Catalytic properties and acidity of 1,2-benzenedisulfonimide and some of its derivatives. An experimental and computational study.

Catalytic properties and acidity of 1,2-benzenedisulfonimide and some of its derivatives. An experimental and computational study.

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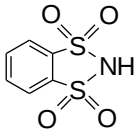
Abstract: 1,2-Benzenedisulfonimide (**1**) has previously been found to be an excellent and, importantly, safe Brønsted acid catalyst. In this work we present the results of a search for derivatives of **1** that are more acidic and effective. Instead of blindly synthesizing a series of analogues, we have carried out a screening process in which the pK_a of **1** and a set of its derivatives were calculated. The calculated pK_a values were confirmed experimentally by carring out determination through potentiometric titrations of some of the compounds: **1**, 4-methyl and 4-nitro derivatives of **1**. The calculations indicated that the dinitro and 4-nitro derivatives are among the best candidates for the synthesis. The latter was obtained in good yields and tested as a catalyst. Results were excellent as the reactions took place more quickly and at lower temperatures in all cases, and in a number of cases it was even possible to reduce the amount of catalyst.

1. Introduction

We have recently reported ~~on~~ the use of 1,2-benzenedisulfonimide[1] (OBS; **1**) in catalytic amounts as a safe, nonvolatile and noncorrosive Brønsted acid in several acid-catalyzed organic reactions that give excellent results.[2]



1

Figure 1. OBS **1**.

The catalyst was easily prepared, recovered and purified, ready to be used in further reactions.

The high acidity of the Brønsted acid **1** is known in the literature. Hendrickson and coauthors stated that it is fully ionized in water.[3] However, no reliable data has been reported as to its acidity.

King and Guo stated that its pK_a is -4.1 (H_0 at half-neutralization determined by UV spectra, at 20 °C in H_2O) but no further details were given;[4] Blaschette, Jones and coauthors reported a value of -1.1 (calculated with the program ACD/pK_a DB).[5]

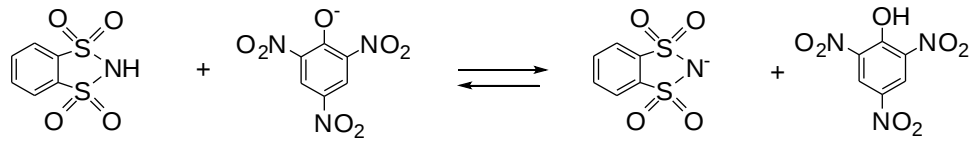
In the light of these results, we propose in this work an estimation of the acidity of OBS and some its derivatives using experimental and theoretical methods. Potentiometric titrations in butanone using ~~using~~ picric acid as reference were performed to obtain an acidity scale for these compounds.

Moreover, in order to synthesise a derivative that is more acidic than the parent **1**, and in order to test and compare it with **1** as a catalyst in some selected reactions, we decided to take advantage of theoretical methods to perform a screening of OBS derivatives based on their pK_a and therefore single out the most promising derivative for synthesis.

2. Results and discussion

2.1. Theoretical calculation

The calculation of absolute pK_a of acids is truly a difficult challenge[6] but because our main goal is limited to an estimation of an acidity scale among the set of substituted OBS, we used a different approach. The pK_a values were obtained as differences (ΔpK_a^A) with respect to the pK_a of ~~the~~ picric acid whose values are available in numerous solvents. With this approach (a sort of "proton-exchange method"[6a]) we should have a self-correction of the errors (mainly due to the *continuum* method used to include the solvent effects) that should be particularly efficient when comparing OBS and its derivatives. The ΔpK_a^A values were calculated using the equilibrium shown in Scheme 1.



1

Scheme 1. Equilibrium between picric acid and **1**

The ΔpK_a^A is then easily calculated as:

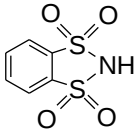
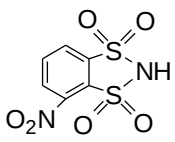
$$\Delta pK_a^A = \frac{\Delta G}{2.303\ RT}$$

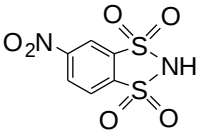
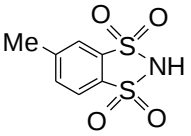
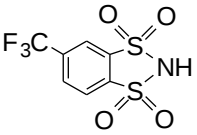
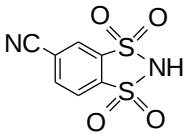
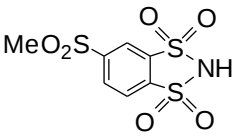
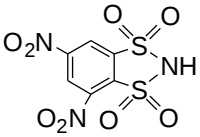
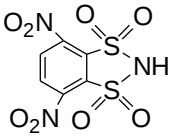
where ΔG is the free energy of the above equilibrium, R the gas constant and T the temperature (25 °C).

Before proceeding with the calculation of the pK_a of **1**, we tested the computational approach (see section 4.6) and calculated a selected number of pK_a values for which the experimental values are available. These includes includes phenols, sulfonic acids and sulfonimides (see Supporting Information, Table 1).[7] The accuracy ($\Delta pK_a = \pm 1$) was satisfactory.

The effect of six different substituents (mostly electron-withdrawing) on **1** pK_a in butanone was calculated. Table 1 shows the ΔG of the above equilibrium, the ΔpK_a with respect to the picric acid (ΔpK_a^A) and with respect to the unsubstituted OBS (ΔpK_a^O). ΔpK_a^A is then used to calculate the absolute pK_a of **1** using the known the pK_a of picric acid (8.2).[8] The last column reports the experimental value (see section 2.3). The error in the calculated ΔpK_a^O (0.2) is below the experimental error.

Table 1. Calculated (pK_a^{calc}) and experimental (pK_a^{exp}) acidity constants in butanone.

1,2-benzenedisulfonimide	ΔG^a	ΔpK_a^A	ΔpK_a^O	pK_a^{calc}	pK_a^{exp} [b]
	-3.2	-2.3	-	5.9	6.09 ± 0.04[c]
	-6.1	-4.5	-2.1	3.7	N/A

	-5.9	-4.4	-2.0	3.8	4.3 ± 0.04[c]
	-2.6	-1.9	+0.5	6.3	6.81 ± 0.01[c]
	-5.7	-4.2	-1.8	4.0	N/A
	-6.4	-4.7	-2.4	3.5	N/A
	-5.8	-4.3	-1.9	3.9	N/A
	-9.8	-7.2	-4.9	1.0	N/A
	-10.0	-7.3	-5.0	0.9	N/A

[a] Kcal mol^{-1}.

[b] Values obtained using the potentiometric method, at T = 25°C.

[c] Standard deviation.

Not surprisingly, the electron withdrawing groups increase acidity by a factor of 100 ($\Delta pK_a^O \sim -2$) for the monosubstituted and by a factor of 10000 ($\Delta pK_a^O \sim -5$) for disubstituted ones. The electronic effects (whether electron donor or electron withdrawing) are hardly dependent on the position of the substituent, and they are almost the same in the acid as in its anion conjugated base (see the group charges in Table 2 of Supporting Information). With the deprotonation of the acid, substituent group charge is reduced (made more negative or less positive) by 0.02 electrons in all cases (for each substituent), testifying that there is no direct effect on the negative charge in the conjugated base. This can also be seen in Figure 2, which shows the highest occupied molecular orbital (HOMO) of the anion of 3,5-dinitrobenzenedisulfonimide. This orbital gives a rough picture of the negative charge distribution and we can see that the nitro groups are not involved.

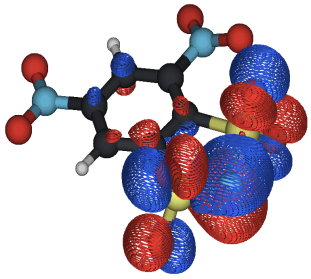
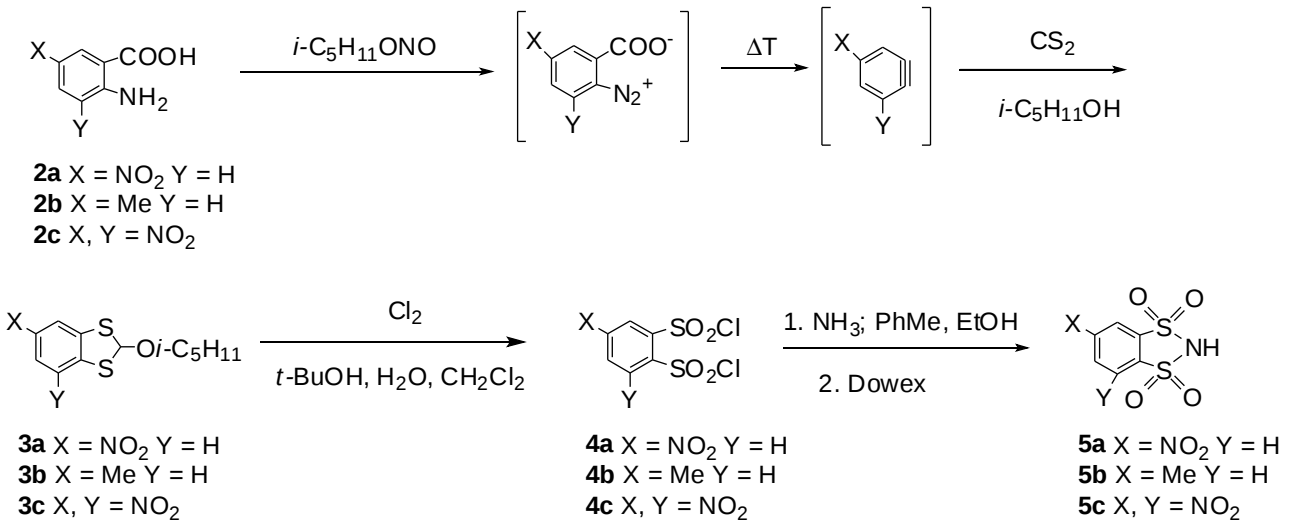


Figure 2. HOMO in 3,5-dinitrobenzenedisulfonimide anion.

2.2 Preparation of 1,2-benzenedisulfonimides 5

We synthesized two derivatives of **1**, one with an electron withdrawing group, 4-nitro-1,2-benzenedisulfonimide (**5a**) and the other with an electron donating group, 4-methyl-1,2-benzenedisulfonimide (**5b**). First of all, the pK_a values of **5a** and **5b** were measured experimentally. Then, the more acidic **5a** (compared to parent **1**) was tested as catalyst in some selected reactions. Compounds **5a** and **5b** were prepared using the same protocol as previously reported, starting from anthranilic acids **2a** and **2b** (Scheme 2).[9]



Scheme 2. Preparation of derivatives of OBS **5a, b**.

The yields of the intermediates **3a** and **3b, 4a** and **4b** and of the imides **5a** and **5b** are reported in Table 2.

Table 2. Synthetic sequence for 1,2-benzenedisulfonimides **5a, b**.

Entry	Reactant	Products and Yields[a] (%)	Products and Yields[a] (%)	Products and Yields[a] (%)
1	**2a**	**3a**, 62	**4a**, 91	**5a**, 94
2	**2b**	**3b**, 88	**4b**, 95	**5b**, 95

[a] Yields refer to the pure and isolated products

Unfortunately, ~~the~~ attempts to prepare 3,5-dinitro-1,2-benzenedisulfonimide (**5c**, a compound which would be more acidic than **5a** from a theoretical point of view) failed. In fact, it was impossible to obtain intermediate **3c** from anthranilic acid **2c** (prepared as reported in the literature [10]) using the standard reaction conditions. Moreover, it must be stressed that the reaction became more difficult even with only one nitro group. In fact, an internal diazonium salt is the key intermediate in the first step (Scheme 1). The presence of a single electron-withdrawing group ~~probably~~ already makes the diazotization reaction more difficult (the yield of **3a** is lower than that of **3b**), and the presence of two completely prevented it and only unreacted **2c** was recovered at the end of the reaction.
It should also be noted that the direct nitration of the intermediates **3a**, **4a** or **5a** also failed

2.3. Measurement of pK_a of 1,2-benzenedisulfonimides 1, 5a, 5b.

As reported by Kütt, Koppel, Leito and coauthors,[7] the acidity measurements of acid molecules turns out to be a useful tool in the design and use of these compounds. However, the choice of a measurement medium in which to obtain the acid strength of a strong acid is no simple matter. Typical solvents (e.g. heptane, DMSO, MeCN) are not convenient for studying strong acids, because of their low polarity, poor ion solvating ability or simply because they are too basic.
We found that butanone is a good solvent; potentiometric titrations in butanone allowed us to differentiate the 1,2-benzenedisulfonimides on the basis of their acid properties. In fact, the large potential range available in butanone affords a useful scale for the potentiometric determination of relative acidity and makes it possible to differentiate strong acids.
Using the method described in the experimental section, ~~paragraph 4.5,~~ it was possible to build a self-consistent acidity scale which was anchored to the pK_a of picric acid using potentiometric apparatus. The pK_a values of compounds **1, 5a** and **5b** were measured and are reported in Table 1. For the first time, an experimental estimation of the acidity of these compounds is obtained and the results are those expected based on the characteristics of the derivative and are in good accordance with those obtained by theoretical calculations.

2.4. 4-Nitro-1,2-benzenedisulfonimide (5a) as a catalyst.

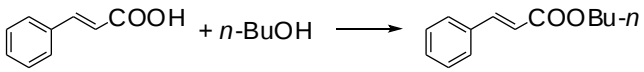
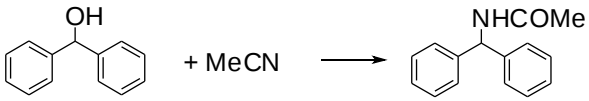
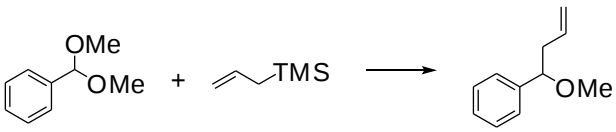
We have recently reported the use of 1,2-benzenedisulfonimide (**1**, Figure 1) in catalytic amounts as a safe, nonvolatile and noncorrosive Brønsted acid in some acid-catalyzed organic reactions such as etherification,[11] esterification,[11,12] acetalization,[11] the Ritter reaction,[13] the Nazarov electrocyclization,[14] the disproportionation of dialkyl diarylmethyl ethers,[15] the Hosomi-Sakurai reaction,[16] the Friedländer annulation,[17] the Pictet-Spengler reaction,[18] the Mukaiyama-aldol reaction,[19] preparation of triaryl and trisindolylmethanes [20] and the Strecker reaction.[2]

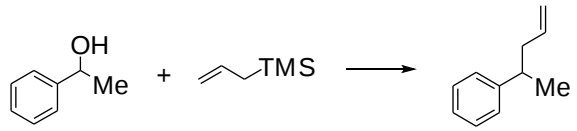
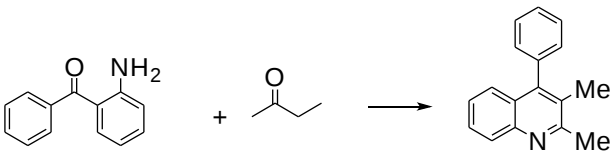
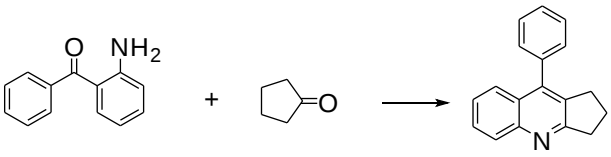
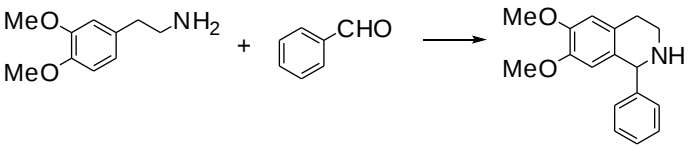
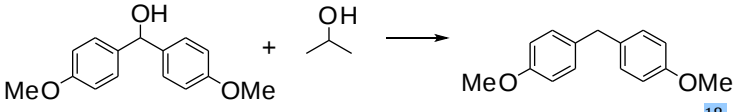
In general, all synthetic methods require mild reaction conditions and short reaction times. It is worth noting that good selectivity and the absence or minimal formation of by-products was observed in all cases. Moreover, **1** can easily recovered from the reaction mixtures in high yield.

In ~~the~~ light of these results, we decided to test **5a** as a catalyst in various selected reactions in order to compare its catalytic activity with the already known activity of **1**.

First of all, we examined the esterification reaction between phenyl acetic acid and butan-1-ol. As reported by us,[11] the reaction catalyzed by **1**, using toluene as a solvent, required the presence of 25 mol-% of catalyst. It was completed after heating at 90 °C for 1.5 hours. The yield of butyl phenylacetate was 90% (Table 3, entry 1).

Table 3. Selected reaction catalyzed by **5a.**

Entry	Reaction and references	Catalysts (mol-%)	Temp (°C)	Time (h)	Yields[a] (%)
1	BnCOOH + *n*-BuOH ⟶ BnCOOBu-*n* [11]	**1** (25)	90	1.5	90[b,c]
		5a (5)	r.t.	3	87[b,c]
2	 [11]	**1** (20)	90	24	37[b,c]
		5a (10)	90	5	84[b,c]
3	 [13]	**1** (10)	82	8	89[d]
		5a (10)	82	3	91[d]
4	*t*-BuOH + MeCN ⟶ *t*-BuNHCOMe [13]	**1** (20)	82	72	83[d]
		5a (20)	82	24	87[d]
5	 [16]	**1** (5)	45	2	90[e,f]
		5a (5)	r.t.	1	92[e,f]

6	 [16]	**1** (30) **5a** (10)	70 80	24 12	72[f,g] 82[f,g]
7	 [17]	**1** (10) **5a** (5)	80 80	28 12	90[b,f] 85[b,f]
8	 [17]	**1** (5) **5a** (5)	80 50	4 2	90[b,f] 86[b,f]
9	 [18]	**1** (10) **5a** (5)	80 80	6 2	89[f,h] 92[f,h]
10	 [18]	**1** (5) **5a** (5)	80 r.t.	3 3	100[b,f] 100[b,f]

[a] Yields refer to the pure and isolated products. The physical and spectroscopic data of the obtained products are in accordance with those previously reported by us.

[b] The reactant ratio was 1: 1.1.

[c] The solvent was toluene.

[d] MeCN was the reactant and the solvent.

[e] The reactant ratio was 1: 1.2.

[f] The reaction was carried out in neat conditions.

[g] The reactant ratio was 1: 1.5.

[h] The reactants was in equimolar amount.

Interestingly, the reaction took place at room temperature in the presence of only 5 mol-% of **5a** as a catalyst, and a good yield (87%) of butyl phenylacetate was obtained ~~nonetheless~~ (Table 3, entry 1). The catalyst **5a** was easy recovered (90%) by simply evaporating the aqueous layer at reduced pressure.

On the basis of this excellent result, **5a** was used as the catalyst in nine other reactions that had previously been performed by us in the presence of **1**. Table 3 shows the results.

It can be stated that **5a** is more effective than **1**. In general, the reactions took place more quickly and at lower temperatures. Moreover, in some cases, a smaller amount of catalyst was needed

(Table 2; entries 2, 6, 7, 9). The yields of the target products were very similar to those obtained using **1,** with the sole exception of entry 2, where a sharp increase in yield was observed.

~~It can be stated that **5a** is more effective than **1**. In general, the reactions took place more quickly and at lower temperatures. Moreover, in some cases, a smaller amount of catalyst was needed (Table 2; entries 2, 6, 7, 9). The yields of the target products were very similar to those obtained using **1,** with the sole exception of entry 2, where a sharp increase in yield was observed.~~

3. Conclusions

The theoretical approach allowed us to calculate the pK_a of OBS (**1**) and a set of its derivatives. The calculated values were confirmed by experimental determination using potentiometric titrations on some of the species; **1**, **5a** and **5b**. The calculations also suggested which derivatives were the best candidates for synthesis. Of them, **5a** was obtained in a good yield and was tested as a catalyst in ten selected reactions, obtaining generally better results than those obtained with **1.**

4. Experimental section

4.1. General

Analytical grade reagents and solvents were used and reactions were monitored, where possible, by GC, GC-MS and TLC. Column chromatography and TLC were performed on ~~a~~ Merck silica gel 60 (70-230 mesh ASTM) and GF 254, respectively. Petroleum ether (PE) refers to the fraction boiling in the range 40–70 °C. Room temperature is 20–25 °C. Mass spectra were recorded on an HP 5989B mass selective detector connected to an HP 5890 GC, cross-linked methyl silicone capillary column. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brüker Avance 200 spectrometer at 200 and 50 MHz respectively. IR spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer as solutions in $CHCl_3$. Potentiometric measurements were performed using a Metrohm mod. 713 potentiometer (resolution of ± 0.1 mV) coupled with a Metrohm 665 Dosimat burette (minimum volume deliverable of ± 0.001 cm^3) and equipped with a Metrohm combined glass electrode suitable for measurements in non aqueous solutions (Solvotrode mod. 6.0229.100). The potentiometric titrations were carried out in a stream of anhydrous nitrogen gently bubbled in the titration cell to avoid O_2 and CO_2 contamination. The measurement cells were thermostated at (25±0.1 °C) by means of a water circulation from a thermocryostat (mod. D1-G Haake).

5-Nitroanthranilic acid, 5-methyanthranilic acid, benzoic acid, calcium sulfate dihydrate, picric acid, butanone and tetrabutylammonium hydroxyde 0.1 mol/l standard solution in 2-propanol/methanol were purchased from Sigma-Aldrich. Thymol blue indicator was a Fluka

product. OBS (**1**)[1] and 3,5-dinitroanthranilic[10] acid were prepared as reported in the literature. Calcium sulfate dihydrate is dried at 240°C for 10-12 hours in order to obtain the anhydrous form. The structures and purity of all the products obtained in this work were confirmed by their spectroscopic (NMR, MS and IR) data. Satisfactory microanalyses were obtained for all the new compounds.

4.2. 2-(3-Methylbutoxy)-1,3-benzodithioles 3. General procedure

As reported by us,[9] 3-methylbutyl nitrite (2.4 mmol, 0.28 g), 3-methylbutan-1-ol (2 mmol, 0.18 g) and CS_2 (16.6 mmol, 1.26 g) were dissolved in 1,2-dichloroethane (15 mL) and heated to reflux at 82 °C. Anthranilic acid **2** (2 mmol) dissolved in 1,4-dioxane (6 mL) was added dropwise to the previously prepared mixture. The resulting mixture was initially stirred at reflux for 45 min and then at room temperature for 1 h. For the preparation of **3a**, it was necessary to stir at reflux for 3.5 h. The reaction mixture was poured into Et_2O–H_2O (100 mL, 1:1). The aqueous layer was separated and extracted with Et_2O (2 × 50 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and a saturated solution of Na_2CO_3 (50 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue, purified by column chromatography (PE–Et_2O 95:5), afforded the pure title compound **3**.

*4.2.1. 5-Nitro-2-(3-methylbutoxy)-1,3-benzodithiole (**3a**)*. Yellow solid; 0.35 g (yield: 62%); mp 69–70 °C (EtOH); R_f = 0.70. IR ($CHCl_3$) ν (cm^{-1}): 3176, 2963, 1815, 1785, 1690, 1560, 1378, 1210, 1100, 795. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.14 (d, J = 2.0 Hz, 1H), 7.90 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 6.85 (s, 1H), 3.37 (t, J = 6.2 Hz, 2H), 1.66–1.50 (m, 1H), 1.40–1.31 (m, 2H), 0.81 (d, J = 6.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.7, 144.9, 138.3, 125.7, 121.4, 120.5, 91.1, 63.2, 37.4, 24.8, 22.3; calcd for $C_{12}H_{15}NO_3S_2$: C 50.51%; H 5.30%; N 4.91%; S 22.47%; found: C 50.47%; H 5.38%; N 4.89% S 22.52%.

*4.2.2. 5-Methyl-2-(3-methylbutoxy)-1,3-benzodithiole (**3b**)*. Viscous yellow oil; 0.45 g (yield: 88%); R_f = 0.80. IR ($CHCl_3$) ν (cm^{-1}): 3160, 2988, 2247, 1820, 1770, 1630, 1390, 1210, 1084, 800 ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.18–7.11 (m, 2H), 6.85 (d, J = 8.2 Hz, 1H), 6.70 (s, 1H), 3.37 (t, J = 6.2 Hz, 2H), 2.24 (s, 3H), 1.64–1.49 (m, 1H), 1.35–1.29 (m, 2H), 0.80 (d, J = 6.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 142.0, 135.5, 133.0, 126.5, 122.6, 121.7, 90.3, 62.8, 37.9, 25.0, 22.6; MS (*m/z*, EI) = 254 (M^+); calcd for $C_{13}H_{18}OS_2$: C 61.38%; H 7.13%; S 25.20%; found: C 61.41%; H 7.18 %; S 25.21%.

4.3. 1,2-Benzenedisulfonyl chlorides 4 . General procedure

As reported by us,[9] 1,3-benzodithiole **3** (2 mmol) was dissolved in *tert*-butyl alcohol (10 mL), CH_2Cl_2 (8 mL) and H_2O (1.5 mL). The resulting mixture was cooled to 0-5 °C. Chlorine was bubbled through while the temperature was maintained at 0-5 °C and the reaction mixture vigorously stirred. The reaction was monitored using TLC (PE-EtOAc 7: 3). After 1 h, the reaction was complete when ~~the spot of~~ **3** disappeared and there was only one other spot. The reaction mixture was poured into CH_2Cl_2–H_2O (100 mL, 1:1) The aqueous layer was separated and extracted with CH_2Cl_2 (2 □× 50 mL). The combined organic extracts were washed with a 5% NaOH solution (2 × 50 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude residue was the pure title compound **4.**

*4.3.1. 4-Nitro-1,2-benzenedisulfonyl chloride (**4a**).* Yellow solid; 0.58 g (yield: 91%); mp 244 °C (EtOH); R_f = 0.31. IR ($CHCl_3$) ν (cm^{-1}): 3015, 1590, 1355, 1220, 1190, 800. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.07 (d, J = 2.0 Hz, 1H), 8.75 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 8.61 (d, J = 8.2 Hz, 1H), ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.6, 144.5, 142.7, 134.0, 130.1, 127.2; calcd for $C_6H_3Cl_2NO_6S_2$: C 22.51%; H 0.94%; Cl 22.15%; N 4.38%; S 20.03%; found: C 22.53%; H 0.90%; Cl 22.55%; N 4.42%; S 16.95%.

*4.3.2. 4-Methyl-1,2-benzenedisulfonyl chloride (**4b**).* White solid; 0.55 g (yield: 95%); mp 106–107 °C (EtOH); R_f = 0.38. IR ($CHCl_3$) ν (cm^{-1}): 3033, 3010, 1340, 1212, 1200, 814 ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.26 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 2.0 Hz, 1H), 7.72 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 148.7, 142.3, 139.4, 136.3, 132.9, 132.6, 21.8; calcd for $C_7H_6Cl_2O_4S_2$: C 29.08%; H 2.09%; Cl 24.52%; S 22.18%; found: C 29.03%; H 2.12%; Cl 24.60%; S 22.25%.

4.4. 1,2-Benzenedisulfonimides 5. General procedure

As reported by us,[9] 1,2-benzenedisulfonyl chloride **4** (2 mmol) was dissolved in toluene (8 mL) and EtOH (12 mL). The resulting mixture was cooled to 0-5 °C. Ammonia was bubbled through while the temperature was maintained at 0-5 °C and the reaction mixture vigorously stirred. The reaction was monitored by TLC (PE–EtOAc 7: 3). After 30 min, the reaction was complete when the spot of **4** disappeared. The mixture was first filtered in order to eliminate NH_4Cl and then the solvent was evaporated under reduced pressure. The crude residue was dissolved in H_2O and passed through a Dowex (HCR–W2) column (H_2O) to afford the pure title compound **5.**

*4.4.1. 4-Nitro-1,2-benzenedisulfonimide (**5a**).* Brown solid; 0.50 g (yield: 94%); mp 160–161 °C (EtOH); IR ($CHCl_3$) ν (cm^{-1}): 3500, 3015, 1630, 1590, 1385, 1218, 818. ^{1}H NMR (200 MHz, MeOH-d_4): δ 8.74 (d, *J* = 2.0 Hz, 1H), 8.69 (dd, J_1 = 8.2 Hz, J_2 = 2.0 Hz, 1H) 8.14 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (50 MHz, MeOH-d_4): δ 154.8, 141.8, 137.0, 128.1, 122.8, 116.9; calcd for $C_6H_4N_2O_6S_2$: C 27.27%; H 1.53%; N 10.60%; S 24.27%; found: C 27.32%; H 1.49%; N 10.67%; S 24.21%.

*4.4.2. 4-Methyl-1,2-benzenedisulfonimide (**5b**).* Pale brown solid; 0.44 g (yield: 95%); mp 121–122 °C (EtOH); IR ($CHCl_3$) ν (cm^{-1}): 3450, 3027, 1625, 1400, 1320, 1235, 810; ^{1}H NMR (200 MHz, MeOH-d_4): δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.68 (s, 1H) 7.62 (d, *J* = 8.2 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (50 MHz, MeOH-d_4): δ 145.2, 141.8, 138.5, 134.2, 121.7, 121.0, 20.3; calcd for $C_7H_7NO_4S_2$: C 36.04%; H 3.02%; N 6.00%; S 27.49%; found: C 36.08%; H 3.05%; N 5.97%; S 27.52%.

4.5 Potentiometric measurements

Solutions of compounds **1**, **5a**, **5b** and picric acid ($2\cdot10^{-3}$ mol/l) in butanone were titrated with tetrabutylammonium hydroxyde 0.1 mol/l standard solution. Each titration was repeated in triplicate. All titrations were carried out with about 2 g of anhydrous calcium sulfate dispersed in the solution in order to avoid water contamination. Under these conditions a good stability of potentials was obtained. The concentration of the tetrabutylammonium hydroxide standard solution was controlled by weekly visual titrations of benzoic acid solutions and thymol blue as indicator.[21]

The pK_a of picric acid obtained by Norberg in butanone (K_a = 6.4·10^{-9})[8,22] was taken as a reference.The pK_a of compounds **1, 5a** and **5b** were then calculated with the equation 1, derived from the Henderson-Hasselbalch equation, using the difference between the half-neutralization potentials measured for OBS and picric acid solutions, assuming that, in the same experimental conditions, the formal potential of the glass electrode is the same for the two solutions. In order to assure that the electrode performance were the same for the reference and the benzenedisulfonimide the titration of picric acid is performed before each titration of **1, 5a** and **5b** solutions.

$$pK_a^{OBS} = pK_a^{PA} + \frac{E_{PA}^{1/2} - E_{OBS}^{1/2}}{59.16} \qquad 1$$

The $E_{PA}^{1/2}$ and $E_{OBS}^{1/2}$ are the half-neutralization potentials (mV) measured for picric acid (PA) and OBS (**1**) solutions respectively; pK_a^{PA} and pK_a^{OBS} are the acidic constants of PA and OBS, and 59.16 mV is the Nernstian slope.

The ΔpK_a between the picric acid and the studied compounds correspond to the chemical equilibrium reported in ~~the~~ paragraph 2.1.

4.6 Computational method

All structures (acids and conjugated anion bases) were optimized using the density functional method (DFT),[23] with the recently developed functional M06-2X[24] with the 6-31+G(d,p)[25a-c] basis set, ~~and~~ and using vibrational analysis to check the nature of the critical points[26] (all data are reported in the Supporting Information). The energy values were then refined using single-point calculations with the basis set 6-311+G(3df,2p),[25d] and combined with the thermal corrections obtained with the smaller basis set to give free energy values. Solvent effects were introduced both in geometry optimization and single point calculations using the Polarized Continuum Method (IEF-PCM)[27] within the universal Solvation Model Density (SMD).[28] Calculations were performed by the quantum package Gaussian 09-A.02.[29] Figure 2 was obtained using the graphical program Molden.[30]

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi...:
Total (in au) and relative (in kcal mol^{-1}) electronic energies and free energy corrections are reported. Nuclear coordinates (in Ångstrom) follows.

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Graphical Abstract

Catalytic properties and acidity
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