JOC*Note*

Synthesis of *o*-Sulfamidotriazobenzenes from 1,1′-Sulfonylbis(benzotriazole)

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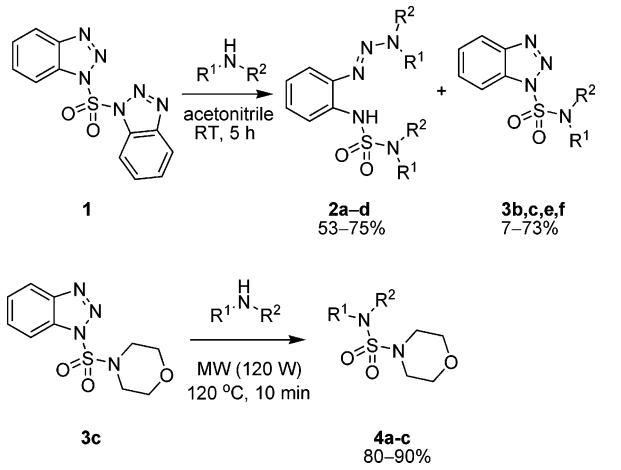
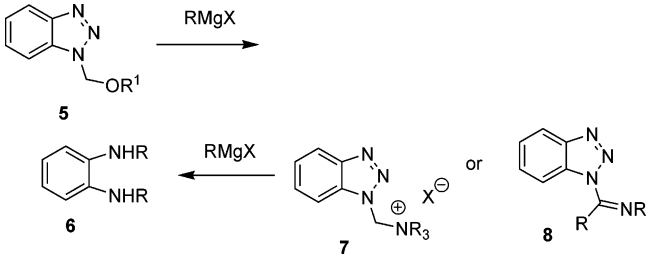


Easily accessible 1,1′-sulfonylbis(benzotriazole) (Bt_2SO_2, **1**) reacts with secondary amines at room temperature to afford (i) the corresponding *o*-sulfamidotriazobenzenes **2a**−**d** (53−75%) via concurrent substitution of the first and ring opening of the second benzotriazolyl group and (ii) *N*-sulfonylbenzotriazoles **3b**,**c**,**e**,**f** (7−73%). 1-(Morpholine-4-sulfonyl)-1*H*-benzotriazole **3c** reacts with piperidine, pyrolidine, and *N*-methylpiperazine under microwave irradiation (120 W) at 120 °C for 10 min to give the unsymmetrical sulfamides **4a**−**c** (80−90%).

Benzotriazole is a useful synthetic auxiliary: it is easily introduced, activates molecules toward numerous transformations, and can be removed readily at the end of the reaction sequence.[1] However, in some reactions cleavage of the triazole ring occurs. The century old classical Graebe−Ullmann synthesis of carbazoles from 1-arylbenzotriazoles occurs at 360 °C via loss of a nitrogen molecule.[2] Pyrolysis of *N*-vinylbenzotriazoles at 500−700 °C gave *N*-phenylketenimines.[3] Recently photodecomposition of tris(benzotriazol-1-yl)methane in benzene gave phenanthridine.[4] Our group encountered benzotriazole ring opening under milder conditions nearly two decades ago; benzotriazolylmethyl phenethyl ether **5** and benzylmagnesium bromide at 110 °C gave *N*-benzyl-*N*′-phenethyl-*o*-phenylenediamine **6** (Scheme 1) via a single nitrogen atom extrusion in low (10%) yield;[5] *N*-(benzotriazol-1-ylmethyl)-*N*-methylpyrrolidinium iodide **7** and ethylmagnesium iodide gave a mixture of unsymmetrically substituted *o*-phenylenediamines[6] (10−40%) (Scheme 1) and 1-(*N*-phenylacetimidoyl)benzotriazole **8** and its propionimidoyl analogue produced corresponding *o*-phenylenediamines in such reactions.[7]

SCHEME 1



Later, ring opening of benzotriazoles with electron-donating substituents and via loss of a nitrogen molecule afforded rearranged heterocycles: quinazolines from 2-(benzotriazol-1-yl)enamines[8] and benzoheterocycles and ortho-substituted anilines from *N*-(α-alkoxyalkyl)benzotriazoles.[9] Ring fragmentation of the diarylbenzotriazolylmethane anion occurred at 20 °C.[10] Acid-catalyzed tandem benzotriazole ring opening/ammonia extrusion of 3-(benzotriazol-1-yl)-1,4-diaryl-1-buten-4-ols gave benzo[*a*]-phenazines.[11] Intramolecular benzotriazole ring opening−ring closure without elimination of nitrogen is preparatively useful for nitrogen-containing fused heterocyclic systems: pyrazolo-[5,1-*b*]benzimidazoles,[12] tetrazolo[1,5-*e*][1,2,5]-triazepines,[13] and 1,2,4-triazolo[1,5-*a*]quinoxalines.[14]

Recently, Zieglar and Subramanian et al. reported the base-catalyzed ring opening of benzotriazoles with electron-withdrawing substituents.[15] 1-[(Nonafluorobutane)sulfonyl]-1*H*-benzotriazole (BtNf, **9**) with a variety of phenols and naphthols in the presence of a base afforded ortho-substituted azobenzenes

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(1) (a) Katritzky, A. R.; Kirichenko, K. *ARKIVOC* **2006**, *iv*, 119. (b) Katritzky, A. R.; Suzuki, K.; Wang, Z. *Synlett* **2005**, 1656. (c) Katritzky, A. R.; Manju, K.; Singh, S. K.; Meher, N. K. *Tetrahedron* **2005**, *61*, 2555. (d) Katritzky, A. R.; Rogovoy, B. V. *Chem. Eur. J.* **2003**, *9*, 4586. (e) Katritzky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, *98*, 409.

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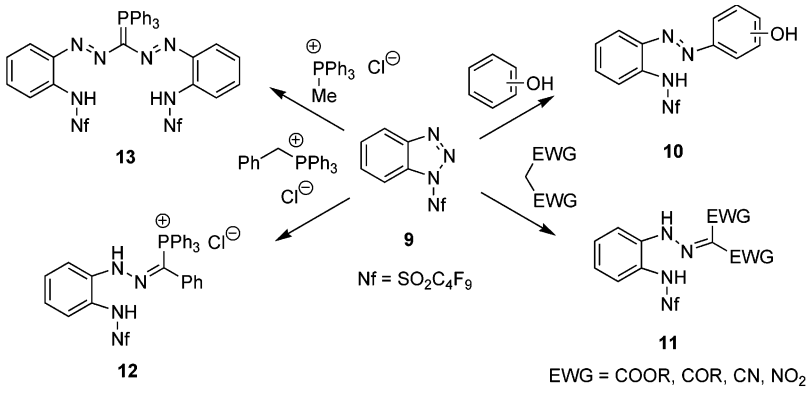
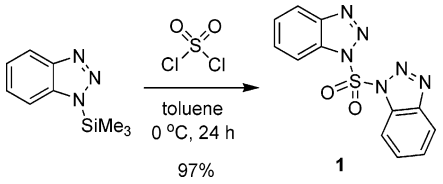
SCHEME 2



SCHEME 3



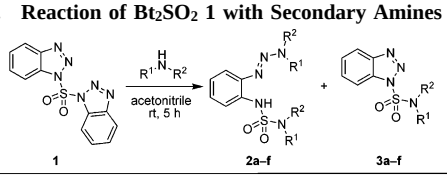
10 (47−94%) (Scheme 2).[15a] This was successfully extended to a mono-triazole-fused phthalocyaninato zinc complex.[15b] Base-catalyzed reactions of BtNf with active methylene compounds afforded α-functionalized *N*-arylhydrazones **11** (72−89%) (Scheme 2);[15c] reactions with alkyl triphenylphosphoranylidenes and methylenetriphenylphosphorylidene gave phenylazomethylenetriphenylphosphoranes **12** and bis-phenylazomethylenetriphenylphosphorane **13**, respectively.[15d]

Herein, we report that Bt_2SO_2 (**1**) with diverse secondary amines involves substitution of one benzotriazolyl group together with ring opening of the second by two molecules of the same amine to give novel *o*-sulfamidotriazobenzenes **2** as the major products along with the expected *N*-sulfonylbenzotriazoles **3** as the minor products.

Synthesis of 1,1′-Sulfonylbis(benzotriazole). Reaction of 1-trimethylsilanyl-1*H*-benzotriazole (2 mol) with sulfuryl chloride in toluene at 0−25 °C for 24 h affords 1,1′-sulfonylbis(benzotriazole) (Bt_2SO_2, **1**) (97%) (Scheme 3),[16] fully characterized by its NMR and elemental analyses. The detailed molecular structure of **1** was established by X-ray diffraction analysis (see the Supporting Information). The molecule possesses a crystallographic 2-fold rotation axis.

Unexpected Reactivity of 1,1′-Sulfonylbis(benzotriazole) (1). Reaction of 1 equiv of 1,1′-sulfonylbis(benzotriazole) (Bt_2SO_2, **1**) with 3 equiv of pyrrolidine in acetonitrile at rt for 5 h gave (*E*)-*N*-(2-(pyrrolidin-1-yldiazenyl)phenyl)pyrrolidine-1-sulfonamide **2a** in 55% yield (Table 1). The expected product 1-(pyrrolidine-1-sulfonyl)-1*H*-benzotriazole **3a** was not obtained. The product **2a** was purified by column chromatography, using silica gel and a mixture of hexanes and ethyl acetate as the eluent, and characterized by ^1H and ^{13}C NMR and satisfactory CHN elemental analysis. The ^1H NMR spectrum of **2a** showed the disappearance of the characteristic Bt signals in the aromatic region, indicating the loss of one of the benzotriazolyl groups during the reaction. Also a different set of signals appeared for the phenyl group protons of the other ring opened Bt moiety.

TABLE 1. Reaction of Bt_2SO_2 1 with Secondary Amines



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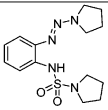
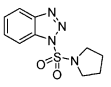
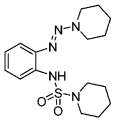
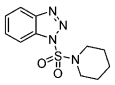
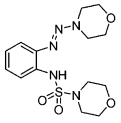
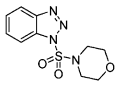
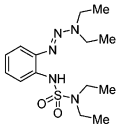
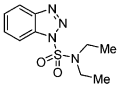
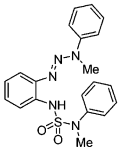
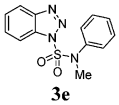
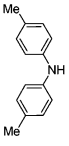
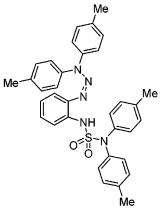
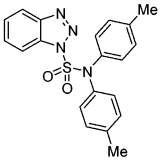
1		 **2a**	55	 **3a**	0
2		 **2b**	53	 **3b**	7
3		 **2c**	63	 **3c**	11
4		 **2d**	75	 **3d**	0
5		 **2e**	0	 **3e**	70[b]
6		 **2f**	0	 **3f**	73[b]

[a] Isolated yields of pure products. [b] No reaction at rt, refluxed for 12 h.

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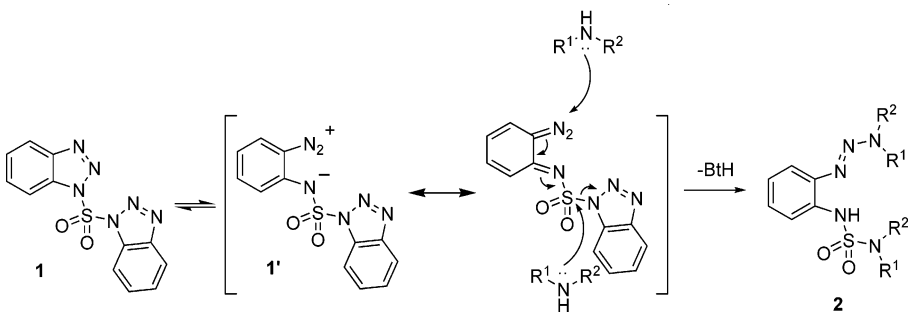
SCHEME 4



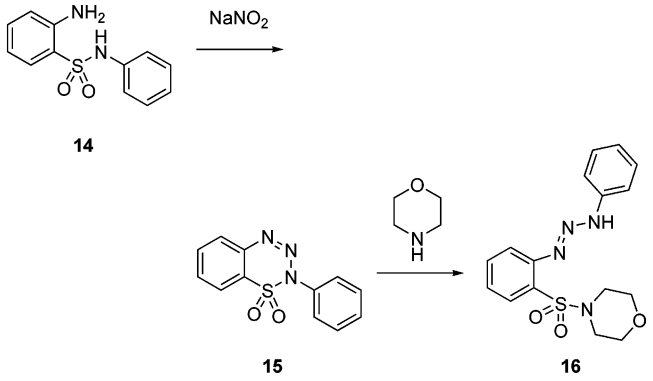
The NH group of **2a** appears downfield at δ 7.81 ppm (singlet) as a result of H-bonding to the neighboring N atom. The ^{13}C NMR spectrum of **2a** showed eight signals corresponding to the product. Further the detailed molecular structure of (*E*)-*N*-(2-(pyrrolidin-1-yldiazenyl)phenyl)pyrrolidine-1-sulfonamide **2a** was established unambiguously by X-ray diffraction analysis (see the Supporting Information). In view of the novelty of the *o*-sulfamidotriazobenzene structure and the mechanism of its formation, we reacted 1 equiv of Bt_2SO_2 (**1**) with 3 equiv of piperidine, morpholine, and diethylamine in acetonitrile at rt for 5 h to give (*E*)-*N*-(2-(piperidin-1-yldiazenyl)phenyl)piperidine-1-sulfonamide (**2b**), (*E*)-*N*-(2-(morpholinodiazenyl)phenyl)-morpholine-4-sulfonamide (**2c**), and (*E*)-*N*-(2-(diethylamino-1-yldiazenyl)phenyl)diethylamine-1-sulfonamide (**2d**) (53%, 63%, and 75%, respectively) along with 1-(piperidine-1-sulfonyl)-1*H*-benzotriazole (**3b**), 1-(morpholine-4-sulfonyl)1*H*-benzotriazole (**3c**), and 1-(diethylamine-1-sulfonyl)-1*H*-benzotriazole (**3d**) (7%, 11%, and 0%, respectively) (Table 1). The structure of **2c** was confirmed by X-ray crystallography but the crystals were all highly twinned and hence the data did not refine to a level suitable for publication. We tried the experiments with a larger excess of secondary amines, but the yields of products **2a**−**d** and **3b**,**c** were not increased. However, the yield of **3c** was increased to 45% when the reaction was heated at 80 °C for 24 h.

Bt_2SO_2 (**1**) did not react with methylphenyl amine or di-*p*-tolylamine at rt; however, refluxing in acetonitrile for 12 h produced 1-(methylphenylamine-1-sulfonyl)-1*H*-benzotriazole (**3e**) and 1-(di-*p*-tolylamine-4-sulfonyl)-1*H*-benzotriazole (**3f**) (70% and 73%, respectively) (Table 1). These results suggest that alkylaryl amines or diaryl amines do not give benzotriazole ring-opened products whereas dialkyl amines easily give *o*-sulfamidotriazobenzenes at rt. This difference in reactivity may be due to a large difference in nucleophilicity between the alkyl and aryl amines.

A possible mechanism for the formation of *o*-sulfamidotriazobenzenes **2** is outlined in Scheme 4: Bt_2SO_2 (**1**) exists in equilibrium with the diazonium betaine structure **1′**.[17] Two molecules of amine attack a single molecule of **1** at different positions—at the diazo group of **1′** assisted by the electron-withdrawing sulfone group, and at the sulfur atom with elimination of a benzotriazole (BtH) moiety. This leads to product **2** after a proton shift (Scheme 4). A similar mechanism of ring opening was proposed for the reactions of BtNf (**9**).[15]

o-Sulfamidotriazobenzenes of type **2** were unknown; however, closely related *o*-sulfonamidotriazobenzenes have been used as color formers.[18] *o*-Sulfonamidotriazobenzenes **16** have been prepared by ring cleavage of cyclic triazosulfones **15**;[19] diazotization of **14** gave the intermediate **15** (Scheme 5).[20]

SCHEME 5



o-Sulfamidotriazobenzenes **2** combine the features of both a triazine and a sulfamide group. Many triazines are known to display potent antitumor activity.[21] Sulfamides on the other hand are of interest as (i) components stable to enzymatic hydrolysis in peptidomimetics,[22] (ii) active components in epinephrine analogues,[23] (iii) agonists of the 5-HT_{1D} receptor (regulating serotonin levels),[24] and (iv) HIV protease inhibitors.[25]

We utilized the byproduct *N*-sulfonylbenzotriazoles **3** for the synthesis of unsymmetrical sulfamides. Thus reaction of 1-(morpholine-4-sulfonyl)-1*H*-benzotriazole (**3c**) with pyrrolidine, piperidine, and *N*-methylpiperazine under microwave irradiation (120 W) at 120 °C for 10 min gave novel 4-(pyrrolidine-1-sulfonyl)morpholine (**4a**) and known 4-(piperidine-1-sulfonyl)-morpholine[26] (**4b**) and 4-(4-methylpiperazine-1-sulfonyl)-morpholine[27] (**4c**) in 90%, 88%, and 80% yields, respectively

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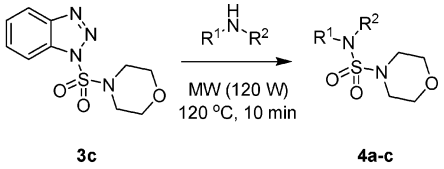
(26) Vandi, A.; Moeller, T.; Audrieth, L. F. *J. Org. Chem.* **1961**, *26*, 1136.

TABLE 2. Reaction of 3c with Secondary Amines



3c 4a-c

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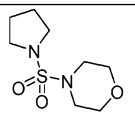
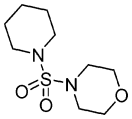
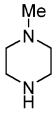
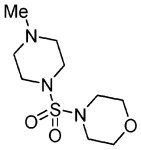
1		 **4a**	90
2		 **4b**	88
3		 **4c**	80

[a] Isolated yields of pure products.

(Table 2). Products **4a**−**c** were purified by flash column chromatography, using silica gel and a mixture of hexanes and ethyl acetate as the eluent, and characterized by their spectral properties.

In summary, the reaction of Bt_2SO_2 (**1**) with secondary amines at room temperature provides the first entry to novel *o*-sulfamidotriazobenzenes **2** in good yields by a convenient straightforward one-step method. Byproduct *N*-sulfonylbenzotriazoles **3** enable the preparation of unsymmetrical sulfamides **4** in high yields.

Experimental Section

1,1′-Sulfonylbis(benzotriazole) (**1**) was prepared by a slight modification of a previously published procedure.[16]

General Procedure for the Preparation of 2a−d and 3b,c,e. To 1,1-sulfonylbenzotriazole (1 g, 3.3 mmol) in anhydrous acetonitrile (15 mL) was added dropwise amine (9.9 mmol, 3 equiv) with stirring at rt for 5 h. The mixture after removal of the solvent was subjected to column chromatography (5−20% ethyl acetate in hexanes) to give pure products **2a**−**d** and **3b**,**c**,**e**,**f**.

(*E*)-*N*-(2-(Pyrrolidin-1-yldiazenyl)phenyl)pyrrolidine-1-sulfonamide (2a): white crystals (55%); mp 109−111 °C (hexanes/dichloromethane); ^{1}H NMR ($CDCl_3$) δ 7.81 (s, 1H), 7.57 (dd, J = 8.0, 1.4 Hz, 1H), 7.43 (dd, J = 7.8, 1.4 Hz, 1H), 7.08 (td, J = 7.4, 1.5 Hz, 1H), 7.01 (td, J = 7.8, 1.5 Hz, 1H), 3.95 (br s, 2H), 3.63 (br s, 2H), 3.29 (t, J = 6.9 Hz, 4H), 2.06 (br s, 4H), 1.75−1.69 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 139.1, 131.8, 125.6, 123.8, 119.1, 115.8, 48.3, 25.6. Anal. Calcd for $C_{14}H_{21}N_5O_2S$: C, 51.99; H, 6.54; N, 21.65. Found: C, 52.16; H, 6.58; N, 21.44.

Crystal data for 2a: $C_{14}H_{21}N_5O_2S$, MW 323.42, monoclinic, space group $P2_1/c$, a = 10.1479(3) Å, b = 10.2295(3) Å, c = 14.7132(4) Å, β = 99.468(1)°, V = 1506.54(7) Å,^{3} $F(000)$ = 688, Z = 4, T = −180 °C, μ(Mo Kα) = 0.231 mm^{-1}, D_{calcd} = 1.426 g·cm^{-3}, $2\theta_{max}$ 55° (CCD area detector, Mo Kα radiation), GOF = 0.96, $wR(F^2)$ = 0.087 (all 1044 data), R = 0.030 (936 data with $I > 2\sigma I$).

(*E*)-*N*-(2-(Piperidin-1-yldiazenyl)phenyl)piperidine-1-sulfonamide (2b): white crystal (53%); mp 74−76 °C (hexanes/dichloromethane); ^{1}H NMR ($CDCl_3$) δ 7.73 (br s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.10 (t, J = 7.3 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 3.80 (br s, 4H), 3.26−3.10 (m, 4H), 1.73 (br s, 6H), 1.58−1.34 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 138.4, 132.1, 126.1, 123.7, 119.1, 116.2, 47.0, 25.2, 24.1, 23.5. Anal. Calcd for $C_{16}H_{25}N_5O_2S$: C, 54.68; H, 7.17; N, 19.93. Found: C, 54.64; H, 7.26; N, 19.75.

(*E*)-*N*-(2-(Morpholinodiazenyl)phenyl)morpholine-4-sulfonamide (2c): white crystal (63%); mp 123−125 °C (hexanes/dichloromethane); ^{1}H NMR ($CDCl_3$) δ 7.70 (br s, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 3.88 (d, J = 4.8 Hz, 4H), 3.82 (d, J = 4.7 Hz, 4H), 3.62 (t, J = 4.0 Hz, 4H), 3.21 (t, J = 4.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 137.9, 132.0, 127.1, 124.2, 119.4, 116.9, 66.1, 46.3. Anal. Calcd for $C_{14}H_{21}N_5O_4S$: C, 47.31; H, 5.96; N, 19.70. Found: C, 47.57; H, 5.99; N, 19.67.

(*E*)-*N*-(2-(Diethylamino-1-yldiazenyl)phenyl)diethylamine-1-sulfonamide (2d): white crystal (75%); mp 54−56 °C (hexanes/dichloromethane); ^{1}H NMR ($CDCl_3$) δ 7.82 (br s, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 3.78 (q, J = 6.3 Hz, 4H), 3.26 (q, J = 7.0 Hz, 4H), 1.28 (br s, 6H), 1.05 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 138.8, 131.8, 125.6, 123.5, 118.6, 116.2, 42.0, 13.5. Anal. Calcd for $C_{14}H_{25}N_5O_2S$: C, 51.35; H, 7.70; N, 21.39. Found: C, 51.51; H, 7.78; N, 21.30.

1-(Piperidine-1-sulfonyl)-1*H*-benzotriazole (3b): white crystal (10%); mp 50−52 °C (hexanes); ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 8.3 Hz, 1H), 8.79 (d, J = 8.3 Hz, 1H), 7.63 (t, J = 8.1 Hz, 1H), 7.48 (t, J = 8.1 Hz, 1H), 3.43 (t, J = 5.4 Hz, 4H), 1.55 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 144.8, 132.5, 129.7, 125.4, 120.2, 112.2, 48.1, 24.8, 23.0. Anal. Calcd for $C_{11}H_{14}N_4O_2S$: C, 49.61; H, 5.30; N, 21.04. Found: C, 49.66; H, 5.27; N, 21.02.

1-(Morpholine-4-sulfonyl)-1*H*-benzotriazole (3c): white crystal (14%); mp 135−137 °C (hexanes); ^{1}H NMR ($CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 8.1 Hz, 1H), 7.51 (t, J = 8.1 Hz, 1H), 3.77 (t, J = 4.8 Hz, 4H), 3.44 (t, J = 4.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 144.7, 132.5, 130.1, 125.6, 120.4, 111.9, 65.7, 46.9. Anal. Calcd for $C_{10}H_{12}N_4O_3S$: C, 44.77; H, 4.51; N, 20.88. Found: C, 45.14; H, 4.44; N, 20.81.

Benzotriazole-1-sulfonic acid *N*-methyl *N*-phenylamide (3e): pink crystal (70%); mp 74−76 °C (hexanes); ^{1}H NMR ($CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.41−7.44 (m, 2H), 7.25−7.28 (m, 3H), 7.11−7.08 (m, 2H), 3.59 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 144.6, 139.3, 132.8, 129.7, 129.5, 128.9, 127.0, 125.4, 120.1, 112.1, 40.8. Anal. Calcd for $C_{13}H_{12}N_4O_2S$: C, 54.15; H, 4.19; N, 19.43. Found: C, 54.07; H, 4.06; N, 19.81.

Benzotriazole-1-sulfonic acid *N*,*N*-di-*p*-tolylamide (3f): white needles (73%); mp 125−127 °C (hexanes); ^{1}H NMR ($CDCl_3$) δ 8.02 (dd, J = 7.4, 1.6 Hz, 1H), 7.53 (dd, J = 7.4, 1.5 Hz, 1H), 7.39 (td, J = 7.0, 1.2 Hz, 2H), 7.34 (td, J = 7.0, 1.2 Hz, 2H), 7.22 (d, J = 8.4 Hz, 4H), 7.02 (d, J = 8.4 Hz, 4H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 144.7, 138.8, 137.4, 132.7, 130.2, 129.6, 127.9, 125.3, 120.0, 112.4, 21.0; HRMS-FAB m/z $[M + Na]^+$ calcd for $C_{20}H_{18}N_4O_2SNa$ 401.1043, found 401.1053.

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Supporting Information Available: Characterization data and details for the crystal structure of **1** and **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Ciba, Ltd., Patent BE 621190; *Chem. Abstr.* **1963**, *59*, 62444.