Acidity of Cyclic Sulfamates: Study of Substituted 1,2,3-Benzoxathiazole 2,2-Dioxides and Theoretical Investigation of the Effect of Conformation on Acidity

Kenneth K. Andersen* and Martin G. Kociolek

Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824

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Sulfamate **1b**, 5-nitro-3-(4-toluenesulfonyl)-1,2,3-benzoxathiazole 2,2- dioxide, was treated with various nucleophiles: imidazole, benzylamine, *tert*-butylamine, sodium azide, potassium fluoride, pyridine, and sodium hydroxide. The first five attacked the exocyclic (tosyl) sulfur atom. No reaction was observed with the pyridine. The hydroxide ion attacked the endocyclic sulfur atom leading to opening of the benzoxathiazole ring. Several N-unsubstituted cyclic sulfamates, X-3*H*-1,2,3-benzoxathiazole 2,2-dioxides (**2a**, X = 5-H; **2b**, X = 5-NO_2; **2c**, X = 5-Me; **2d**, X = 5-Br; **2e**, X = 5-Cl; **2f**, X = 6-NO_2; **2g**, X = 5,6-Cl,Cl) and the naphtho-fused cyclic sulfamate (**2h**), were prepared by treatment of the respective *N*-tosyl compounds (**1a–h**) with sodium azide or potassium fluoride. The pK_a values for these compounds were determined by potentiometric titration in 60% v/v EtOH/H_2O. A Hammett plot using σ_m for **2a–e**, σ_p for **2f**, and both σ_m and σ_p for **2g** gave a $\rho = 2.74$. *Ab initio* calculations were done using sulfamic acid as a simple sulfamate model to test the effect of the geometry changes on pK_a. The calculations showed that the sulfamate with the ringlike geometry should be 3.6 pK_a units more acidic than the acyclic sulfamate. This overall change was broken down into three factors affecting the pK_a. The N–S bond rotation accounted for a change of 0.22 units, O–S bond rotation for 2.03 units, and ring strain for 1.36 units.

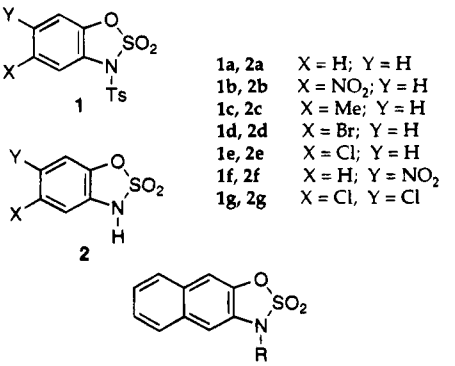
Introduction

Cyclic sulfur(VI) and sulfur(IV) esters and amides have been studied in order to compare their properties with those of their acyclic analogues.[1] These investigations have shown that cyclic compounds often differ markedly in reactivity compared to their acyclic analogues.

The reactivity of 3-tosyl-1,2,3-benzoxathiazole 2,2-dioxide (**1a**) with various nucleophiles has been examined previously.[2] Results of that study showed that the site of attack could be either the exocyclic or endocyclic sulfur atom depending on the nucleophile. Hydroxide ion and amines attacked the endocyclic sulfur atom, resulting in ring opening. Methoxide ion attacked both the endocyclic and exocyclic sulfur atoms. Organolithiums, as well as fluoride ion, attacked the exocyclic sulfur atom, cleaving off the tosyl group. In the latter cases it was suggested that **2a** was unusually acidic, since its conjugate base was a good leaving group. A variety of compounds, including sulfamides,[3] sulfonamides,[4] and disulfonamides,[5] show enhanced acidity when these functional groups are incorporated into five- or six-membered rings. This "acid strengthening" has been suggested to arise from stereoelectronic effects resulting from the ring geometry.[3a,5]

This paper reports the reaction of **1b** with several nucleophiles. The addition of the nitro group on the aromatic ring should make **2b** a stronger acid and, in turn, its conjugate base a better leaving group than the conjugate base of **2a**. This might increase the reactivity of the tosyl sulfur atom in **1b** compared to **1a**.

In addition, several of these substituted cyclic sulfamates (**2a–h**) were synthesized and their pK_a values determined. The effects of the substituents on the pK_as of these sulfamates were correlated by a Hammett plot.



1h R = Ts; **2h** R = H

The acid strengthening effect was examined by *ab initio* calculations using sulfamic acid as a simple sulfamate model. By calculating the energies for a variety of conformations, we were able to calculate the overall pK_a change going from an acyclic to a ring-like geometry. The overall change was broken down into three additive contributions: (1) O–S bond rotation; (2) N–S bond rotation, and (3) ring strain.

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Results and Discussion

Reaction of 1b with Various Nucleophiles. The reaction of **1b** with 2 equiv of imidazole in acetonitrile gave the *N*-unsubstituted cyclic sulfamate **2b** (69%) and *p*-toluenesulfonyl imidazole which arose from attack of the imidazole on the exocyclic *N*-tosyl sulfur atom. Similarly, the reaction of **1b** with two equivalents of benzyl- or *tert*-butylamine resulted in **2b** and the tosylated amines.

These reactions all required 2 equiv of the nitrogen nucleophile in order for the reactions to go to completion. One equivalent was necessary to form the *N*-tosylated compound, and the second equivalent formed an ammonium salt with the cyclic sulfamate anion. The use of 1 equiv resulted in the above mentioned products as well as recovery of half of the starting sulfamate.

Treatment of **1b** with 1 equiv of sodium azide in an aqueous acetonitrile solution gave the *N*-unsubstituted cyclic sulfamate **2b** (93%) and *p*-toluenesulfonyl azide. As monitored by TLC, this reaction went to completion in several minutes. Similarly, the reaction of **1b** with 1 equiv of potassium fluoride in aqueous acetonitrile resulted in **2b** (81%) and *p*-toluenesulfonyl fluoride. This reaction time was significantly longer.

The reaction of **1b** with 1 equiv of pyridine in acetonitrile was also attempted, but after the mixture had been stirred for 24 h at room temperature, TLC showed only starting material.

The treatment of **1b** with sodium hydroxide in aqueous acetonitrile resulted in the formation of sulfonamide **3** (92%) and a small amount of **2b** (6%). The formation of the major product arose from attack on the ring sulfur atom with cleavage of either the S–N or S–O bond. Ultimately, the acidic workup resulted in loss of a sulfate group, yielding the sulfonamide. This attack at the ring sulfur is analogous to that reported for the treatment of **1a** with sodium hydroxide, where it had been determined experimentally that the ring opening proceeded by way of N–S bond cleavage. Hammett correlation of the rate constants for the saponification of these *N*-tosyl sulfamates suggested that the ring opening of **1b** also proceeded by way of N–S bond cleavage. The reaction of **1a** with hydroxide ion, however, showed no evidence for attack on the *N*-tosyl sulfur atom.

The exocyclic sulfur atom of **1b** was the site of reaction when the nucleophiles were imidazole, azide ion, fluoride ion, or amines, and the endocyclic sulfur atom when the nucleophile was hydroxide ion. These results are analogous with those previously reported for the reaction of **1a** with fluoride ion and hydroxide ion.[2] However, in the case of the amines, opposite results were observed: endocyclic attack for **1a** and exocyclic for **1b**. The cyclic sulfamide **5a** has been shown to be quite acidic, which suggests that **2a** would also be quite acidic. The addition of a nitro group would only serve to increase the acidity of sulfamate **2b**. The conjugate base of **2b** would therefore be a better leaving group than that of **2a**. This might explain the increased reactivity of the exocyclic sulfur in **2b**. The difference in selectivity of the various nucleophiles remains unexplained.

These results led to an investigation of the acidity of a series of these NH cyclic sulfamates (**2a–h**).

Synthesis of N–H Cyclic Sulfamates. Treatment of **1a** with sodium azide in aqueous acetonitrile resulted in removal of the tosyl group and formation of the NH cyclic sulfamate, as well as *p*-toluenesulfonyl azide.

Table 1. Experimentally Determined pK_a Values

no.	pK_a[a]	scatter[b]	n[c]	no.	pK_a[a]	scatter[b]	n[c]
2a	4.62	0.03	6	**2e**	3.72	0.05	6
2b	2.76	0.07	5	**2f**	2.33	0.04	5
2c	4.73	0.03	7	**2g**	2.87	0.04	6
2d	3.47	0.05	5	**2h**	3.84	0.02	5

[a] pK_a determined at 25 °C in 60% v/v EtOH/H_2O. [b] The scatter or spread was determined as described in ref 6. [c] n = number of pK_a values averaged to obtain the value shown.

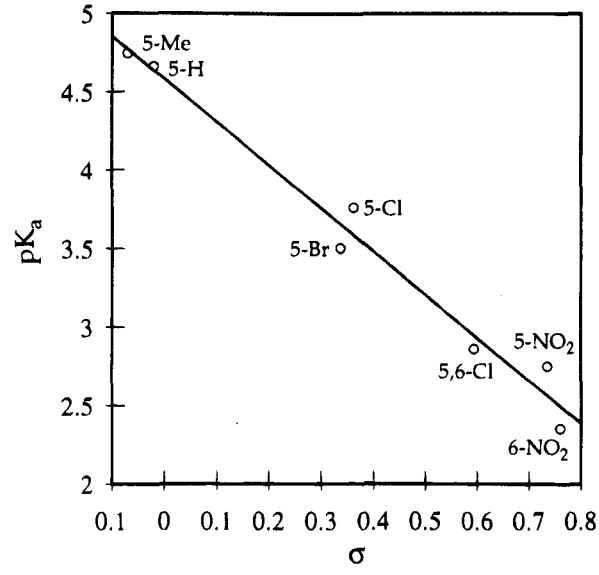

Figure 1. Hammett plot for the ionization of **2a–g** in 60% EtOH/H_2O.

Similar results were seen upon treatment of **1a** with potassium fluoride. The cyclic sulfamates **1c–h** were all treated in a similar manner, with either sodium azide or potassium fluoride, to give the N-unsubstituted cyclic sulfamates **2c–h**. The reactions of these compounds with sodium azide, in general, were faster and proceeded with very good yields. The reaction with potassium fluoride generally involved longer reaction times and resulted in lower yields.

pK_a Determinations. The pK_a values for the series of substituted cyclic sulfamates were determined in 60% v/v EtOH/H_2O. Potentiometric methods[6] were utilized with the pK_a values being calculated by using eq 1 which includes a correction for hydrogen ion activity $\{H^+\}$ (eq 2). This correction was applied only for pH values below 4.0; for values above 4.0 the hydrogen ion activity is essentially 0.

$$pK_a = pH + \log_{10}([HA] + \{H^+\}/[A^-] - \{H^+\}) \quad (1)$$

$$\{H^+\} = 10^{-pH} \quad (2)$$

The pK_a values for a series of substituted cyclic sulfamates (**2a-h**), as well as the scatter and number of pK_a values averaged, are shown in Table 1.

Hammett Plot. Several Hammett correlations using least squares analyses were carried out by plotting the experimental pK_a values (-log K) vs Hammett σ values (Figure 1). The pK_a values for compounds **2a–g** were plotted using σ_m for **2a–e**, σ_p for **2f**, and $\sigma_p + \sigma_m$ for **2g**.[7]

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Table 2. Energies (hartree) and Relative Energies (kcal mol^{-1})

no.	$E(NH_2)$	$E_{rel}(NH_2)$	$E(NH^-)$	$E_{rel}(NH^-)$
6a	−674.929742	0	−674.376334	0
6b	−674.921973	4.9	−674.369018	4.6
6c	−674.9053229	15.3	−674.356589	12.4
6d	−674.889493	25.2	−674.343595	20.6

The straight line provided a ϱ value of 2.74, correlation coefficient (r) of 0.975 with a standard error (s) of 0.16. Similar plots were constructed using only values for **2a**−**e** and **2a**−**f**. The ϱ,r,s values showed little change when the 6-NO_2 (**2f**) and 5,6-dichloro (**2g**) compounds were omitted. The value for these plots were as follows: (**2a**−**e**) $\varrho = 2.74$, $r = 0.975$, $s = 0.16$; (**2a-f**) $\varrho = 2.71$, $r = 0.974$, $s = 0.17$. The ϱ value for this series of cyclic sulfamates, 2.74, is in the same range as the value of 2.8 observed for a series of substituted cyclic sulfamides.[3]

Computational Investigation of a Simple Sulfamate Model. Sulfamic acid was chosen as a simple model to investigate the effect of O−S, N−S, and ring strain on the pK_a of sulfamate systems. By applying various constraints to the molecule, we could assess the degree to which each of these changes in geometry effected the acidity. The geometries of all the conformations (applying appropriate constraints where necessary) was optimized at the RHF/3-21+G* level. This level incorporates d-orbitals on the sulfur atom and also diffuse functions necessary for proper treatment of the anionic species. By calculating the energies for both the neutral and anionic species (Table 2), ΔH could be obtained for the reaction (deprotonation of H_5 at nitrogen). This could be used comparatively to judge the relative acidity of each conformation. Initially, the model was allowed to optimize to its lowest energy conformation (**6a**), in which the $H-O_2-S-N$ dihedral = 180° (hydroxyl hydrogen bisects the sulfonyl oxygens) and the O_2-S-N-(lone pair) dihedral = 180° (lone pair on nitrogen bisects the sulfonyl oxygens). The model was then subjected to a series of sequential conformational changes until the ring like geometry was reached (Figure 2). Each step was evaluated to compare its contribution to the overall pK_a change.

N−S Bond Rotation. The O_2-S-N-(lone pair) dihedral angle was constrained to 90° while holding the $H-O_2-S-N$ dihedral at 180°. The result of the 90° rotation of the S−N bond was a difference in energy between the two neutral species (**6a** to **6b**) of +4.9 kcal mol^{-1} and a difference between the anions of 4.6 kcal mol^{-1}. The difference between the two ΔH values of the two conformations was −0.3 kcal mol^{-1}. This translates to a ΔpK_a of −0.22 units resulting from rotation of the N−S bond; i.e., the acidity was increased on going from **6a** to **6b**.

O−S Bond Rotation. The O_2-S bond was rotated and the $H-O_2-S-N$ dihedral angle constrained at 0. This change resulted in a change in energy from **6b** to **6c** of 10.4 kcal mol^{-1} for the neutral compounds and 7.8 kcal mol^{-1} for the anions. The difference between the two ΔH values was −2.65 kcal mol^{-1}, which leads to a ΔpK_a of −2.03; i.e., an increase in acidity in going from **6b** to **6c**.

Ring Strain. The internal angles of compound **6c** were then constrained to resemble the ring geometry of the five-membered cyclic sulfamate using angles taken from a crystal structure of **1a** previously reported.[8] The angles were constrained as follows: $H-O_2-S$ = 112°, O_2-S-N = 95°, $S-N-H_6$ = 108°. The effect of constraining these angles were changes of 9.9 and 8.2 kcal mol^{-1} in the energies for the neutral molecules and anions, respectively. The ΔH value going from **6c** to **6d** was calculated to be −1.78 kcal mol^{-1}, which leads to a difference between the two ΔpK_a values of −1.36; i.e., an increase in acidity going from **6c** to **6d**.

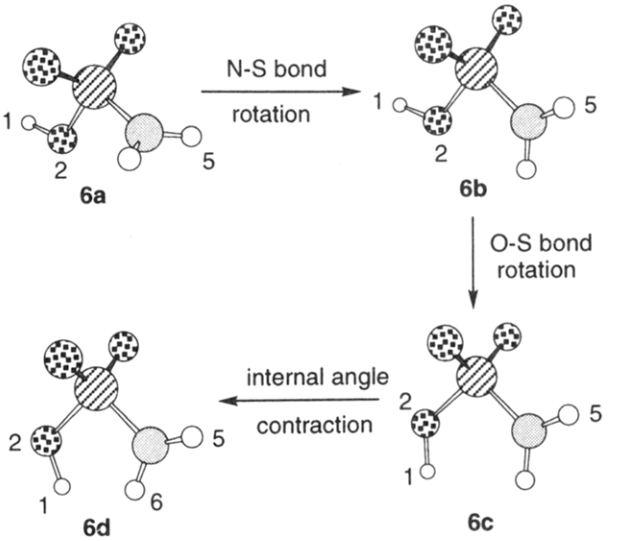

Figure 2. Representation of conformations of sulfamate model. **6a**: H_1-O_2-S-N dihedral = 180°, O_2-S-N-(lone pair) dihedral = 180°. **6b**: O_2-S-N-(lone pair) dihedral rotated to 90°. **6c**: H_1-O_2-S-N dihedral rotated to 0°. **6d**: internal angles contrained to ringlike geometry, $\angle H_1-O_2-S$ = 112°, $\angle O_2-S-N$ = 95°, $\angle S-N-H_6$ = 108°.

These results show that the change in geometry going from an acyclic to a ringlike structure has a profound effect on the energies of the compounds and, in turn, on the acidity. Overall, the neutral ringlike structure **6d** is 25 kcal mol^{-1} higher in energy than its acyclic analogue. The anion is slightly less effected with the structure having ringlike geometry being 20 kcal mol^{-1} higher. These calculations suggest that this change in geometry may be responsible for a lowering of the pK_a for the ring structure by about 3.6 units, thus acounting for the increase in acidity of the cyclic sulfamates compared to their acyclic analogues. The rotation of the N−S bond seems to have the smallest effect, a change of −0.22 units. The O−S bond rotation has the most profound effect with a change of −2.03 units. The ring strain also contributed greatly to the overall ΔpK_a, providing a change of −1.36 units.

To properly test the validity of these results, the experimentally determined pK_a for a cyclic sulfamate must be compared to an acyclic analogue. A proper compound to compare to cyclic sulfamate **2a** would be phenyl (*N*-phenyl amino)sulfonate (**4a**). The pK_a value for this compound has not yet been reported. A similar compound, **4b**, has been reported to have a pK_a in 50% EtOH/H_2O of 10.53.[9] This value is approximately 5.8 units higher that that of the cyclic compound **2a**. The computational results suggest that the difference should be smaller, around 3.6 pK_a units. It is conceivable,

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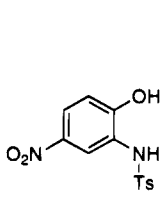
however, that the presence of a phenyl group attached to the nitrogen in place of the methyl could increase the acidity as much as 2.5 pK_a units. This has been shown experimentally in the case of $PhNHSO_2Ph$ versus $MeNHSO_2Ph$ where the pK_a values differ by 2.67 units, with the former sulfonamide being more acidic.[10] If the sulfamate were analogous to the sulfonamide, then the pK_a of **4a** is predicted to be around 8 (10.53−2.67). This would bring the change in pK_a between the cyclic and acyclic sulfamates in the range of the theoretical model (3.6). These results are analogous to experimental results seen in cyclic sulfamides; cyclic sulfamide **5a** (pK_a = 6.4)[3a,b] is approximately 3.7 pK_a units more acidic than its acyclic analogue **5b** (pK_a = 10.1).[11]



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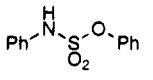
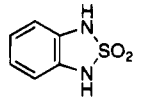
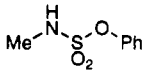


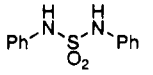
4a



5a



4b



5b

One other factor which may serve to lower the pK_a of the cyclic structure is the conformation of the aromatic ring in regard to the adjacent heteroatoms. In the acyclic compound the aromatic ring can adopt a conformation maximizing the interaction between the ring and the lone pairs on the heteroatoms. The constrained geometry of the cyclic structure might change this interaction, having a subsequent effect on the acidity of the compound.

It appears that this increase in acidity for the five-membered sulfamates is directly dependent on the amount of delocalization present between the lone pairs on the heteroatoms and the sulfur atom. This delocalization is directly effected by bond rotation and angle contraction going from **6a** to **6d**. This effect is reflected in the calculated N−S bond lengths for the neutral and anionic species of the four compounds which are as follows: (**6a**) 1.58, 1.52 Å; (**6b**) 1.60, 1.52 Å; (**6c**) 1.62, 1.53 Å; (**6d**) 1.65, 1.58 Å. As we change the conformation of the neutral species to provide for less and less delocalization, there is a corresponding increase in the N−S bond length. This inhibition of N−S delocalization has a direct effect on the acidity of the compound. We also see the expected shortening of the N−S bond length in the anion compared to the neutral compound resulting from an increase in N−S delocalization. Evidence for this type of delocalization has been determined by X-ray crystallography. Cotton and Stokely[12] reported the crystal structures of $(PhSO_2)_2NH$ and $(PhSO_2)_2N^-Na^+$ whose N−S bond lengths were 1.65 and 1.58 Å, respectively.

Similar arguments were suggested by King[5] to explain the acidity of a variety of sulfonamides. Laughlin[13] and co-workers also cited this effect to explain the basicity of *N,N*-dialkyl sulfonamides. King[14] also pointed to stereoelectronic effects of this type to explain the conformation and reactivity of sultones.

This delocalization has been considered for a number of similar compounds. Lipscomb[15] and co-workers' study of the rotational barriers in $(CH_3)_2NSO_2N(CH_3)_2$ suggested that interactions of the nitrogen lone pair and sulfur d-orbital has a profound effect on the conformations and rotational barriers of these compounds. Jennings and Spratt[16] came to similar conclusions for $ClSO_2NR_2$ and related compounds. By analogy it appears that there is a similar effect for the neutral sulfamates.

The effect of this d-orbital interaction involving anions next to a sulfonyl group is a source of some controversy. Wolfe[17] and co-workers have completed theoretical studies on carbanions adjacent to sulfur centers and suggested that these d-orbitals may indeed play some role in the stabilization of these compounds. In contrast, Streitwieser[18] has completed theoretical studies on the anion of dimethyl sulfone which suggested that the d-orbital interaction plays little role in the stabilization of the anion next to sulfonyl sulfur. Most recently,[19] Streitwieser has reported a study of the acidities of dimethyl sulfide, sulfoxide, and sulfone. They concluded that the relative acidity is inherent in the acid and is not dependent on charge delocalization within the anion.

Conclusion. The reactions of nucleophiles with **1b** did not prove totally analogous to those reaction with **1a**. The addition of the nitro group, making the conjugate base of **2b** a better leaving group, seems to have changed the reactivy of the exocyclic (tosyl) sulfur atom. Nitrogen nucleophiles, as well as fluoride ion, attack the tosyl sulfur atom and cleave the tosyl moiety, whereas hydroxide ion attacks the endocyclic sulfur atom and opens the ring. The selectivity between these two sulfur atoms remains unexplained.

The cyclic sulfamates **2a−h** have proven to be quite acidic in comparison to their acyclic analogues. This effect is analogous to that seen in sulfamides, sulfonamides, and disulfonamides. *Ab initio* studies of a simple sulfamate model suggest that the increase in acidity may arise from stereoelectronic effects which are controlled by the geometry of the system.

Experimental Section

General Methods. Melting points were determined in capillary tubes and are uncorrected. NMR spectra were obtained at 360 MHz for ^1H and at 90.6 MHz for ^{13}C on a Bruker spectrometer. All samples are in acetone−d_6 unless otherwise noted and are reported in parts per million from internal TMS. Mass spectra were obtained on a Hewlett Packard Model 5988−A GC/MS quadrupole spectrometer. IR spectra were obtained on a Nicolet model 205 FT spectrometer. Solvents were purified and dried via standard techniques.

Computational Methods. *Ab intio* calculations were carried out using Spartan (version 1.0.3) on a Silicon Graphics workstation with all compounds being optimized (applying constraints where necessary) at the HF/3-21+G* level.

Hammett Plots. The Hammett plots were constructed using the Least Squares 1.0 program, as well as DeltaGraph (version 2.0.2). Hammett σ values were obtain from ref 7.

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Acidity Measurements. Experimental pK_a values were obtained by potentiometric titration as outlined in Albert and Serjeant.[6] The pK_a values were determined in 60% v/v ethanol/water mixtures, primarily due to the low solubility of the compounds in water. The samples were typically run at 0.01 M concentrations (0.25 mmol in 25 mL) and titrated with 0.1 N NaOH (standardized with KHP) at 25° C. The measurements of pH were taken at nine intervals from 10–90% ionization.

Known Starting Materials. The syntheses of **1a–f** have been previously reported.[2] Compound **1h** was synthesized by similar methods: treatment of 3′-*N*-(2′-hydroxynaphthyl)-4-toluenesulfonamide with triethylamine and sulfuryl chloride. Compound **1g** was isolated as a product in the synthesis of **1e**.

Reaction of 1b with Imidazole. A solution of imidazole (0.050 g, 0.730 mmol) in H_2O (2 mL) was added to a solution of **1b** (0.135 g, 0.365 mmol) in acetonitrile (10 mL). The solution was stirred at room temperature for 30 min. The solvent was evaporated and the residue was triturated with $CHCl_3$ (10 mL) and filtered. The organic layer yielded *p*-toluenesulfonyl imidazole (0.072 g, 89%), whose mp, IR, and ^{1}H NMR spectra matched those in the literature. The bright yellow solid, removed by filtration, was dissolved in H_2O (10 mL), and the solution was acidified with 6 N HCl. The aqueous solution was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried over magnesium sulfate and evaporated to yield **2b** (0.054 g, 69%): mp 147–50 ×a1C dec; MS *m*/*z* 216 (M^+); IR (KBr) 3272 (NH, sharp), 1600, 1525 (NO_2), 1475, 1430, 1375, 1345 (NO_2, SO_2), 1230, 1220, 1180 (SO_2); ^{1}H NMR δ 8.08 (dd, 1H, J = 2.5, 8.5 Hz), 8.00 (d, 1H, J = 2.5 Hz), 7.25 (d, 1H, J = 8.5 Hz); ^{13}C NMR δ 108.5, 112.2, 120.0, 131.3, 145.5, 147.2. Anal. Calcd for $C_6H_4N_2O_5S$: C, 33.34; H, 1.87; N, 12.96. Found: C, 33.30; H, 1.89; N, 12.92.

Reaction of 1b with Benzylamine. Benzylamine (0.040 mL, 0.260 mmol) was added to a solution of **1b** (0.050 g, 0.135 mmol) in acetonitrile (10 mL). The solution was stirred at room temperature for 30 min. The solvent was evaporated and the residue triturated with $CHCl_3$ (15 mL) and filtered. Removal of the $CHCl_3$ yielded *N*-benzyl-*p*-toluenesulfonamide (0.031 g, 88%) whose mp and ^{1}H NMR spectra matched those in the literature. The undissolved solid was dissolved in H_2O and acidified with 6 N HCl and extracted with $CHCl_3$ (3 × 10 mL). Removal of the $CHCl_3$ yielded **2b** (0.025 g, 86%).

Reaction of 1b with *t*-Butylamine. An analogous reaction to the one with benzylamine was carried out with **1b** (0.100 g, 0.270 mmol) and *tert*-butylamine (0.057 mL, 0.540 mmol). Workup yielded **2b** (0.031 g, 53%). The *N*-*tert*-butyl-*p*-toluenesulfonamide was not isolated.

Reaction of 1b with Pyridine. An analogous reaction was carried out using **1b** (0.050 g, 0.135 mmol) and pyridine (0.011 mL, 0.135 mmol). The reaction was stirred for 24 h with only starting material detected by TLC.

Reaction of 1b with Sodium Azide. An analogous reaction was carried out using **1b** (0.100 g, 0.270 mmol) in acetonitrile (5 mL) and sodium azide (0.018 g, 0.260 mmol) in H_2O (1 mL). The reaction was complete in 15 min. Similar workup, using acetone in place of chloroform, yielded *p*-toluenesulfonyl azide, whose mp and ^{1}H NMR matched those in the literature. The reaction also yielded **2b** (0.052 g, 93%).

Reaction of 1b with Potassium Fluoride. An analogous reaction was carried out using **1b** (0.100 g, 0.270 mmol) in acetonitrile (5 mL) and potassium fluoride (0.018 g, 0.260 mmol) in H_2O (1 mL). The reaction was complete in 12 h. Workup yielded *p*-toluenesulfonyl fluoride, whose mp and ^{1}H NMR matched those in the literature. The reaction also yielded **2b** (0.045 g, 81%).

Reaction of 1b with Sodium Hydroxide. A solution of sodium hydroxide (6.4 mg, 0.16 mmol) in H_2O (2 mL) was added to **1b** (0.058 g, 0.16 mmol) in acetonitrile (10 mL), and the mixture was stirred at room temperature for 2 h. The solution was acidified with 6 N HCl and extracted with chloroform (3 × 5 mL) which upon removal of the solvent yielded **2b** (2 mg, 6%). The aqueous layer was then extracted with diethyl ether (3 × 5 mL); concentration of the organic solution yielded **3** (0.045, 92%) whose mp, IR, ^{1}H NMR, and ^{13}C NMR matched those previously reported.[2]

Synthesis of 2a,c–h. The compounds **2a,c–h** were synthesized by methods analogous to the reactions of **1b** with sodium azide or potassium fluoride as mentioned above. The IR spectra for the compounds below all showed the characteristic absorption bands of the cyclic sulfamate ring, most notably the single sharp NH stretch around 3200 cm^{-1}.

3*H*-1,2,3-Benzoxathiazole 2,2-dioxide (2a): mp 76–79 °C dec; MS *m*/*z* (relative intensity) 171 (35, M^+), 106 (6), 79 (100); ^{1}H NMR δ 7.07 (m, 5H); ^{13}C NMR δ 111.4, 113.5, 124.3, 124.9, 129.1, 143.6. Anal. Calcd for $C_6H_5NO_3S$: C, 42.10; H, 2.94; N, 8.18. Found: C, 41.91; H, 3.04; N, 8.02.

3*H*-5-Methyl-1,2,3-benzoxathiazole 2,2-dioxide (2c): mp 99–100 °C dec; MS *m*/*z* (relative intensity) 185 (37, M^+), 93 (100); ^{1}H NMR δ 2.31 (s, 3H), 6.93(dd, 1H, J = 2, 8 Hz), 6.96 (d, 1H, J = 2 Hz), 7.11 (d, 1H, J = 8 Hz); ^{13}C NMR δ 21.1, 111.4, 114.0, 124.3, 130.8, 135.8, 142.0. Anal. Calcd for $C_7H_7NO_3S$: C, 45.40; H, 3.81; N, 7.56. Found: C, 45.40; H, 3.84; N, 7.44.

3*H*-5-Bromo-1,2,3-benzoxathiazole 2,2-dioxide (2d): mp 178–181 °C dec; MS *m*/*z* (relative intensity) 251 (34, M^+), 249 (35), 159 (37), 157 (44), 78 (100); ^{1}H NMR δ 7.23 (d, 1H, J = 8.6 Hz), 7.30 (dd, 1H, J = 2.1, 8.6 Hz), 7.33 (d, 1H, J = 2.1 Hz); ^{13}C NMR δ 113.1, 115.8, 117.0, 126.1, 131.9, 142.3. Anal. Calcd for $C_6H_4BrNO_3S$: C, 28.82; H, 1.61; N, 5.60. Found: C, 28.73; H, 1.55; N, 5.44.

3*H*-5-Chloro-1,2,3-benzoxathiazole 2,2-dioxide (2e): mp 168–170 °C dec; MS *m*/*z* (relative intensity) 207 (79, M^+), 205 (32), 113 (100), 111 (34); ^{1}H NMR δ 7.27 (d, 1H, J = 8.9 Hz), 7.19 (d, 1H, J = 2.1 Hz), 7.14 (dd, 1H, J = 8.9, 2.1 Hz); ^{13}C NMR δ 113.1, 113.5, 123.6, 130.3, 131.9, 142.3. Anal. Calcd $C_6H_4ClNO_3S$: C, 35.05; H, 1.96; N, 6.81. Found: C, 35.00; H, 2.01; N, 6.80.

3*H*-6-Nitro-1,2,3-benzoxathiazole 2,2-dioxide (2f): mp 200–202 °C dec; MS *m*/*z* 216 (M^+); ^{1}H NMR δ 7.33 (d, 1H, J = 9.4 Hz), 8.16 (m, 2H); ^{13}C NMR δ 107.5, 111.7, 112.9, 135.9, 141.8, 143.1. Anal. Calcd for $C_6H_4N_2O_5S$: C, 33.34; H, 1.87; N, 12.96. Found: C, 33.40; H, 1.76; N, 12.99.

3*H*-5,6-Dichloro-1,2,3-benzoxathiazole 2,2-dioxide (2g): mp 177–181 °C dec; MS *m*/*z* (relative intensity) 241 (27, M^+), 239 (37), 149 (59), 147 (100), 112 (75). ^{1}H NMR δ 7.59 (s, 1H), 7.39 (s, 1H); ^{13} C NMR δ 113.6, 114.3, 123.2, 128.2, 130.2, 141.9. Anal. Calcd for $C_6H_3Cl_2NO_3S$: C, 30.02; H, 1.26; N, 5.84. Found: C, 29.94; H, 1.32; N, 5.77.

3*H*-1,2,3-Naphtho[2,3-*d*]oxathiazole 2,2-dioxide (2h): mp 167–170 °C dec; MS *m*/*z* (relative intensity) 221 (15, M^+), 129 (93), 102 (100); ^{1}H NMR δ 7.47 (m, 2H), 7.53 (s, 1H), 7.72 (s, 1H), 7.88 (m, 2H); ^{13}C NMR δ 107.8, 108.9, 125.9, 126.5, 127.6, 128.2, 130.0, 130.1, 131.4, 143.0. Anal. Calcd for $C_{10}H_7NO_3S$: C, 54.29; H, 3.19; N, 6.33. Found: C, 54.38;, H, 3.15; N, 6.38.

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Supplementary Material Available: Cartesian coordinates for compounds **6a–d** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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