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Analyses of Reaction Mechanisms among Different Sulfonation Reagents and *m*-Diphenylamine and Crystal Structures of the Formed Compounds

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Abstract

In the traditional process, *m*-phenylenediamine reacts with fuming sulfuric acid at high temperature to get intermediates, and then after dehydration occurs intramolecular rearrangement to get 2,4-diaminobenzenesulfonic acid. Traditional methods need to consume a lot of fuming sulfuric acid or concentrated sulfuric acid, resulting in high industrial large-scale production cost, more waste, and posing a serious environmental pollution risk. In this thesis, three different sulfonation reagents were used for the sulfonation reaction of *m*-phenylenediamine, and the reaction mechanisms and crystal structures of the three pathways were investigated. The three routes are: 1) one-step synthesis of monosulfonated compound **1** from raw material and sulfur trioxide (SO_3); 2) rapid reaction of raw material and chlorosulfonic acid to synthesize bisulfonated compound **2**; 3) direct eutectic crystallization of raw material and ordinary sulfuric acid to obtain compound **3**. The crystal structure of the compounds synthesized by three paths was analyzed by X-ray single crystal diffraction, and compound **1** was characterized by NMR, Fourier infrared spectra, UV-visible spectrum and Mass spectrometry. The one-step synthesis of SO_3 as a sulfonation reagent has the advantages of mild reaction conditions, simple operation and low cost.

Keywords

2,4-Diaminobenzenesulfonic Acid, Sulfur Trioxide (SO_3), Spectrometry, Crystal Structure

1. Introduction

2,4-Diaminobenzenesulfonic acid (DBSA) is an important organic intermediate widely used in textile, chemical and pharmaceutical applications. Especially in the textile industry, it can be used as a dye derivative for direct printing of fiber/cotton blended textiles, providing a wide range of color options and excellent color brightness [1] [2] [3] [4]. The physical and chemical properties of DBSA are characterized by its high solubility in water and slight solubility in methanol and ethanol. However, purification by recrystallization from these solvents usually takes at least three weeks and often yields only poor quality crystals [5]. At present, the laboratory synthesis of 2,4-diaminobenzene sulfonic acid is generally not suitable for pilot scale amplification, the specific reasons are mainly the following three aspects: 1) The synthesis of DBSA through the iron powder acid system, which will produce a large number of waste acids and residues, leading to environmental problems and not conducive to green development; 2) The use of concentrated sulfuric acid or fuming sulfuric acid as an oxidant directly involved in the reaction or hydrogen as a reducing agent, and the reaction temperature is high, the reaction process has a high risk [6] [7]; 3) High-boiling solvents such as dichloroethane are used in the synthesis process for the experiments, and their recovery costs are large in the post-treatment process [8].

There are generally two synthesis methods of DBSA: one is formed by sulphonation of m-phenylenediamine, and the other is formed by reduction of 2, 4-dinitrobenzene sulfonic acid. The Japanese publication Teppei 04-013657 [9] synthesizes DBSA by liquid phase method. The specific process is to use a large amount of sulfuric acid (fuming sulfuric acid) as the solvent, and then use fuming sulfuric acid as the sulfonation reagent to sulfonate *m*-phenylenediamine. After that, Tang *et al.* [10]. patented in Japan basically reduced environmental pollution and high costs by solid-phase reaction with a specific amount of sulfuric acid or fuming sulfuric acid and *m*-phenylenediamine at a specific temperature to generate DBSA. In another synthetic route, YU *et al.* [11] synthesized 2,4-diaminobenzenesulfonic acid from 2,4-dinitrobenzenesulfonic acid by catalytic hydrogenation, and the optimal reaction conditions were determined by orthogonal tests.

When the product is considered in the direction of pilot scale, the key issue to be considered is whether it meets the requirements of safe production, green environmental protection, low cost and so on. Obviously, this kind of experimental small trial of synthesizing DBSA cannot meet these requirements [12]; because the production process requires the use of a large amount of concentrated sulfuric acid at high temperatures, which leads to greater production risk; and, a large amount of waste acid and residue produced in the process of production will seriously pollute the environment; finally, the steps are more complicated, and the more raw materials involved increase the cost [13]. This is not in line with the concept of sustainable development and green development advocated by our society today.

In this paper, m-phenylenediamine was used as a raw material and reacted with three different sulfonation reagents, monosulfonated compound **1** (2,4-diaminobenzenesulfonic acid) was obtained by reacting with sulfur trioxide, bisulfonated compound **2** was obtained by reacting with chlorosulfonic acid, and compound **3** was obtained by co-crystallization with ordinary sulfuric acid, and sulfonate group of compound **3** existed in the free form. The sulfonation of *m*-phenylenediamine with sulfur trioxide to obtain 2,4-diaminobenzenesulfonic acid was found to have the advantages of fewer reaction steps, lower production cost, and higher yield than the conventional process.

2. Experimental Section

2.1. General Considerations

All solvents were commercial products of high purity and used as received. The *m*-phenylenediamine (99% purity) used in this paper was purchased from Sinopharm Chemical Reagent Co., Ltd. NMR spectra were recorded on a Bruker ALX 400 Plus spectrometer operating at 400 MHz for ^{1}H NMR. Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with use of pressed KBr pellets. Electronic absorption spectra were obtained on a Shimadzu UV-2600 spectrophotometer. Positive-ion ESI mass spectra were recorded with Thermo ScientificTM Q ExactiveTM Focus mass spectrometer.

2.2. Synthesis of Compound 1

In a 250 mL three-necked flask, 1,2-dichloroethane (138 g, 1.4 mol) was added, *m*-phenylenediamine (32 g, 0.3 mol) was added, stirring was done to dissolve it, and sulfur trioxide (48 g, 0.6 mol) was added slowly under stirring condition, and the temperature was raised to 60˚C, the reaction was carried out for 10 hours. The reaction was stopped, and solids were generated, filtered, washed, and dried to obtain the white 2,4-diaminobenzenesulfonic acid, and then it is recrystallized to obtain compound **1**, and compound 1 is characterized for testing. Yield: 95% (53.58 g), ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, J = 8.3 Hz, 1H), 6.48 (d, J = 2.1 Hz, 1H), 6.44 (dd, J = 8.3, 2.1 Hz, 1H). IR spectrum (KBr disc, cm^{-1}): υ(N–H) 3383, 3327, υ(C–H) 3058, υ(C–N) 1302, 1008. MS (ESI): $m/z = 189.0330$ [M+H]$^+$.

2.3. Synthesis of Compound 2

The reaction of *m*-phenylenediamine and chlorosulfonic acid was referred to the method of literature [14], the specific reaction steps: in a 500 mL three-necked flask add 1,2-dichlorobenzene (191 g, 1.3 mol), and then add *m*-phenylenediamine (30 g, 0.28 mol), stirring to dissolve, heating to 110˚C to react for 1 hour; and then reduce the temperature to 70˚C, with a constant pressure buretting funnel to add a slow drop of chlorosulfonic acid (45 g, 0.39 mol) , the end of the drop, and continue the react for 2 hours, measure the end point, not reached, continue to heat for 2 hours, measure the end point, the end point reached (*m*-phenylenediamine content: 0.05%).

After treatment, add 40 mL water to the flask to remove excess chlorosulphonic acid, then add about 1000 mL water (water temperature 85˚C) and dilute it to 2000 mL beaker, stir for 0.5 hour, then place it in the separator funnel, let it stand overnight. The next day, it was found that there was obvious stratification, the upper water phase was stationary on the upper part of the refrigerator for a period of time, there was crystal precipitation, centrifugal filtration, to produce compound 2: Yield: 95% (26 g).

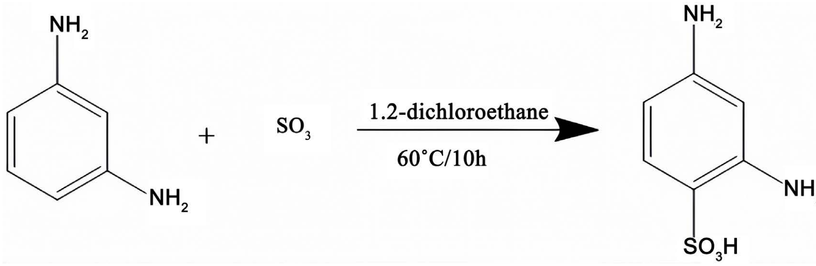
2.4. X-Ray Diffraction Measurements

Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The collected frames were processed with the software SAINT [15]. The data were corrected for absorption using the program SADABS [16]. Structures were solved by the direct methods and refined by full-matrix least-squares on *F*2 using the SHELXTL software package [17] [18]. All non-hydrogen atoms expect for the lattice solvent molecules were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3}–H = 0.96 Å), assigned isotropic thermal parameters and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

3. Results and Discussion

3.1. Synthetic Reactions

The equation for the monosulfonation reaction is shown in **Figure 1**. In 1,2-dichloroethane, the direct reaction of *m*-phenylenediamine with SO_3 was performed in one step to obtain the monosulfonated compound **1**. The reaction mechanism is shown in **Figure 2**, *m*-phenylenediamine directly onto two sulfonic acid groups, after a period of reaction, a water molecule and sulfuric acid molecule fall off to get monosulfonated compound **1**. The equation for the dual sulfonation reaction is shown in **Figure 3**, *m*-phenylenediamine was first incorporated into the solvent 1,2-dichloroethane, then chlorosulfonic acid was added, and after a period of reaction, filtration was carried out, and the bissulfonated compound **2** was obtained by spinning. The reaction mechanism is shown in **Figure 4**, the chlorosulfonic acid method is fast, and it will react quickly with aniline compounds to produce chloroaniline compounds, mainly because the molecular structure of chlorosulfonic acid is very active, easy to lose electrons, forming a new chemical bond, that is, the sulfonic acid group (-HSO_3) in the chlorosulfonic acid molecule will replace the hydrogen atoms on the aniline molecule. *m*-Phenylenediamine and chlorosulfonic acid react rapidly, with two sulfonic acid groups (-HSO_3) replacing hydrogen atoms on the carbon atoms of the *m*-phenylenediamine ring almost simultaneously. The reaction mechanism between *m*-phenylenediamine and chlorosulfonic acid is shown in **Figure 4**. Since *m*-phenylenediamine could not be directly reacted with normal sulfuric acid, the reaction was performed by mixing *m*-phenylenediamine with concentrated sulfuric acid and stirring, after the stirring was finished it was left at room temperature and after some time it was found that a crystal compound **3** appeared.



1

Figure 1. Reaction route of compound **1**.

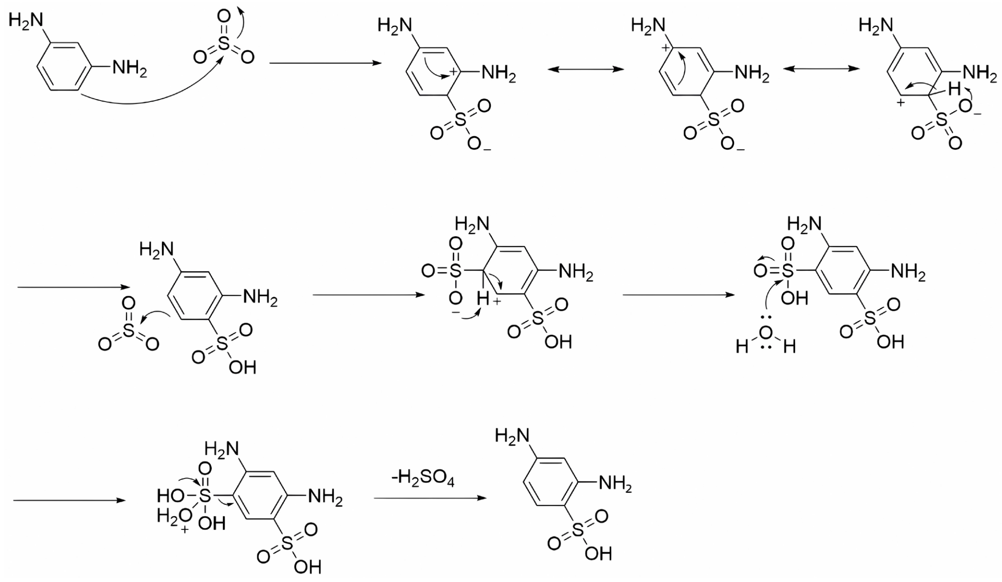
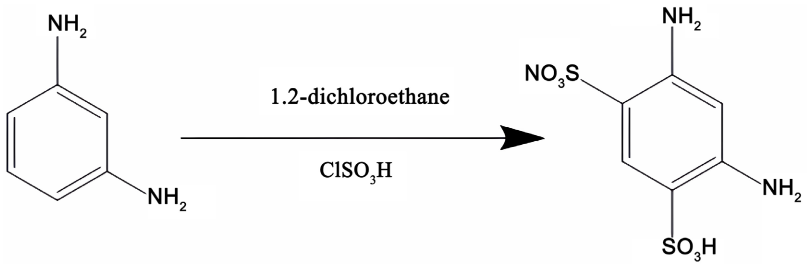


Figure 2. Reaction mechanism of compound **1**.



2

Figure 3. Reaction route of compound **2**.

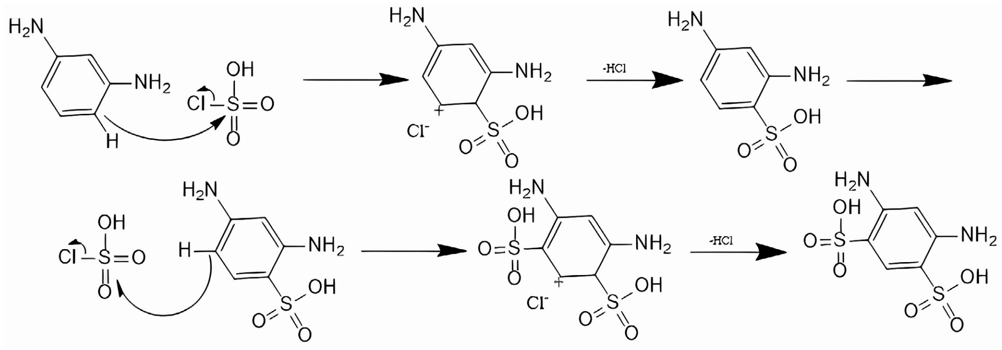


Figure 4. Reaction mechanism of compound **2**.

3.2. Crystal Structures

Three crystal structures have been confirmed by x-ray crystallography. The views of the molecular structures of compounds **1**, **2** and **3** are shown in **Figures 5-11**, respectively. In compound **1**, the benzene ring is connected to two NH_2

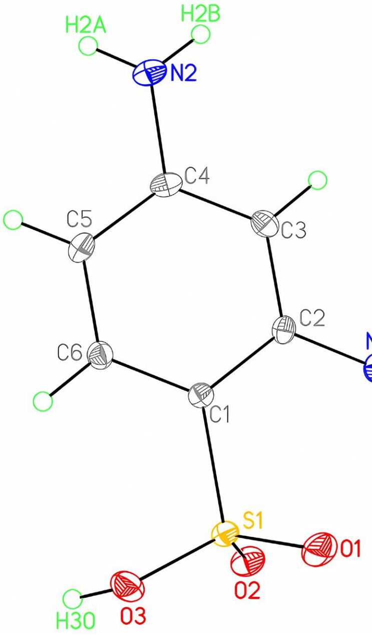


Figure 5. Molecular structure of compound **1**.

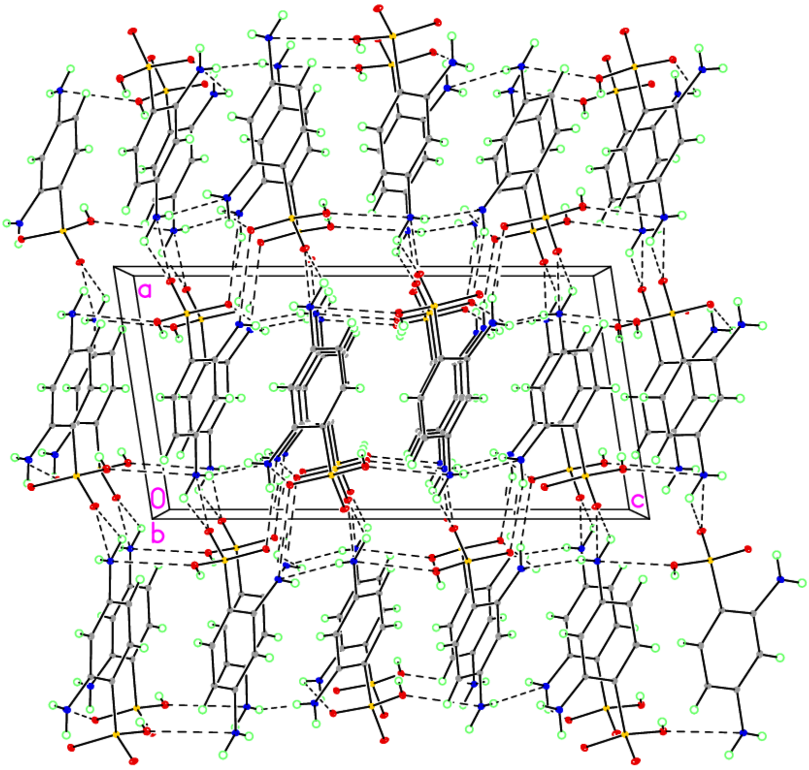


Figure 6. Hydrogen bond molecular packing diagram of compound **1**.

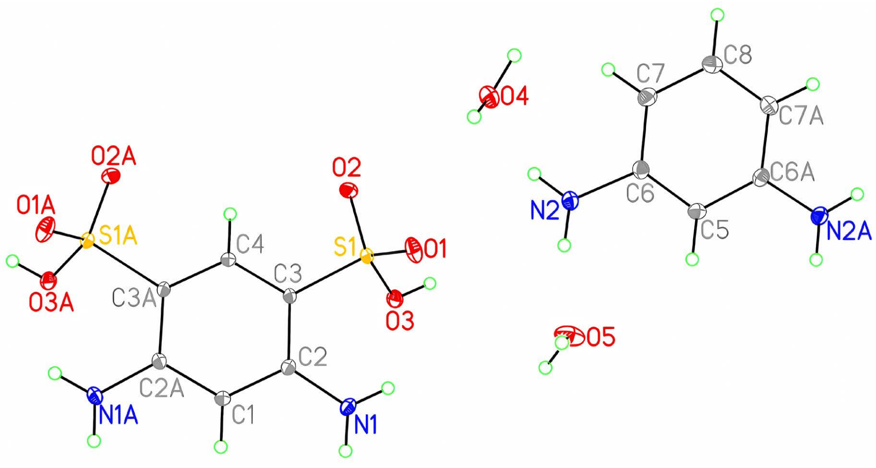


Figure 7. Molecular structure of compound **2**.

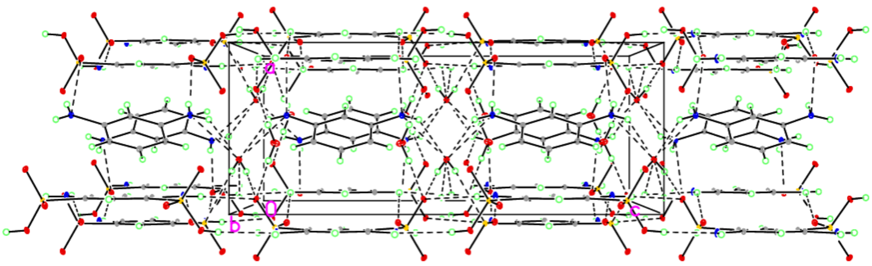


Figure 8. Hydrogen bond molecular packing diagram of compound **2**.

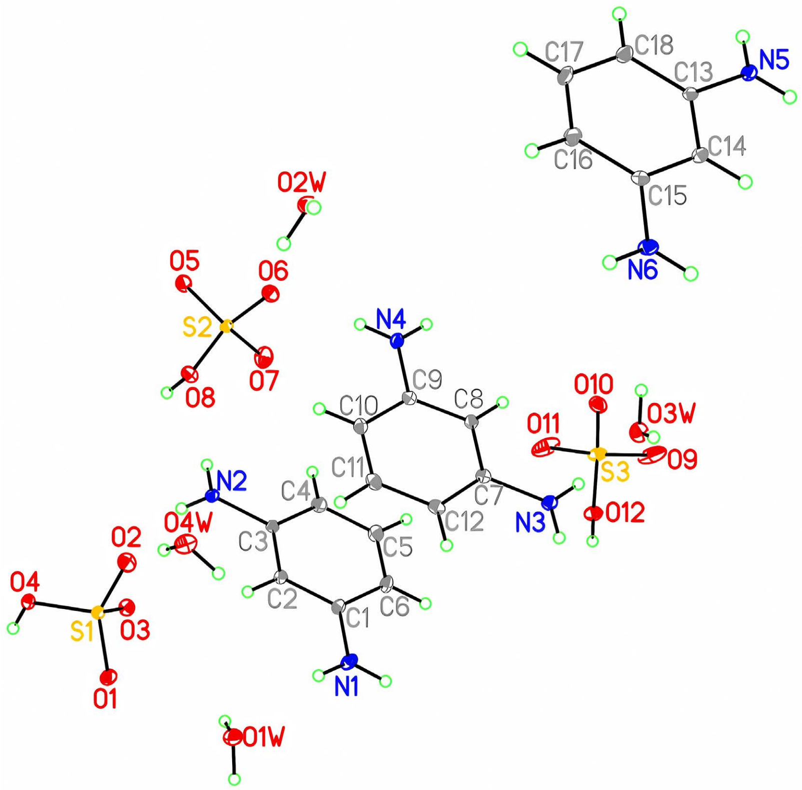


Figure 9. Molecular structure of compound **3**.

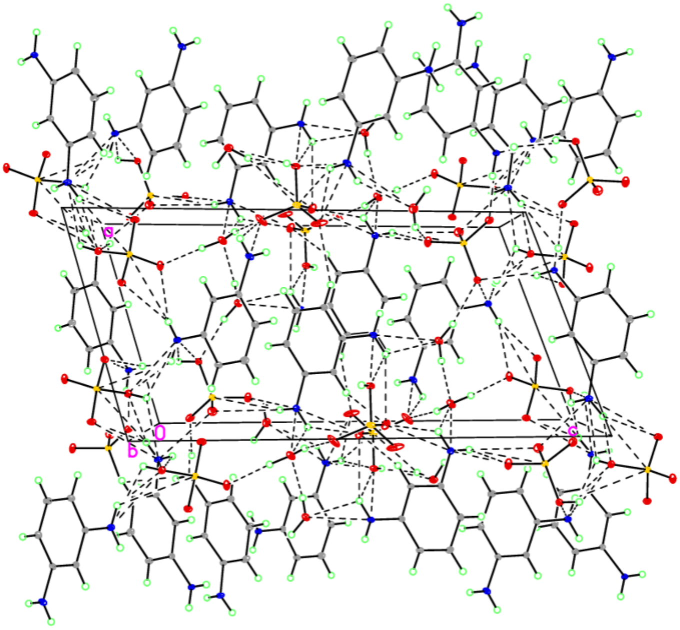


Figure 10. Hydrogen bond molecular packing diagram of compound **3**.

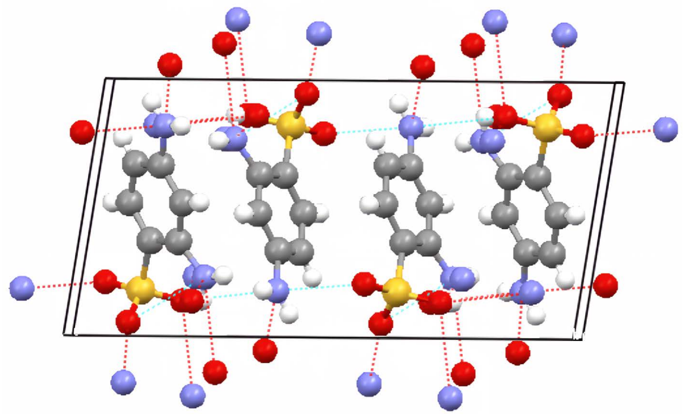


Figure 11. Accumulation diagram of compound **1**.

and two HSO_3-sulfonic acid groups. In compound **2**, the benzene ring is connected to two NH_2 functional groups as well as one HSO_3-sulfonic acid group, while in compound **3**, the two sulfonic acid groups are present in the free form. The average S-O length of these products range from 1.453(3) - 1.461(4) Å, which are similar to those in the previous report (1.4454(13) - 1.4762(10) Å) [19]. The average C-N length in compounds **1**, **2** and **3** is 1.413(2) - 1.462(6) Å. The bond angles of O-S-O are 108.7(2)˚, 112.52(10)˚, 111.33(10)˚. Selected bond lengths and angles for compounds **1**-**3** are collected in Table 1 for comparison. The crystallographic data of the three crystals are shown in **Appendix** (Table A1).

3.3. Spectroscopic Properties

The ^1H NMR spectrum of 2,4-diaminobenzenesulfonic acid compound **1** is shown in Figure 12. It can be obtained by nuclear magnetic resonance hydrogen

Table 1. Comparions of bond parameters data of compounds **1**-**3**.

product	S-O/Å	O-S-O/deg	C–N/Å	N-C-C/deg
1	1.459(6)	174.5(8)	1.413(2)	122.8(17)
2	1.453(17)	176.4(4)	1.428(3)	122.4(2)
3	1.461(4)	173.5(17)	1.162(6)	120.5(4)

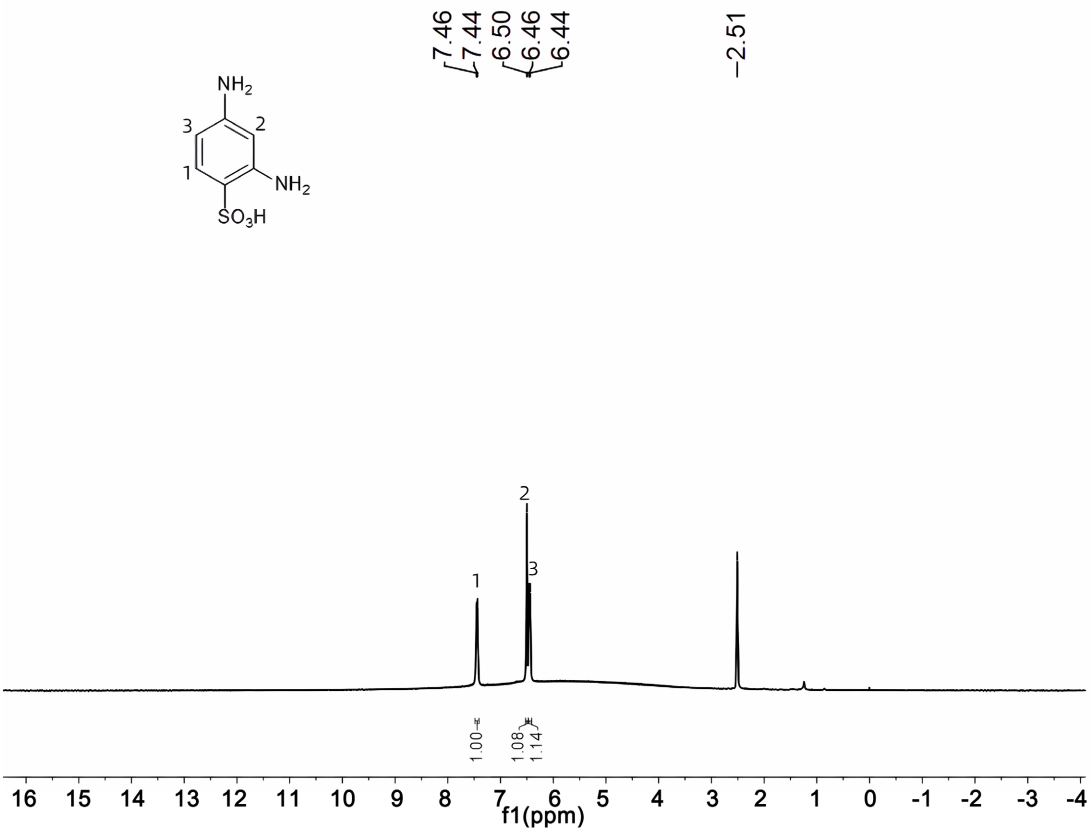


Figure 12. ^{1}H NMR spectrum of compound **1**.

spectra that the chemical shift of 6 - 7 ppm belongs to the characteristic peak in the aromatic region. A total of three groups of peaks were found, among which 7.44 and 6.48 ppm were double peaks, and the signal belonged to the characteristic peak on the hydrocarbon adjacent to the benzene ring. There were two double peaks at the 6.44 ppm signal, which were cracked due to the influence of the connection of amino groups by the adjacent carbon. In summary, the characteristic peak in the aromatic region of the product was in line with that of the product. In addition, the nuclear magnetic carbon spectrum further verified the structure of the compound, and the peaks at 109.06, 110.49, 120.10, 129.21, 139.27, 140.31 ppm in the **Figure 13** corresponded to the peaks of carbon in six different environments on the benzene ring.

The infrared spectrum of compound **1** is shown in **Figure 14**; the spectral bands near 3383 cm^{-1} and 3327 cm^{-1} are N-H asymmetric stretching vibration peaks and symmetric stretching vibration peaks of the amino group in aromatic

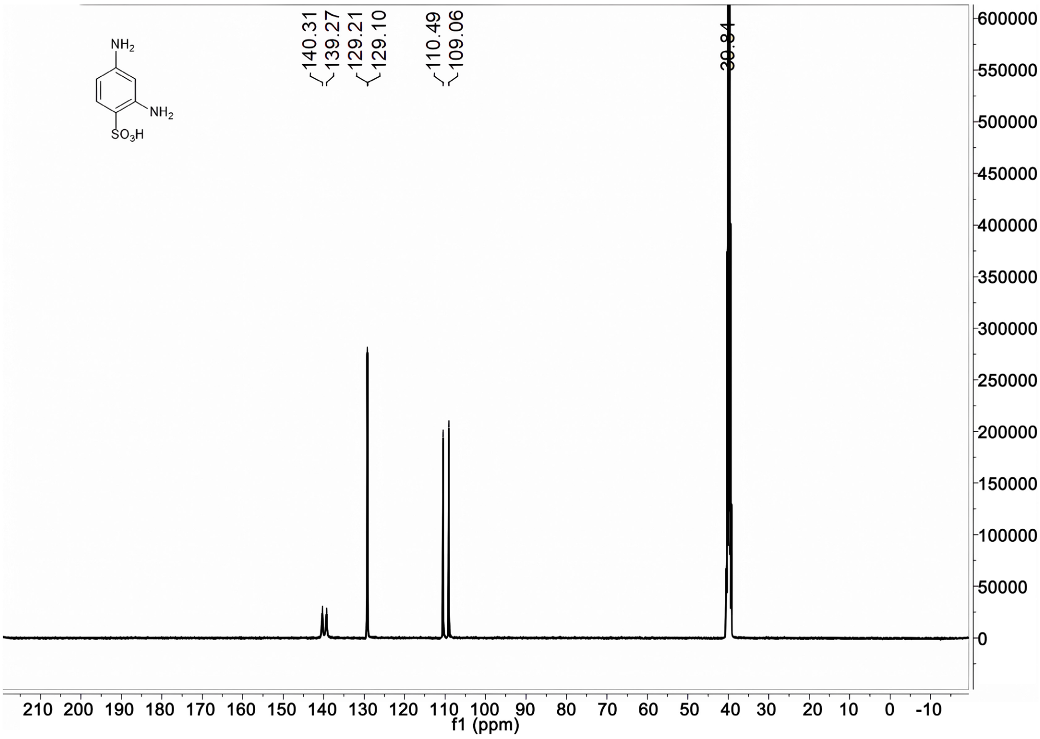


Figure 13. ^{1}C NMR spectrum of compound **1**.

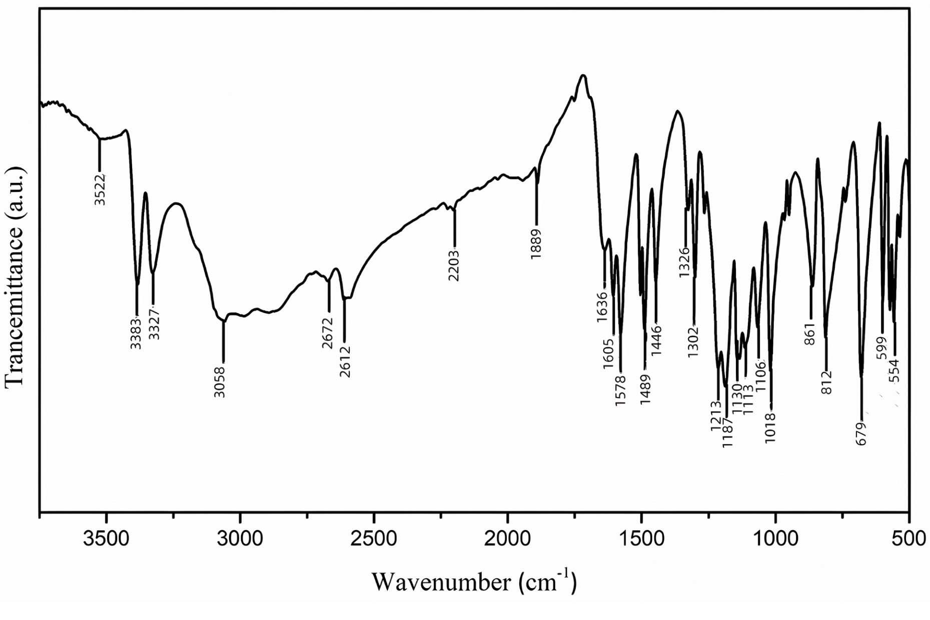


Figure 14. FT-IR spectrum of compound **1**.

primary amine. At 3058 cm^{-1} is the aromatic ring C-H stretching vibration peak. The absorption peak of sulfonyl SO_2^- is around 1187 cm^{-1}. The C-N stretching vibration peak on the aromatic ring is at 1302 cm^{-1}. The out-of-plane bending vibration absorption peak of two adjacent hydrogens on the benzene ring is at 812 cm^{-1}. The out-of-plane bending vibration absorption peak of three adjacent hydrogen on the benzene ring is at 679 cm^{-1}. The upward absorption of the amino group is a hill-like wide peak near 1018 - 861 cm^{-1}, so it overlaps with some characteristic peaks belonging to the benzene ring near this band, and the sulfonyl group attached to the benzene ring also has a certain influence on some characteristic peaks on the benzene ring.

The ultraviolet spectra of compound **1** in water and DMSO solvents display an intense absorption band at around 300 nm as shown in **Figure 15**, the peak near 300 nm is the absorption peak on the benzene ring, which has a red-shift compared with the absorption peak on the general benzene ring. This is because the benzene ring of 2,4-diaminobenzenesulfonic acid is connected with two auxochromic group N and S atoms. The interaction between N and S atoms and the benzene ring makes p-π conjugated and expands the range of electron activity. The absorption peak on the benzene ring moves towards the long wave direction, and the absorption intensity is also increased. The polarity of different solvents is different, and the position of the absorption peak, absorption intensity and spectral shape are also different. As shown in the figure, when the polar solvent increases, it can move $n \rightarrow \pi^*$ transition to the short-wave direction, because the polarity of the ground state is large, and a strong hydrogen bond can be formed between non-bonding electrons (n electrons) and polar solvents. The ground state energy reduction is greater than the energy reduced by the interaction between the anti-bond orbital and the polar solvent, so the energy required for the transition becomes larger, so the absorption wavelength shifts short.

The mass spectrum of compound **1** is shown in **Figure 16**, it shows that the excimer ion peak *m*/*z* 189.0330 [M+H] + (calcd $[M+H]^+$, *m*/*z* 189.0256) has a molecular weight of 188. The molecular formula is $C_6H_8N_2O_3S$ when combined with the results of ^1H NMR.

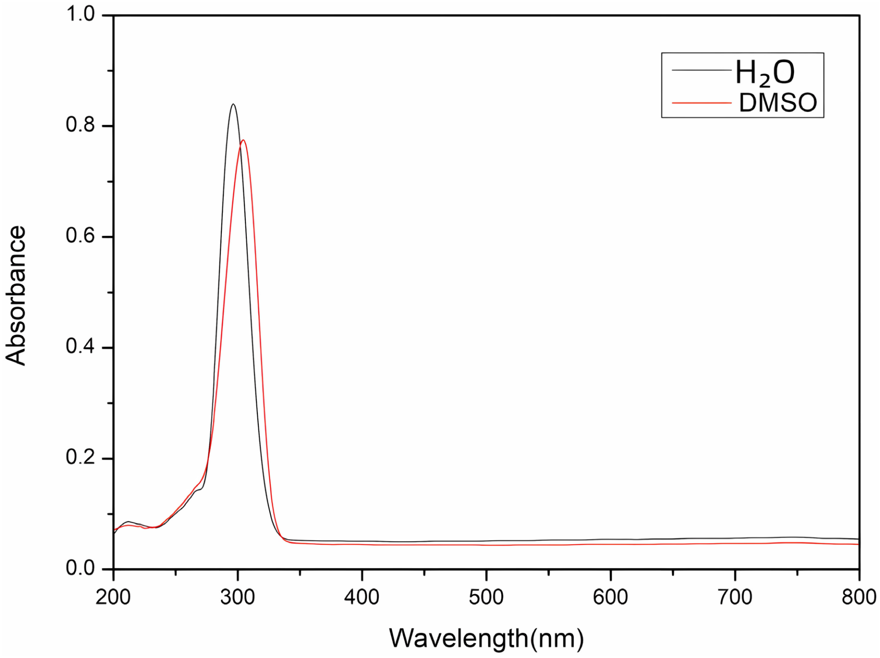


Figure 15. Ultraviolet spectra of compound **1** in water and DMSO solvents.

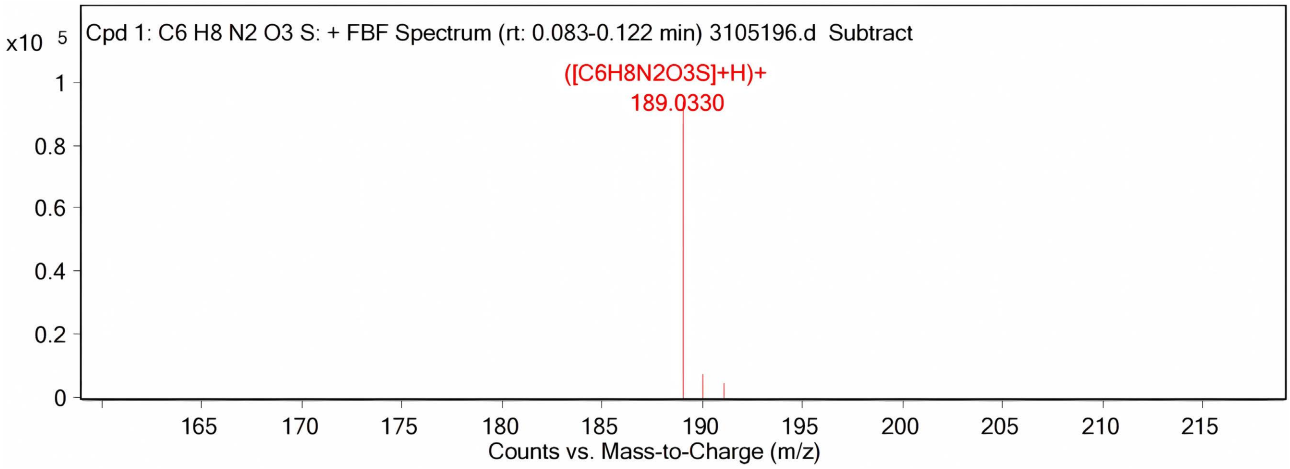


Figure 16. Mass spectrum of compound **1**.

4. Conclusion

In this paper, *m*-phenylenediamine was used as a raw material and reacted with three different sulfonation reagents, monosulfonated compound **1** (2,4-diaminobenzenesulfonic acid) was obtained by reacting with sulfur trioxide, bisulfonated compound **2** was obtained by reacting with chlorosulfonic acid, and compound **3** was obtained by co-crystallization with ordinary sulfuric acid, and sulfonate group of compound **3** existed in the free form. The crystal structure of the three products was analyzed by X-ray single crystal diffraction, and compound **1** was characterized by ^{1}H NMR, Fourier infrared spectrum, UV-visible spectrum and mass spectrometry. Three sets of characteristic peaks attributed to benzene ring were obtained from ^{1}H NMR spectra at the chemical shift of 6 - 7 ppm. The N-H asymmetric stretching vibration peak and symmetric stretching vibration peak belonging to the amino group in aromatic primary amine are obtained from the FT-IR spectra near 3383 cm^{-1} and 3327 cm^{-1}. Compared with traditional craft, the results show that the SO_3 method has the advantages of fewer reaction steps, higher conversion rate and higher selectivity, and has the prospect of industrial application.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Appendix

Table A1. The crystallographic data of the reaction products of *m*-phenylenediamine with sulfur trioxide, chlorosulfonic acid and ordinary sulfuric acid.

Complex	**Compound 1**	**Compound 2**	**Compound 3**
Empirical formula	$C_6H_8N_2O_3S$	$C_{12}H_{22}N_4O_9S_2$	$C_{18}H_{35}N_6O_{16}S_3$
Formula weight	188.20	430.46	687.70
Temperature (K)	296.15	296.15	296.15
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	*Pbcm*	*P*-1
a (Å)	7.9728(8)	6.8818(19)	9.102(4)
b (Å)	5.8389(6)	14.739(4)	11.718(5)
c (Å)	15.5022(16)	17.508(5)	16.835(8)
α (˚)	90	90	100.291(6)
β (˚)	98.7230(10)	90	102.983(6)
γ (˚)	90	90	111.707(4)
Volume $(\text{Å})^3$	713.32(13)	1775.8(8)	1556.3(13)
Z	4	4	2
D_{calc} (g·cm^{-3})	1.752	1.610	1.468
μ (Mo-Kα) (mm^{-1})	0.416	0.357	0.316
F(000)	392.0	904	722.0
Total refln	4205	10549	9763
R_{int}	0.0156	0.0190	0.0411
GoF^c	1.056	1.060	1.063
$R1^a$, $wR2^b$ $(I > 2\sigma(I))$	0.0411, 0.1154	0.0393, 0.1149	0.0814, 0.2180
$R1$, $wR2$ (all data)	0.0457, 0.1200	0.0448, 0.1206	0.1168, 0.2623

[a] $R1 = ||F_o| - |F_c||/|F_o|$; [b] $wR2 = \left[w\left(\left|F_o^2\right| - \left|F_c^2\right|\right)^2 / w\left|F_o^2\right|^2 \right]^{1/2}$; [c] $GoF = [w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.