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Insertion Reaction of Azidosulfonyl Azo Dye with Model Alicyclic and Heterocyclic Compounds*

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Abstract—Thermal reactions of 4-(2-hydroxynaphthalen-1-yldiazenyl)benzenesulfonyl azide with cyclohexane, benzene, toluene, anisole, *p*-xylene, mesitylene, dihydropyran, and pyridine were studied. Structures of the resulting azo dyes were confirmed by FT-IR, UV, ^{1}H and ^{13}C NMR, and mass spectra and elemental analyses, and their solvatochromic properties were examined. Probable mechanisms of nitrene insertion were discussed.

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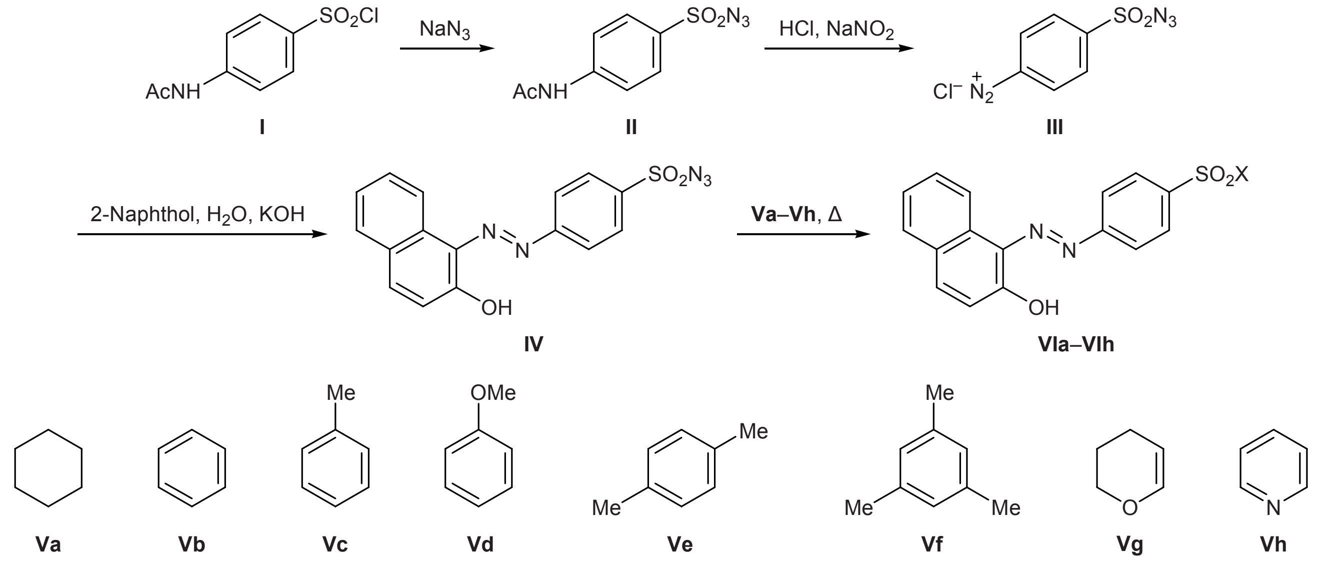
The chemistry of azo dyes was discussed in detail by Zollinger [1]. Thermal decomposition of sulfonyl azides and their reactions with monosubstituted benzenes [2] and other aromatic compounds were reported [3]. Reactions of sulfonyl azides with olefins, [4] some hydrocarbons [5–10], benzo-fused cyclic β-keto esters [11, 12], alkyl radicals [13], and vinyl ethers [14], as well as addition of sulfonyl azides to dihydropyran, were also described [14, 15]. Abramovitch et al. [16, 17] studied thermolysis of benzene-1,2-disulfonyl azide in benzene and cyclohexane and addition of aromatic sulfonyl azides to simple acyclic and cyclic dienes. Both aliphatic and aromatic sulfonyl azides were found to insert into carbon–hydrogen bond of saturated hydrocarbons [18]. The mechanism of fixation of reactive azide dyes containing an azidosulfonyl

Scheme 1.



X = *cyclo*-$C_6H_{11}NH$ (**a**), PhNH (**b**), 2-MeC_6H_4NH (**c**), 2-$MeOC_6H_4NH$ (**d**), 2,5-$Me_2C_6H_3NH$ (**e**), 2,4,6-$Me_3C_6H_2NH$ (**f**), tetrahydro-2*H*-pyran-2-ylideneamino (**g**), pyridin-1-ioimino (**h**).

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* The text was submitted by the authors in English.

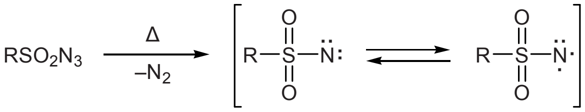
group on nylon and polyesters was proposed in [19]. Thermal decomposition of imidoyl azides in the presence of various substituted benzenes was studied by us in [20]. We recently reported on the synthesis of a new group of reactive azo dyes containing an azido group [21] and proposed a new method for the preparation of azo dyes using clay catalysts [22].

In the present work we examined thermal reactions of a reactive azidosulfonyl azo dye, 4-(2-hydroxynaphthalen-1-yldiazenyl)benzenesulfonyl azide with some model compounds (cyclohexane, benzene, toluene, anisole, *p*-xylene, mesitylene, dihydropyran, and pyridine) with a view to get a deeper insight into the mechanism of its insertion reactions.

Initial 4-(2-hydroxynaphthalen-1-yldiazenyl)benzenesulfonyl azide (**IV**) was prepared starting from 4-acetylaminobenzenesulfonyl chloride (**I**). Compound **I** was converted into sulfonyl azide **II** by treatment with sodium azide, deprotection of the amino group in **II** and subsequent diazotization gave azidosulfonylbenzenediazonium salt **III**, and the latter was brought into azo coupling with β-naphthol (Scheme 1). Thermal decomposition of azide **IV** in the presence of model compounds **Va**–**Vh** led to the formation of new azo dyes **VIa**–**VIh** whose structure was established on the basis of their elemental analyses and spectral data.

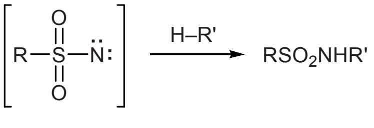
Thermal decomposition of sulfonyl azides in organic solvents and mineral oil was studied in detail [18–23]. Generally, sulfonyl azides decompose at elevated temperatures to form sulfonyl nitrene as shown in Scheme 2.

Scheme 2.



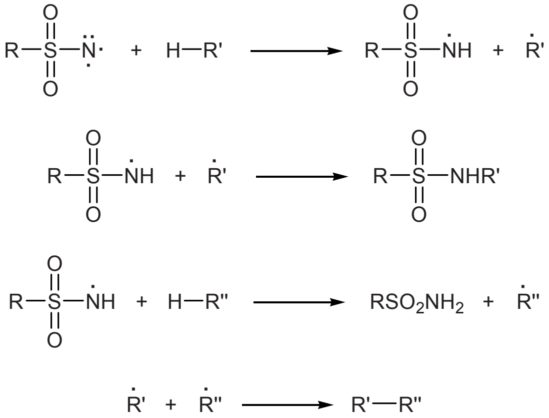
The nitrene can exist in both singlet and triplet states that are capable of reacting with hydrocarbons in different ways. The reaction involving the singlet nitrene occurs as insertion into C–H bond to give N-substituted sulfonamide (Scheme 3).

Scheme 3.



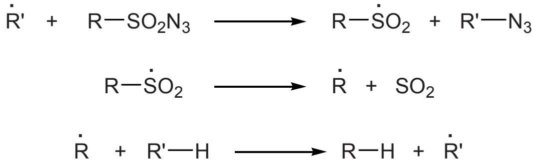
The triplet nitrene reacts via abstraction of a proton from hydrocarbon resulting in the formation of a macroradical. Next follows either recombination of the two radicals to form the same product as in the reaction of singlet nitrene or abstraction of a proton from another hydrocarbon to give primary sulfonamide (Scheme 4).

Scheme 4.



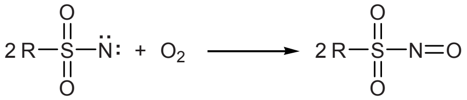
Another possible reaction path involves loss of the sulfonyl azide moiety with formation of SO_2. This path was observed in the thermal decomposition of various sulfonyl azides in mineral oil and organic solvents [18, 23]. Presumably, the formation of SO_2 is in some way catalyzed by nitrenes or substances formed in reactions involving nitrenes. The reaction is likely to involve radical species, but the origin of the latter has not been determined, and it could depend on the reaction system (possible radical sources are nitrenes in the triplet state). There are many puzzling features concerning the formation of SO_2. A probable reaction path is shown in Scheme 5 [18, 23].

Scheme 5.



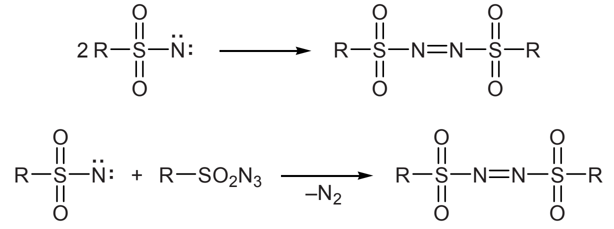
It is also important that oxygen should be absent since it easily reacts with nitrenes to form nitroso compounds according to Scheme 6 [24]. Other undesirable reactions are formation of azo dimers from

Scheme 6.



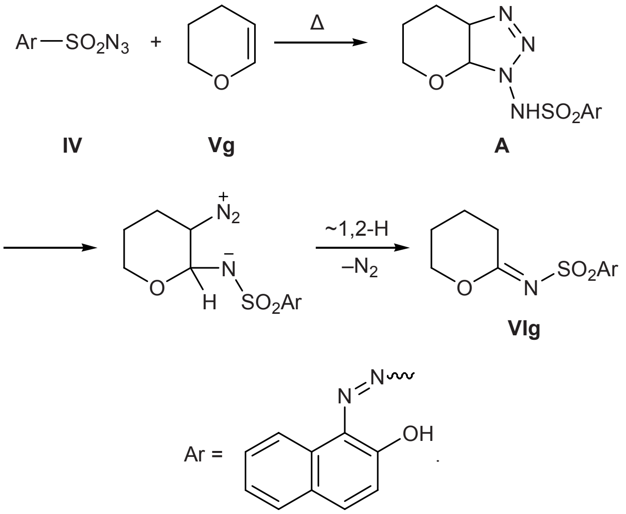
two nitrenes and nitrene coupling with the initial azide (Scheme 7). These reactions are more likely to occur in pure sulfonyl azides or in highly concentrated solution [25].

Scheme 7.



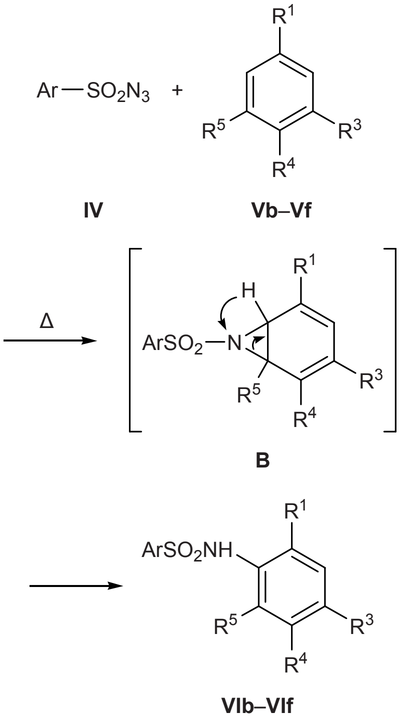
Model substrates studied in the present work contained both C_{sp^3}–H and C_{sp^2}–H bonds. Aromatic compounds **Vb**–**Vf** reacted with azide **IV** via formation of nitrene intermediate which inserted into the C_{sp^2}–H bond. By contrast, the reaction of **IV** with dihydropyran **Vg** did not involve nitrene formation. Insofar as the azido group is an 1,3-dipole, azides are capable of reacting with many unsaturated compounds, especially with electron-rich olefins, following the 1,3-dipolar cycloaddition pattern. The reaction of azide **IV** with dihydropyran **Vg** was complete at room temperature. Presumably, the primary adduct, pyranotriazole **A**, decomposed with elimination of nitrogen molecule, and the subsequent 1,2-H shift gave the final product (Scheme 8). This mechanism resembles that proposed previously [15].

Scheme 8.



The reactions with substituted benzenes were presumed to involve nitrene addition, followed by rearrangement. Thermal decomposition of sulfonyl azide **IV** in benzene (or other aromatic compound) occurs slowly at 170–178°C; nitrene addition gives benzo[*b*]-aziridine intermediate **B**, and the subsequent cleavage of the three-membered ring produces N-substituted sulfonamides **VIb**–**VIf** (Scheme 9).

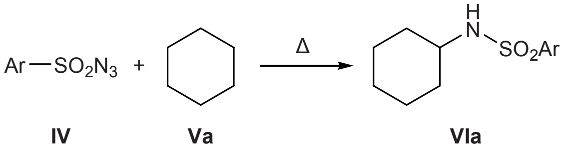
Scheme 9.



Analogous patter was observed by us previously while studying thermal decomposition of imidoyl azides in the presence of various substituted benzenes [21]. Here, the major products were the corresponding *ortho*-substituted derivatives. Isolation of minor products (*para*- and *meta*-substituted) was difficult because of formation of other by-products (see Schemes 4–7).

In the reaction with cyclohexane at 175°C under pressure, insertion into the C_{sp^3}–H bond occurred (Scheme 10), as in the reactions of sulfonyl azides with aliphatic hydrocarbons reported previously [6, 10]

Scheme 10.



We recorded the electronic absorption spectra of azo dyes **VIa**–**VIg** in different solvents; the results are summarized in Table 1. Compounds **VIa**–**VIg** charac-

Table 1. Electronic absorption spectra of azo dyes **VIa**–**VIh** in different solvents

Compound no.	λ_{max}, nm				
	ethanol	acetone	dimethylformamide	methylene chloride	acetonitrile
VIa	210, 323, 474	210, 323, 474	210, 324, 478	211, 324, 477	210, 323, 475
VIb	210, 321, 477	210, 321, 478	210. 323. 480	210, 321, 478	210, 321, 476
VIc	211, 323, 477	212, 323, 477	212, 325, 480	212, 324, 476	211, 324, 477
VId	213, 324, 478	213, 324, 478	213, 326, 482	212, 323, 479	213, 324, 476
VIe	211, 322, 476	211, 324, 477	211, 327, 481	211, 323, 478	211, 322, 476
VIf	211, 323, 477	211, 324, 477	211, 327, 480	212, 325, 478	211, 323, 476
VIg	211. 321, 477	211, 322, 475	211, 323, 479	211, 322, 476	211, 323, 474
VIh	211, 320, 477	211, 323, 476	211, 325, 480	211, 323, 475	211, 322, 475

teristically displayed absorption maxima in the regions λ 210–213, 320–327, and 475–480 nm. The first two bands originate from the aromatic rings, and the long-wave absorption maximum was assigned to π–π* type transition involving the whole conjugated system consisting of naphthyl and phenyl rings and azo group. The long-wave maximum was located at λ 475–478 nm in ethanol, 474–479 nm in acetone, 478–482 nm in dimethylformamide (DMF), 476–479 nm in methylene chloride, and 474–477 nm in acetonitrile. It is seen that these dyes show weak solvatochromism: the red shift in going from weakly to strongly polar solvents does not exceed 6 nm.

The IR spectra of azo dyes **VIa**–**VIh** lacked azide absorption but contained absorption bands due to stretching vibrations of the OH (3427–3553 cm^{-1}), NH (3218–3308 cm^{-1}), N=N (1343–1565 cm^{-1}), and SO_2 groups (1162–1398 cm^{-1}). The ^{1}H NMR spectra of **VIa**–**VIh** are given in Experimental. The most abundant ions in the mass spectra of dyes **VIa**–**VIh** had *m*/*z* values 247, 171, and 143. They were formed via elimination of the sulfonyl group from the molecular ion and cleavage of the naphthylazophenyl fragment.

Thus the thermal reaction of 4-(2-hydroxynaphthalen-1-yldiazenyl)benzenesulfonyl azide (**IV**) with cyclohexane, benzene, toluene, anisole, *p*-xylene, and mesitylene gives the corresponding N-substituted sulfonamides as a result of insertion of intermediate nitrene into the C–H bond of the substrate. In the reaction with pyridine, nitrene addition at the nitrogen atom occurs, while the reaction with dihydropyran follows 1,3-dipolar cycloaddition pattern with subsequent elimination of nitrogen from intermediate pyranotriazole with formation of *N*-(tetrahydro-2*H*-pyran-2-ylidene) sulfonamide.

EXPERIMENTAL

The IR spectra were recorded in KBr on a JASCO FT/IR-680 PLUS spectrometer. The ^{1}H NMR spectra were measured on a Bruker 500 Ultrashield spectrometer (500 MHz) using DMSO-d_6 as solvent. The mass

Table 2. Elemental analyses of azo dyes **VIa**–**VIh**

Compound no.	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
VIa	64.32	5.50	10.12	$C_{22}H_{23}N_3O_3S$	64.53	5.66	10.26
VIb	65.37	4.11	10.28	$C_{22}H_{17}N_3O_3S$	65.50	4.25	10.42
VIc	66.09	4.46	9.91	$C_{23}H_{19}N_3O_3S$	66.17	4.59	10.07
VId	63.53	4.30	9.49	$C_{23}H_{19}N_3O_4S$	63.73	4.42	9.69
VIe	66.61	4.77	9.63	$C_{24}H_{21}N_3O_3S$	66.80	4.91	9.74
VIf	67.25	5.11	9.29	$C_{25}H_{23}N_3O_3S$	67.40	5.20	9.43
VIg	61.42	4.73	10.07	$C_{21}H_{19}N_3O_4S$	61.60	4.88	10.26
VIh	62.13	4.31	14.10	$C_{21}H_{16}N_4O_3S$	62.36	3.99	13.85

spectra (electron impact, 70 eV) were obtained on a Fisons Trio 1000 spectrometer (UK). The UV spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer. The elemental compositions were determined at the Research Institute of Petroleum Industry (Pazhouheshgah Bld., Qom Road, Tehran, Iran). The melting points were determined on a Gallenkamp apparatus and are uncorrected. Analytical TLC was performed on silica gel F254 plates (Merck) and silica gel 60 (40–63 μm, Merck) was used for column chromatography. 4-Acetylaminobenzenesulfonyl chloride, cyclohexane, toluene, anisole, mesitylene, 3,4-dihydro-2*H*-pyran, and pyridine were commercial products (Merck) which were used without further purification. The elemental analyses of azo dyes **VIa**–**VIh** are listed in Table 2.

***N*-(4-Azidosulfonylphenyl)acetamide (II).** A solution of 48.6 g (208 mmol) of 4-acetylaminobenzenesulfonyl chloride in 500 ml of acetone was cooled to 0°C, a cold solution of 20 g (312 mmol) of sodium azide in 200 ml of water was added dropwise under stirring over a period of 1 h, and the mixture was stirred for 1 h at 0°C. The mixture was then poured into 1.5 l of an ice–water slurry, and the precipitate was filtered off, washed with ice water, and dried under reduced pressure. The product can be used in the next step directly or recrystallized from aqueous acetone. Yield 75%, colorless crystals, mp 108–110°C. IR spectrum (KBr), ν, cm^{-1}: 2125, 1674, 1160. ^{1}H NMR spectrum, δ, ppm; 8.4 s (1H, NH), 7.82 d.d (4H, *J* = 13.58, 8.3 Hz, H_{arom}), 2.23 s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 169.5, 144.1, 132.3, 128.9, 119.6, 24.7. Mass spectrum: *m*/*z* 240 $[M]^+$.

4-(2-Hydroxynaphthalen-1-yldiazenyl)benzenesulfonyl azide (IV). A mixture of 2.4 g (10 mmol) of sulfonyl azide **II** and 9 ml of concentrated hydrochloric acid was heated for 35 min under reflux. The resulting solution was cooled to 0°C in an ice–salt bath, a solution of 0.76 g (11 mmol) of sodium nitrite in 20 ml of water was added dropwise under stirring, maintaining the temperature below 5°C, and the mixture was stirred for an additional 30 min on cooling. The solution was then neutralized with a saturated solution of sodium hydrogen carbonate, 1.44 g (10 mmol) of 2-naphthol was slowly added under stirring to the resulting suspension of diazonium salt **III** (10 mmol), the mixture was stirred for 30 min, neutralized with a saturated solution of sodium carbonate, and stirred until complete precipitation (1–3 h). The precipitate was filtered off with suction, dried, and recrystallized from toluene. Yield 87%, red plates, mp 172–174°C. IR spectrum, ν, cm^{-1}: 3545, 2110, 1379. ^{1}H NMR spectrum, δ, ppm: 15.6 s (1H, OH), 8.04 d (2H, C_6H_4, *J* = 8.83 Hz), 7.98 d (2H, C_6H_4, *J* = 8.83 Hz), 6.66–8.37 m (6H, $C_{10}H_6$). ^{13}C NMR spectrum, δ_C, ppm: 117.4, 122.9, 126.7 (2C), 128, 129, 129.6, 129.9 (2C), 130.2, 132.4, 133.4, 134.1, 144.0, 148.4, 180.7. UV spectrum (CH_2Cl_2), λ_{max}, nm: 224, 313, 479. Mass spectrum: *m*/*z* 353 $[M]^+$.

***N*-Cyclohexyl-4-[2-(2-hydroxynaphthalen-1-yl)-diazenyl]benzenesulfonamide (VIa).** A stainless steel high-pressure reactor was charged with a degassed solution of 0.653 g (1.8 mmol) of azo dye **IV** in 20 ml (0.185 mol) of anhydrous cyclohexane, and the mixture was heated for 3 h at 170–175°C, the progress of the reaction being monitored by TLC. The mixture was treated with acetone, the resulting solution was evaporated to dryness, and the residue was subjected to chromatography on silica gel using cyclohexane–ethyl acetate (80:20) as eluent to isolate an orange–red solid whose IR spectrum lacked azide band. Yield 52%, mp 192–194°C. IR spectrum, ν, cm^{-1}: 3548, 3308, 3065, 2966, 1613, 1565, 1385, 1178. ^{1}H NMR spectrum, δ, ppm: 15.77 s (1H, OH), 8.46 d (1H, *J* = 9.63 Hz), 7.94 d (1H, *J* = 7.87 Hz), 7.94 d (2H, *J* = 8.5 Hz), 7.88 d (2H, *J* = 5.56 Hz), 7.65 d (1H, *J* = 7.92 Hz), 7.59 t (1H, *J* = 7.72 Hz), 7.46 t (1H, *J* = 7.53 Hz), 6.78 d (1H, *J* = 9.56 Hz). ^{13}C NMR spectrum, δ_C, ppm: 23.23 (2C), 28.43, 33.54 (2C), 42.84, 118.60 (2C), 122.19, 126.13, 127.62, 128.45, 129.39, 129.42 (2C), 129.74, 131.12, 132.57, 132.59, 143.63, 148.34, 178.98. Mass spectrum: *m*/*z* 409 $[M]^+$.

4-[2-(2-Hydroxynaphthalen-1-yl)diazenyl]-*N*-phenylbenzenesulfonamide (VIb) was obtained in a similar way from 0.790 g (2.2 mmol) of azide **IV** and 20 ml (0.226 mol) of anhydrous benzene. Yield 41%, orange–red solid, mp 256–258°C. IR spectrum, ν, cm^{-1}: 3551, 3228, 3075, 1623, 1563, 1343, 1182. ^{1}H NMR spectrum, δ, ppm: 15.83 s (1H, OH), 8.41 d (1H, *J* = 8.2 Hz), 7.92 d (1H, *J* = 9.72 Hz), 7.88 d (2H, *J* = 8.79 Hz), 7.80 d (2H, *J* = 8.39 Hz), 7.67 d (1H, *J* = 10.45 Hz), 7.56 t (1H, *J* = 8.42 Hz), 7.45 t (1H, *J* = 6.82 Hz), 7.21 t (2H, *J* = 7.44 Hz), 7.01 t (1H, *J* = 8.06 Hz), 6.92 d (1H, *J* = 8.43 Hz), 6.73 d (1H, *J* = 8.70 Hz). ^{13}C NMR spectrum, δ_C, ppm: 116.80 (2C), 117.76, 118.66, 123.14, 126.12, 127.71, 128.21, 128.41, 129.29, 129.38 (2C), 131.11, 132.51, 132.59, 137.52, 143.54, 148.02, 170.13. Mass spectrum: *m*/*z* 403 $[M]^+$.

4-[2-(2-Hydroxynaphthalen-1-yl)diazenyl]-*N*-(2-methylphenyl)benzenesulfonamide (VIc) was obtained in a similar way from 0.664 g (1.9 mmol) of azide **IV** and 20 ml (0.188 mol) of anhydrous toluene. The mixture was dissolved in hot acetonitrile, the solution was evaporated to dryness, and the residue was subjected to chromatography on silica gel using cyclohexane–ethyl acetate (80:20) as eluent. Yield 53%, orange–red solid, mp 198–200°C. IR spectrum, ν, cm^{-1}: 3547, 3219, 3060, 2951, 1613, 1565, 1382, 1181. ^{1}H NMR spectrum, δ, ppm: 15.65 br.s (1H, OH), 9.34 br.s (1H), 8.36 d (1H, J = 7.75 Hz), 7.90 d (1H, J = 9.50 Hz), 7.81 d (2H, J = 8.59 Hz), 7.65 d (1H, J = 7.63 Hz), 7.73 d (2H, J = 8.87 Hz), 7.49 t (1H, J = 8.75 Hz), 7.12 t (1H, J = 7.83 Hz), 6.93 d (1H, J = 8.84 Hz), 6.85 t (1H, J = 9.16 Hz), 6.77 d (1H, J = 8.78 Hz), 6.71 d (1H, J = 8.77 Hz), 2.25 s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 27.33, 114.15, 116.59, 117.65, 118.21, 121.35 122.19 (2C), 126.10, 127.81, 128.14, 128.35, 129.36, 129.45 (2C), 130.02, 131.25, 132.56, 132.95, 143.66, 145.30, 149.09, 177.87. Mass spectrum: m/z 417 $[M]^+$.

4-[2-(2-Hydroxynaphthalen-1-yl)diazenyl]-*N*-(2-methoxyphenyl)benzenesulfonamide (VId) was obtained in a similar way from 0.650 g (1.8 mmol) of compound **IV** and 20 ml (0.184 mol) of anhydrous anisole. Yield 44%, red solid, mp 186–188°C. IR spectrum, ν, cm^{-1}: 3432, 3266, 3055, 2926, 1609, 1566, 1398, 1162. ^{1}H NMR spectrum, δ, ppm: 15.70 br.s (1H), 9.30 br.s (1H), 8.42 d (1H, J = 7.55 Hz), 7.92 d (1H, J = 9.57 Hz), 7.87 d (2H, J = 8.62 Hz), 7.75 d (1H, J = 8.74 Hz), 7.72 d (2H, J = 8.53 Hz), 7.45 t (1H, J = 8.74 Hz), 7.09 t (1H, J = 7.88 Hz), 6.97 d (1H, J = 8.89 Hz), 6.87 t (1H, J = 9.18 Hz), 6.79 d (1H, J = 8.78 Hz), 6.72 d (1H, J = 8.78 Hz), 3.64 s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 65.83, 114.23, 116.61, 117.70, 118.11, 121.31, 122.17 (2C), 126.13, 127.61, 128.12, 128.41, 129.37, 129.38 (2C), 129.77, 131.11, 132.50, 132.58, 143.54, 145.41, 148.03, 178.13. Mass spectrum: m/z 433 $[M]^+$.

***N*-(2,5-Dimethylphenyl)-4-[2-(2-hydroxynaphthalen-1-yl)diazenyl]benzenesulfonamide (VIe)** was obtained in a similar way from 0.572 g (1.6 mmol) of sulfonyl azide **IV** and 20 ml (0.162 mol) of anhydrous *p*-xylene. Yield 56 %, red solid, mp 210–212°C. IR spectrum, ν, cm^{-1}: 3427, 3265, 3072, 2969, 1635, 1558, 1388, 1169. ^{1}H NMR spectrum, δ, ppm: 15.57 s (1H, OH), 12.50 br.s (1H), 8.45 d (1H, J = 7.93 Hz), 7.93 d (1H, J = 9.53 Hz), 7.88 d (2H, J = 8.45 Hz), 7.72 d (2H, J = 7.95 Hz), 7.70 d (2H, J = 8.53 Hz), 7.57 t (1H, J = 7.70 Hz), 7.44 t (1H, J = 7.53 Hz), 7.06 d (1H, J = 8.17 Hz), 6.95 d (1H, J = 8.09 Hz), 6.84 q (1H), 6.77 d (1H, J = 2.31 Hz), 2.45 s and 2.35 s (3H each, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 16.30, 25.36, 115.72, 117.68, 119.77, 122.13 (2C), 126.13, 126.24, 127.39, 128.51, 129.39 (2C), 129.76, 129.88, 130.93, 131.11, 132.53, 132.59, 136.01, 136.31, 143.45, 148.06, 178.33. Mass spectrum: m/z 431 $[M]^+$.

4-[2-(2-Hydroxynaphthalen-1-yl)diazenyl]-*N*-(2,4,6-trimethylphenyl)benzenesulfonamide (VIf) was obtained in a similar way from 0.511 g (1.4 mmol) of azide **IV** and 20 ml (0.144 mol) of anhydrous mesitylene. Yield 61%, mp 216–218°C. IR spectrum, ν, cm^{-1}: 3553, 3263, 3061, 2919, 1615, 1561, 1393, 1186. ^{1}H NMR spectrum, δ, ppm: 15.75 br.s (1H, OH), 12.50 br.s (1H), 8.45 d (1H, J = 7.93 Hz), 7.91 d (1H, J = 7.87 Hz), 7.89 d (2H, J = 8.53 Hz), 7.86 d (2H, J = 8.51 Hz), 7.71 d (1H, J = 7.75 Hz), 7.56 t (1H, J = 7.53 Hz), 7.41 t (1H, J = 7.51 Hz), 6.79 d (1H, J = 7.95 Hz), 6.79 d (1H, J = 7.95 Hz), 2.51 s (6H, CH_3), 2.35 s (3H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 16.35, 25.75, 118.11, 123.44 (2C), 124.15, 126.36, 127.12, 127.25, 127.30, 128.24, 128.44, 129.13, 129.55 (2C), 130.43, 132.12, 142.31, 147.22, 149.10, 150.06, 175.20. Mass spectrum: m/z 445 $[M]^+$.

4-[2-(2-Hydroxynaphthalen-1-yl)diazenyl]-*N*-(tetrahydro-2*H*-pyran-2-ylidene)benzenesulfonamide (VIg). A thoroughly degassed solution of 0.747 g (2.1 mmol) of azide **IV** in 20 ml (0.211 mol) of anhydrous dihydropyran was stirred at a moderate rate for 3 days at room temperature. When the reaction was complete (TLC), the mixture was washed with acetone and evaporated to dryness, and the residue was subjected to chromatography on silica gel using cyclohexane–ethyl acetate (80:20) as eluent to isolate compound **VIg** as an orange–red solid. Yield 37 %, mp 264–266°C. IR spectrum, ν, cm^{-1}: 3549, 3062, 2897, 1613, 1557, 1382, 1184. ^{1}H NMR spectrum, δ, ppm: 15.79 br.s (1H), 8.46 d (1H, J = 8.11 Hz), 7.94 d (1H, J = 7.95 Hz), 7.93 d (1H, J = 8.70 Hz), 7.90 d (1H, J = 8.74 Hz), 7.73 d (1H, J = 7.74 Hz), 7.59 t (1H, J = 7.51 Hz), 7.46 t (1H, J = 7.57 Hz), 6.78 d (1H, J = 8.15 Hz), 4.55 m (2H), 2.75 m (1H), 0.89 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 21.37, 35.35, 68.42, 118.31, 123.10 (2C), 126.13, 128.42, 129.37 (2C), 129.77, 131.11, 132.50, 132.57, 143.55, 148.04, 170.11. Mass spectrum: m/z 409 $[M]^+$.

4-[2-(2-Hydroxynaphthalen-1-yl)diazenyl]-*N*-pyridiniobenzenesulfonimide (VIh). A thoroughly degassed solution of 0.871 g (2.5 mmol) of sulfonyl azide **IV** in 20 ml (0.247 mol) of anhydrous pyridine was heated for 3 h at 170–175°C in a stainless steel high-pressure reactor. When the reaction was complete

(TLC), the mixture was treated as described above to isolate compound **VIh** as an orange–red solid. Yield 40%, mp 246–248°C. IR spectrum, ν, cm^{-1}: 3477, 2979, 1635, 1508, 1379, 1176. ^1H NMR spectrum, δ, ppm: 15.74 br.s (1H), 8.54 d (1H, J = 8.26 Hz), 8.22 d (2H, C_6H_4, J = 8.83 Hz), 8.16 d (2H, J = 8.81 Hz), 7.95 d (1H, J = 9.31 Hz), 7.86 t (2H, J = 8.13 Hz), 7.78 d (1H, J = 7.87 Hz), 7.60 t (1H, J = 7.77 Hz), 7.55 t (2H, J = 7.66 Hz), 7.45 t (1H, J = 7.48 Hz), 7.37 d (1H, J = 7.33 Hz), 6.92 d (1H, J = 8.37 Hz). ^{13}C NMR spectrum, δ_C, ppm: 119.72 (2C), 122.77, 126.13, 127.63 (2C), 128.31, 129.37, 129.48, 129.78, 131.10, 132.50, 132.57, 142.78, 143.55, 145.53, 148.03, 176.33. Mass spectrum: m/z 404 $[M]^+$.

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