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Sensitivities of Some Imidazole-1-sulfonyl Azide Salts

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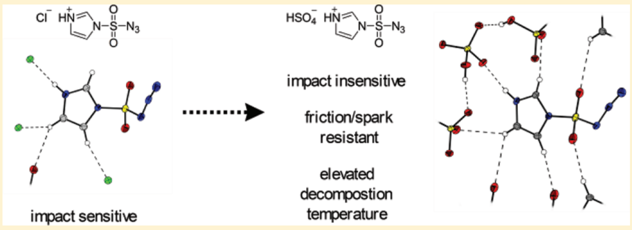
S Supporting Information

ABSTRACT: Imidazole-1-sulfonyl azide hydrochloride, an inexpensive and effective diazotransfer reagent, was recently found to be impact sensitive. To identify safer-to-handle forms of this reagent, several different salts of imidazole-1-sulfonyl azide were prepared, and their sensitivity to heat, impact, friction, and electrostatic discharge was quantitatively determined. A number of these salts exhibited improved properties and can be considered safer than the aforementioned hydrochloride. The solid-state structures of the chloride and less sensitive hydrogen sulfate were determined by single-crystal X-ray diffraction in an effort to provide some insight into the different properties of the materials.



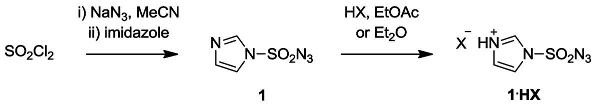
■ INTRODUCTION

In recent times, organic azides have attracted considerable attention because of the facile reactions that these high energy, kinetically stable molecules undergo.[1] Their use in dipolar cycloadditions, investigated in detail by Huisgen and coworkers in the 1960s[2] and popularized in the past decade by the revelation that such reactions are catalyzed by various metals,[3] is particularly noteworthy. As a consequence of this popularity, there is a considerable interest in synthetic methodologies for the preparation of organic azides. The diazo-transfer reaction is one such method and involves the conversion of a primary amine into an organic azide by the action of a powerful diazo donor (most commonly a sulfonyl azide). For the reaction to proceed in a facile manner, the sulfonyl azide must be adjoined to a strong electron-withdrawing group; trifluoromethanesulfonyl azide is most commonly used because arylsulfonyl azides are, for the most part, simply not reactive enough. To circumvent the problems of high cost and instability associated with using trifluoromethanesulfonyl azide, imidazole-1-sulfonyl azide hydrochloride **1·HCl** was developed as an inexpensive and shelf-stable alternative diazo-transfer reagent with comparable efficacy.[4] The shock sensitivity and thermal stability of activated, low-molecular weight azides has always been cause for concern,[1,5,6] and after hearing of an explosion that occurred during the synthesis of **1·HCl**[4] we sought to quantify the sensitivity of **1** and a number of its salts toward impact, friction, and electrostatic discharge to provide a rational assessment of the relative safety of these compounds. It was anticipated that the sensitivity of reagent **1** to various stimuli could be "tuned", for better or worse, by crystallization with different acids.

■ RESULTS AND DISCUSSION

Imidazole-1-sulfonyl azide **1** is easily prepared by the addition of 2 molar equiv of imidazole to chlorosulfonyl azide preformed in situ by the reaction of equimolar quantities of sodium azide and sulfuryl chloride in acetonitrile (Scheme 1).[4] This product can be precipitated from the crude solution as the pure hydrochloride salt **1·HCl** by treatment with ethanolic hydrogen chloride. Partitioning **1·HCl** between an organic solvent and aqueous sodium bicarbonate proved to be a convenient method for obtaining organic solutions of pure **1**. Solutions of **1** in ethyl acetate were treated with sulphuric acid, toluenesulfonic acid, perchloric acid, or tetrafluoroboric acid to precipitate the corresponding salts **1·H$_2$SO$_4$**, **1·TsOH**, **1·HClO$_4$**, and **1·HBF$_4$**, respectively. Similarly, treatment of a solution of **1** in diethyl ether with methanesulfonic acid provided the corresponding salt **1·MsOH**.

Scheme 1. Synthesis of Different Salts of 1



X = Cl, HSO$_4$, MsO, TsO, ClO$_4$, BF$_4$

The ability of these salts to act as diazo donors was confirmed by the conversion of 4-aminobenzoic acid into 4-azidobenzoic acid under standard diazo-transfer reaction conditions (Table 1).[4] All of the reactions provided product in

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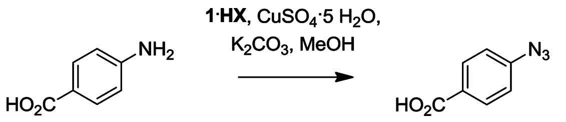
Table 1. Different Anions Do Not Significantly Affect the Efficacy of Reagent 1



	1·HCl	**1·H$_2$SO$_4$**	**1·MsOH**	**1·TsOH**	**1·HClO$_4$**	**1·HBF$_4$**
yield (%)	63	63	61	70	57	64

comparable isolated yield, demonstrating that the different anions do not significantly affect the efficacy of the reagent.

Differential scanning calorimetry (DSC) was performed on **1** and all of its salts to determine their melting points and decomposition onset temperatures. The thermal behavior of these materials is displayed as DSC plots in a temperature range from 20 to 400 °C in Figure 1. Since none of the compounds crystallized as hydrates or with included solvent, as indicated by elemental analyses, the small endothermic peaks of each DSC curve can be assigned as the melting point for each salt, while the exothermic peaks can be ascribed to decomposition. Decomposition temperatures for each compound are defined by the lowest onset temperature of the exotherms.

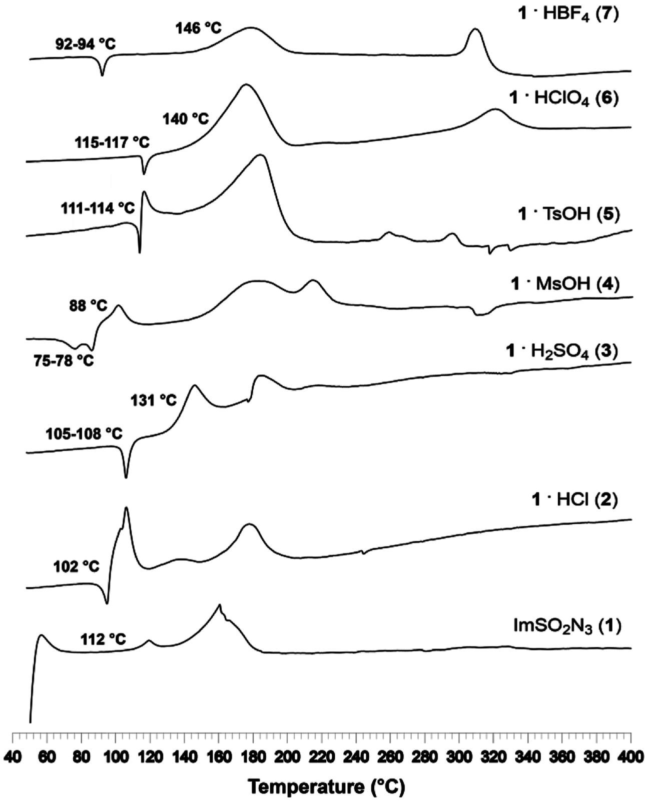


Figure 1. DSC plots of compound **1** and its various salts (exothermic = ↑, endothermic = ↓).

Interestingly, the temperature at which decomposition commences varies considerably; from the low value of 88 °C for **1·MsOH**, to the parent compound **1** at 112 °C, up to 146 °C, as observed for **1·HBF$_4$**. The only salt with a relatively large liquid range (>50 °C) was **1·HBF$_4$**, which melted at 92–94 °C but did not begin to decompose until it reached a temperature of 146 °C. From the DSC data, it is evident that all of the materials can be used at a temperature less than 88 °C and some even higher. However, in practice, when drying samples, using or storing the materials, it is advisible to use temperatures less than 60 °C. This provides a particularly large margin for error for the more thermostable salts like **1·HBF$_4$** and **1·H$_2$SO$_4$**.

The sensitivities of each substance to mechanical stimuli were assessed. Impact sensitivity tests were carried out according to STANAG 4489[7] modified instructions[8] using a BAM (Bundesanstalt für Materialforschung) drophammer,[9] while friction sensitivity tests were carried out according to STANAG 4487[10] modified instructions[11] using the BAM friction tester. The sensitivity of each compound toward electrical discharge was also determined using the electric spark tester ESD 2010 EN.[12] These data, together with decomposition temperatures and nitrogen content (percentage by weight) of each material, are presented in Table 2. When interpreting the data presented in Table 2, one should note that the larger a value is for a given test, the less sensitive that material is to that given form of stimulus. Further, subsequent descriptions of materials as "insensitive", "less sensitive", "sensitive", "very sensitive", or "extremely sensitive" are based on the UN Recommendations on the Transport of Dangerous Goods.[13]

Table 2. Sensitivity Data for 1 and Its Salts[a]

	sensitivity				
compd	impact (J)	friction (N)	ESD (J)	percentage nitrogen (w/w, %)	dec temp (°C)
1	<1	72		40.5	112
1·HCl	6	240	0.50	33.4	102
1·H$_2$SO$_4$	40	240	0.30	25.8	131
1·MsOH	40	192	0.10	26.0	88
1·TsOH	30	>360	0.70	20.3	114
1·HClO$_4$	<1	<5	0.15	25.6	140
1·HBF$_4$	40	240	0.50	26.8	146

[a]ESD is an acronym for electrostatic discharge. The technique used to determine these values cannot be applied to **1** because it is a liquid under standard conditions.

What is quite remarkable about the data in Table 2 is that the properties of the materials vary significantly, ranging from extremely sensitive to insensitive, even though they all contain the same energetic species. The parent compound **1**, as well as the perchlorate **1·HClO$_4$**, is *very sensitive* toward impact, as one would expect. The previously reported chloride **1·HCl** and the tosylate **1·TsOH** are *sensitive* to impact and should be handled with care. The hydrogen sulfate **1·H$_2$SO$_4$**, mesylate **1·MsOH**, and tetrafluoroborate **1·HBF$_4$** are *insensitive* to impact. A similar trend is observed for the friction sensitivity of the compounds. The parent sulfonyl azide **1** and its perchlorate salt **1·HClO$_4$** are again of concern: classified as *very sensitive* and *extremely sensitive*, respectively. The other salts have higher values and are only considered *sensitive* to friction, except for the tosylate **1·TsOH**, which is *insensitive* to friction. Values determined for electrostatic discharge (ESD) are strongly dependent on the grain size of the crystalline material, thus differing between batches of each material and for technical reasons cannot be determined for a liquid like **1**. Nevertheless, all of the salts returned values in the range of 0.10–0.70 J, indicating that none were particularly sensitive toward electrostatic discharge.

From these results, several recommendations can be made. The parent compound **1**, as a neat liquid, should be handled with extreme caution and ideally would never be isolated but instead prepared and used only in solution. As expected, the perchlorate **1·$HClO_4$** is even more hazardous than **1** and should not be prepared by those without expertise in handling energetic materials. The hydrochloride salt **1·HCl** has comparable impact sensitivity (not to be confused with energetic yield) to RDX (cyclotrimethylenetrinitramine), a commonly used high explosive, and must be handled with caution. On the other hand, the relatively high decomposition temperature, impact insensitivity, low friction, and ESD sensitivities of the hydrogensulfate **1·H_2SO_4** and the tetrafluoroborate **1·HBF_4** make these two materials safe to manipulate, although all the usual precautions taken when handling energetic laboratory reagents should still be observed.

Another issue worthy of consideration, especially if these reagents are to be kept in bulk, is the question of shelf stability. If not stored with desiccation, the hygroscopic hydrochloride **1·HCl** discolors and liquefies over the course of a few weeks, producing a brown oil that smells of hydrazoic acid. The hydrogensulfate **1·H_2SO_4** is less hygroscopic, remaining unchanged after storage for several months under ambient conditions. However, after more than one year, this salt also discolored and liquefied with the liberation of hydrazoic acid. Only the tetrafluoroborate **1·HBF_4** remained unaffected by storage under ambient conditions for one year. Thus, one can conclude that **1·HBF_4** has the most favorable characteristics of all the salts investigated but that **1·H_2SO_4** is a less expensive, viable alternative if stored with the exclusion of moisture.

The solid-state structures of **1·HCl** and **1·H_2SO_4**, two salts with quite different sensitivities, were determined by single-crystal X-ray diffraction to see if some insight might be gained into why the former salt is more sensitive to mechanical stimuli than the latter. The structures of both materials were solved (see the Experimental Section for details) and found to crystallize in the monoclinic space group $P2_1/c$ with four molecules to each unit cell. The molecular moiety of each solid is depicted in the Supporting Information (Figure S1). The bond lengths and angles associated with both imidazole moieties and counterions are commensurate with literature values,[14] while those associated with the sulfonyl azide moiety did not differ significantly between structures.

The main difference between these materials lies in their molar volumes, density and the number of intermolecular hydrogen bonding contacts made (Table 3, Figure 2). The more sensitive salt, **1·HCl**, has a smaller molar volume, lower density, and fewer hydrogen bonds than the less sensitive salt, **1·H_2SO_4**. The greater molar volume of **1·H_2SO_4** leads to a lower calculated lattice enthalpy (according to Jenkins' equation[15,16] $\Delta_L H$ (**1·H_2SO_4**) = 484.5 kJ mol^{-1}, $\Delta_L H$ (**1·HCl**) = 506.4 kJ mol^{-1}) but translates to fewer high energy azide groups per unit volume in the solid. Its greater density and more extensive network of hydrogen bonds may act as an energy sink to suppress decomposition.

Table 3. Molar Volume, Density, And Hydrogen Bonding in 1·HCl and 1·H_2SO_4

	V_M (cm^{3}mol^{-1})	ρ (g cm^{-3})	classical H-bonds per molecule	nonclassical H-bonds per molecule
1·HCl	122.4	1.713	1	3
1·H_2SO_4	144.8	1.873	2	4

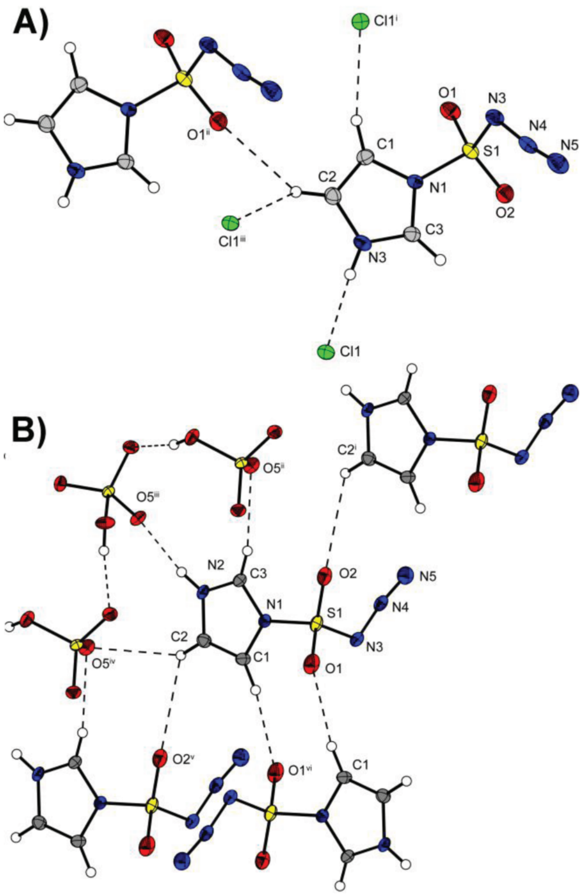


Figure 2. Comparison of the intermolecular interactions in crystals of **1·HCl** and **1·H_2SO_4**. (A) View on the hydrogen bonds in the structure of **1·HCl**. Symmetry codes: (i) x, $1.5 - y$, $0.5 + z$; (ii) $-1 + x$, y, z; (iii) $-x$, $2 - y$, $1 - z$. (B) View on the hydrogen bonds in the structure of **1·H_2SO_4**. Symmetry codes: (i) x, y, $1 + z$; (ii) $-1 + x$, y, z; (iii) $-1 + x$, $0.5 - y$, $-0.5 + z$; (iv) $-1 + x$, $0.5 - y$, $-0.5 + z$; (v) x, y, $-1 + z$; (vi) $-x$, $-y$, $2 - z$.

■ CONCLUSION

Since all of the compounds investigated were equally good diazo donors, the choice of ideal reagent comes down to a consideration of their safety. All things considered, the tetrafluoroborate **1·HBF_4** and the hydrogen sulfate **1·H_2SO_4** are the safest-to-handle materials, although the tetrafluoroborate **1·HBF_4** is superior in that it has a longer shelf life than the hydrogen sulfate **1·H_2SO_4**. However, the hydrogen sulfate **1·H_2SO_4** is easier and less expensive to prepare than the tetrafluoroborate **1·HBF_4** and can be stored with the exclusion of moisture to prolong its shelf life, making it the recommended alternative to the hydrochloride **1·HCl**. None of these compounds were found to be completely insensitive, which restricts options for transportation and thereby commercialization. Formulation of one of these salts with additives may provide a solution to this problem and further extend shelf life.[17]

■ EXPERIMENTAL SECTION

Caution! Imidazole-1-sulfonyl azide and its salts are energetic materials with sensitivities toward shock and friction. Therefore, proper safety precautions (safety glass, face shield, earthened equipment and shoes, Kevlar gloves, and ear plugs) should be employed while synthesizing and handling the compounds described. Specifically, neat imidazole-1-sulfonyl azide and its chloride and perchlorate salts are very sensitive and have to be handled with great care. Plastic suction filters and spatulas are recommended for the isolation of the crystalline materials described. Mother liquors and other waste, which may contain the highly explosive sulfonyl diazide, should be treated with excess sodium nitrite and acidified to destroy azide-containing species.

Imidazole-1-sulfonyl azide (**1**) as well as its hydrochloride (**2**) was prepared according to literature procedures.[4] Unfortunately, all described compounds suffer from partial decomposition during the NMR experiments in DMSO-d_6, so that in all cases remaining undecomposed material besides a decomposition product can be observed. Presumably from the 3-azidosulfonyl-3*H*-imidazol-1-ium cation the azidosulfonyl moiety is cleaved off resulting in the respective 1,3*H*-imidazol-1-ium salts. Because of the polar character of the described compounds and resulting solubility problems, it was not possible to gain NMR data from different solvents such as $CDCl_3$, CD_3OD, or acetone-d_6. The NMR signals of the decomposition product can be identified in all recorded spectra and are marked with an asterisk in the experimental procedures.

3-Azidosulfonyl-3*H*-imidazol-1-ium Hydrogen Sulfate (1·H_2SO_4). Sulfuric acid (3.9 g, 39.85 mmol; in 20 mL EtOAc) was added slowly to a solution of imidazole-1-sulfonyl azide **1** (6.9 g, 39.85 mmol; in 20 mL EtOAc) at 0 °C. The reaction mixture was stirred for 1 h at rt. The precipitate was filtered, washed, and dried in vacuo to give 9.3 g (29.52 mmol, 74%) of **1·H_2SO_4** as a white, crystalline powder. DSC (5 °C min^{-1}, °C): 105−108 °C (mp), 131 °C (dec). IR (KBr, cm^{-1}) 3110 (s), 3084 (s), 2969 (s), 2864 (s), 2177 (s), 1586 (m), 1516 (m), 1460 (w), 1431 (s), 1302 (m), 1233 (vs), 1191 (s), 1152 (vs), 1127 (vs), 1100 (vs), 1067 (s), 1018 (s), 983 (m), 872 (m), 834 (m), 774 (s), 740 (m); Raman (1064 nm, 400 mW, 25 °C, cm^{-1}): 3187 (13), 3157 (23), 3113 (13), 2174 (100), 1588 (20), 1518 (23), 1462 (70), 1426 (26), 1329 (19), 1304 (44), 1236 (24), 1192 (35), 1146 (12), 1129 (18), 1103 (13), 1071 (48), 1021 (83), 984 (41), 899 (24), 780 (67), 646 (15), 617 (18), 599 (19), 585 (90), 486 (36), 467 (55), 430 (15), 411 (26), 372 (71), 362 (48), 322 (25), 203 (26). ^1H NMR (DMSO-d_6, 25 °C, ppm): δ = 14.30 (s, br, NH^+), 12.42 (s, br, HSO_4^-), 9.06* (t, CH, J = 1.1 Hz), 8.69 (dd, CH, J_1 = 0.8 Hz, J_2 = 1.5 Hz), 7.98 (dd, CH, $J_{1/2}$ = 1.5 Hz), 7.66* (d, CH, J = 1.2 Hz), 7.37 (dd, CH, J_1 = 0.9 Hz, J_2 = 1.7 Hz). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 138.3, 134.9*, 130.6, 119.8*, 119.5. *m/z* (FAB^+): 174.0 [$HImSO_2N_3^+$]. *m/z* (FAB^-): 96.9 [HSO_4^-]. Anal. Calcd for $C_3H_5N_5O_6S_2$: C, 13.28; H, 1.86; N, 25.82; S, 23.64. Found: C, 13.61; H, 2.03; N, 26.11; S, 23.29. BAM drophammer: >40 J; friction tester: >240 N; ESD: 0.3 J.

3-Azidosulfonyl-3*H*-imidazol-1-ium Methanesulfonate (1·MsOH). Imidazole-1-sulfonyl azide **1** (8.66 g, 50 mmol) was diluted with 10 mL of Et_2O. Then methanesulfonic acid (4.81 g, 50 mmol) was added dropwise under stirring at 0 °C. The precipitate was filtered off, washed with EtOH and Et_2O, and dried in vacuo, yielding 11.50 g (42.7 mmol, 85%) of **1·MsOH** as a white powder. DSC (5 °C min^{-1}, °C): 75−78 °C (mp), 88 °C (dec). IR (KBr, cm^{-1}): 3439 (br), 3107 (s), 3058 (s), 2908 (s), 2761 (s) 2704 (s), 2661 (s), 2577 (m), 2173 (vs), 1629 (w), 1580 (m), 1508 (m), 1449 (m), 1428 (vs), 1322 (m), 1195 (vs), 1161 (vs), 1135 (vs), 1103 (m), 1059 (vs), 981 (w), 834 (s), 780 (vs), 638 (s), 584 (s), 562 (s), 535 (m). Raman (1064 nm, 400 mW, 25 °C, cm^{-1}): 3178 (17), 3120 (28), 3035 (49), 3020 (41), 2947 (100), 2179 (100), 1582 (10), 1514 (10), 1471 (66), 1444 (32), 1424 (21),1321 (25), 1302 (24), 1244 (11), 1189 (28), 1124 (12), 1058 (26), 1031 (59), 981 (30), 966 (12), 785 (96), 769 (25), 581 (60), 555 (22), 546 (21), 523 (12), 482 (22), 467 (28), 375 (29), 357 (36), 343 (24), 320 (11). ^1H NMR (DMSO-d_6, 25 °C, ppm): δ = 14.88 (s, br, $MeSO_3H$), 14.28 (s, br, NH), 9.03* (t, CH, J = 1.2 Hz), 8.76 (dd, CH, J_1 = 0.8 Hz, J_2 = 1.6 Hz), 7.99 (dd, CH, $J_{1/2}$ = 1.6 Hz), 7.63* (d, CH, J = 1.4 Hz), 7.39 (dd, CH, J_1 = 0.8 Hz, J_2 = 1.6 Hz), 2.46 (s, $CH_3SO_3^-$). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 138.4, 134.9*, 129.9, 119.8*, 119.6, 40.9 ($CH_3SO_3^-$). *m/z* (FAB^+): 174.1 [$HImSO_2N_3^+$]. *m/z* (FAB): 95.0 [$MeSO_3^-$]. Anal. Calcd for $C_4H_7N_5O_5S_2$: C, 17.84; H, 2.62; N, 26.01. Found: C, 17.46; H, 2.76; N, 25.88. BAM drophammer: >40 J; friction tester: >192 N; ESD: >0.1 J.

3-Azidosulfonyl-3*H*-imidazol-1-ium 4-Toluenesulfonate (1·TsOH). Imidazole-1-sulfonyl azide hydrochloride **1** (4.19 g, 20 mmol) was suspended in EtOAc (50 mL). Under stirring, a saturated solution of $NaHCO_3$ (50 mL) was added. After **1** dissolved under gas evolution, the phases were separated. The organic phase was dried over $MgSO_4$ and subsequently treated with a solution of *p*-toluenesulfonic acid monohydrate (3.8 g, 20 mmol) in EtOAc (35 mL). Then the reaction mixture was cooled with an ice bath, and a small amount of hexane was added. The precipitate was filtered off and washed with Et_2O to give 3.29 g (9.53 mmol, 48%) of **1·TsOH** as a white powder. DSC (5 °C min^{-1}, °C): 111−114 °C (mp); 114 °C (dec 1); 155 °C (dec 2). IR (KBr, cm^{-1}): 3440 (br), 3157 (s), 3086 (s), 3058 (s), 2969 (m), 2554 (m), 2418 (m), 2305 (m), 2172 (vs), 1584 (m), 1495 (m), 1438 (vs), 1226 (vs), 1173 (vs), 1119 (vs), 1057 (s), 1011 (vs), 874 (m), 817 (m), 778 (vs), 682 (vs), 644 (vs), 566 (vs). Raman (1064 nm, 400 mW, 25 °C, cm^{-1}): 3185 (12), 3158 (11), 3065 (100), 2984 (16), 2924 (53), 2872 (13), 2177 (58), 1601 (45), 1496 (18), 1450 (28), 1383 (22), 1318 (16), 1244 (10), 1213 (41), 1182 (20), 1123 (72), 1086 (27), 1060 (18), 1035 (27), 1014 (34), 982 (42), 803 (98), 777 (40), 685 (24), 651 (13), 637 (27), 605 (13), 584 (36), 483 (30), 466 (33), 402 (27), 363 (79), 318 (26), 293 (84), 232 (37). ^1H NMR (DMSO-d_6, 25 °C, ppm): δ = 14.28 (s, br, NH), 9.08* (t, CH, J = 1.2 Hz), 8.73 (dd, CH, J_1 = 0.9 Hz, J_2 = 1.7 Hz), 8.00 (dd, CH, $J_{1/2}$ = 1.1 Hz), 7.67* (d, CH, J = 1.4 Hz), 7.51 (d, CH (*p*-$TolSO_3^-$, J = 8.0 Hz), 7.39 (dd, CH, J_1 = 0.9 Hz, J_2 = 1.7 Hz), 7.14 (d, CH, (*p*-$TolSO_3^-$, J = 8.0 Hz), 2.29 (s, CH_3). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 145.4 (C_1, *p*-$TolSO_3^-$), 138.8 (C_4, *p*-$TolSO_3^-$), 138.4, 134.9*, 130.5, 128.8 ($C_{3/5}$, *p*-$TolSO_3^-$), 126.1($C_{2/6}$, *p*-$TolSO_3^-$), 119.9*, 119.5, 21.3 (CH_3). *m/z* (FAB^+): 174.2 [$HImSO_2N_3^+$]. *m/z* (FAB^-): 171.1 [$C_7H_7SO_3^-$]. Anal. Calcd for $C_{10}H_{11}N_5O_5S_2$: C, 34.78; H, 3.21; N, 20.28; S, 18.57. Found: C, 34.62; H, 3.34; N, 20.14; S, 18.81. BAM drophammer: >30 J; friction tester: >360 N; ESD: 0.7 J.

3-Azidosulfonyl-3*H*-imidazol-1-ium Perchlorate (1·$HClO_4$). Imidazole-1-sulfonyl azide (**1**) (13.8 g, 79.7 mmol) and perchloric acid (60%, 5.2 mL, 79.7 mmol) were dissolved in 30 mL of EtOAc each. Then the perchloric acid solution was slowly added to the imidazole-1-sulfonyl azide solution at 0 °C. After the reaction mixture was stirred for 1 h at rt, the white precipitate was filtered off and dried in vacuo to give 3.9 g (14.25 mmol, 18%) of **1·$HClO_4$** as a white powder. DSC (5 °C min^{-1}, °C): 115−117 °C (mp); 140 °C (dec). IR (KBr, cm^{-1}): 3168 (s), 2172 (s), 1581 (m), 1512 (m), 1446 (s), 1327 (m), 1284 (m), 1222 (m), 1197 (s), 1157 (s), 1121 (s), 1083 (vs), 1059 (vs), 981 (m), 888 (w), 779 (vs), 746 (m). Raman (1064 nm, 400 mW, 25 °C, cm^{-1}): 3183 (9), 3170 (8), 2171 (47), 1580 (5), 1512 (8), 1444 (42), 1328 (14), 1286 (15), 1224 (23), 1196 (16), 1156 (7), 1134 (9), 1113 (17), 1078 (14), 983 (32), 938 (101), 930 (43), 910 (11), 788 (49), 627 (28), 590 (59), 485 (24), 462 (46), 365 (35), 359 (48), 330 (20), 210 (16). ^1H NMR (DMSO-d_6, 25 °C, ppm): δ = 14.52 (s, br, $HClO_4$), 14.27 (s, br, NH), 9.04* (CH), 8.76 (CH), 8.00 (CH), 7.66* (s, CH), 7.41 (CH). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 138.4, 134.8*, 130.4, 119.8*, 119.6. *m/z* (FAB^+): 174.0 [$HImSO_2N_3^+$]. *m/z* (FAB^-): 98.9 [ClO_4^-]. Anal. Calcd for $C_3H_4ClN_5O_6S$: C, 13. 17; H, 1.47; N, 25.60; S, 11.72. Found: C, 13.11; H, 1.53; N, 25.55; S, 11.47. BAM drophammer: <1 J (!); friction tester: <5 N (!); ESD: 0.15 J.

3-Azidosulfonyl-3*H*-imidazol-1-ium Tetrafluoroborate (1·HBF_4). At 0 °C, a solution of 54% fluoroboric acid in Et_2O (3.25 g, 20 mmol) was slowly added to a solution of imidazole-1-sulfonyl azide (**1**) in 25 mL of EtOAc (3.46 g, 20 mmol). A white precipitate instantly formed. It was filtered off and washed with Et_2O to give 3.20 g (12.3 mmol, 61%) of **1·HBF_4** as a white powder. DSC (5 °C min^{-1}, °C): 92−94 °C (mp); 146 °C (dec). IR (KBr, cm^{-1}): 3426 (s), 3168 (m), 3059 (m), 2167 (s), 1629 (w), 1580 (m), 1509 (w), 1438 (s), 1322 (w), 1294 (m), 1195 (vs), 1124 (vs), 1105 (vs), 1083 (vs), 1064 (vs), 1036 (vs), 834 (vw), 778 (s), 640 (s), 601 (m), 584 (m). Raman (1064 nm, 400 mW, 25 °C, cm^{-1}): 3198 (15), 3173 (11), 3132 (10), 2166 (83), 1586 (11), 1446 (63), 1432 (29), 1324 (15), 1287 (14), 1230 (23), 1198 (20), 1143 (11), 1068 (16), 976 (31), 783 (64), 771 (51), 649 (21), 597 (102), 483 (34), 465 (42), 361 (71), 325 (30). ^1H NMR (DMSO-d_6, 25 °C, ppm): δ = 14.21 (s, br, NH), 9.04* (t, CH, J = 1.2 Hz), 8.80 (dd, CH, J_1 = 1.1 Hz,

J_2 = 2.2 Hz), 8.02 (dd, CH, $J_{1/2}$ = 1.3 Hz), 7.66* (d, CH, J = 1.5 Hz), 7.43 (dd, CH, J_1 = 1.1 Hz, J_2 = 2.1 Hz). ^{13}C NMR (DMSO-d_6, 25 °C, ppm): δ = 138.4, 134.9*, 130.0, 119.8*, 119.6. m/z (FAB$^+$): 174.1 [$HImSO_2N_3^+$]. m/z (FAB$^-$): 87.0 [BF_4^-]. Anal. Calcd for $C_3H_4BF_4N_5O_2S$: C, 13.81; H, 1.54; N, 26.84; S, 12.29. Found: C, 13.78; H, 1.77; N, 26.43; S, 12.59. BAM drophammer: >40 J; friction tester: >240 N; ESD: 0.5 J.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal structures (discussion, ORTEP figure of molecular unit, and crystallographic data and parameters) of **1**·HCl and **1**·H_2SO_4. ^{1}H and ^{13}C NMR spectra of **1**·H_2SO_4, **1**·MsOH, **1**·TsOH, **1**·$HClO_4$, and **1**·HBF_4. This material is available free of charge via the Internet at http://pubs.acs.org/.

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