5.25, N 14.25, S 8.29.

4.2.12. (6-Nitro-benzothiazol-2-yl)-(4,6,8-trimethyl-azulen-1-yl)-diazene, **5e**

Dark crystals. UV–vis (methanol): λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}): 230 (4.34), 247 (4.23), 257 (4.14), 346 (3.80), 539 (4.35). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.76$ (s, 3H, Me_4), 2.93 (s, 3H, Me_8), 3.39 (s, 3H, Me_6), 7.46 (d, $^3J = 5.2$ Hz, 1H, 3H), 7.54 (s, 1H, 5H), 7.67 (s, 1H, 7H), 8.05 (d, $^3J = 9.2$ Hz, 1H, 4′-H), 8.25 (t, $^3J = 8.8$ Hz, $^4J = 2.8$ Hz, 1H, 5′-H), 8.29 (d, $^3J = 5.2$ Hz, 1H, 2H), 8.71 (d, $^4J = 2.0$ Hz, 1H, 7′-H). IR (KBr) ν (cm^{-1}) = 725 (m), 747 (m), 825 (m), 880 (m), 910 (m), 1040 (m), 1125 (m), 1170 (m), 1235 (m), 1255 (m), 1290 (m), 1330 (m), 1452 (m), 1500 (m), 1530 (m), 1645 (m), 3080 (m). MS (ESI): 377 [$M^+ + 1$, 100]. $C_{20}H_{16}N_4OS$: calcd C 63.81, H 4.28, N 14.88, S 8.52; found C 63.75, H 4.25, N 14.69, S 8.63.

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