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Synthesis, characterization, and quantum chemical calculation studies on 3-(3-nitrophenylsulfonyl)aniline

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ABSTRACT

A novel partially reduced polynitro aromatic compound, 3-(3-nitrophenylsulfonyl)aniline (III), was found during the catalytic transfer hydrogenation of 3,3'-sulfonylbis(nitrobenzene) (I) to 3,3'-sulfonyldianiline (II). III was identified and characterized by elemental analysis, IR, ¹H NMR, and X-ray single crystal diffraction. The optimized geometries of III calculated by DFT-B3LYP/6-31G* and HF/6-31G* closely resemble the crystal structure. The frontier orbital gap and the electrostatic potential isosurface map of III were calculated and compared with those of I. HF/6-31G* method is better than DFT-B3LYP/6-31G* method to predict the vibrational frequencies by the comparisons between the calculated results and the experimental data. The present study of III, in general, may lead to the better understanding of the mechanisms and intermediates of the reduction of polynitro aromatic compounds, especially the nitro groups at the different aromatic rings, and may also help in designing and synthesizing new partial reduction products for technological applications.

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1. Introduction

Aromatic amines are important organic raw materials and widely used in chemical, pharmaceutical, agricultural chemicals, photographic chemicals, additives, surfactants and polymer production. Aromatic amines are generally made by the reduction of aromatic nitro compounds. The main reduction methods include catalytic hydrogenation, reduction with CO/H₂O, reduction with metal, reduction with sulfide, reduction with metal hydride, electro-chemical reduction, and photo-chemical reduction [1]. In these methods, catalytic hydrogenation is environmentally friendly and has a high yield and good selectivity, showing promising prospect of application.

Catalytic transfer hydrogenation (CTH) is a special variation of catalytic hydrogenation, in which hydrogen gas is replaced with a hydrogen donor such as hydrazine hydrate [2]. CTH has potential advantages including a small investment in equipment, mild reaction conditions, operational simplicity, and partially reduced product. It is particularly suitable for small batch, short-line production of aromatic amines.

The reaction of nitro compounds to amines is usually through the following process: $-RNO_2 \rightarrow -RNO \rightarrow RNHOH \rightarrow RNH_2$ [3]. Most of the research on the mechanisms and intermediates was about the nitrobenzenes [4]. Little has been published on the

* Corresponding authors. E-mail addresses: fangshi.li@njut.edu.cn (F. Li), xiaoningliu@163.com (X. Liu). mechanisms and intermediates of the reduction of polynitro aromatic compounds, especially the nitro groups at the different aromatic rings. It is urgent to identify CTH intermediates, because of the requirement of the mechanism of the CTH reaction and the potential usage of the partial reduction products.

Recently, we focus our attention on synthesis and characterization various aromatic amines [5-10] and study their special properties [11,12]. During our study on the CTH of 3,3'-sulfonylbis(nitrobenzene) (I) to 3,3'-sulfonyldianiline (II), we found a partially reduced intermediate (III) (Fig. 1). To the best of our knowledge, neither the synthesis nor the theoretical studies on III has been available till now.

In the present work, we wish to report the synthesis and characterization of the novel compound **III** as well as the theoretical studies on it by using DFT-B3LYP/6-31G^{*} and HF/6-31G^{*} methods.

2. Experimental

2.1. Materials and instruments

Starting material 3,3'-sulfonylbis(nitrobenzene) (I) was commercially available. All chemicals were reagent grade and were used without further purification. The ferrihydrite catalyst was prepared according to the method described in the literature [13].

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike, China) and were uncorrected. Fourier's transformation infrared (FTIR) spectra were recorded in KBr pellets





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Fig. 1. Scheme of the catalytic transfer hydrogenation of 3,3'-sulfonylbis(nitrobenzene) (I) to 3,3'-sulfonyldianiline (II).

using an AVARTE360 FTIR spectrometer (Thermo Nicolet). ¹H NMR spectra were recorded on a Bruker AV-300 spectrometer at 300 MHz. The elemental analysis was performed with a Vario El III elemental analyzer. The TLC was performed on the commercial GF₂₅₄ plates. The "spots" were located by a ZF-1 UV analyzer (Shengke, Shanghai). The X-ray crystallographic analysis was performed on a Nonius CAD4 single-crystal diffractometer equipped with a graphite-monochromated Mo K α radiation (λ = 0.71073 Å) by using an $\omega/2\theta$ scan mode at 293 K.

2.2. Synthesis

The reduction reaction was performed by heating a solution of I (24.35 mmol) and ferrihydrite catalyst (4.50 mmol) in anhydrous ethanol (150 mL) under reflux (78 °C) followed by slowly dropping in hydrazine hydrate (146.7 mmol) in 0.5 h. The mixture was refluxed for a specified time.

The reaction course was monitored by TLC using the solvent system of ethyl acetate-petroleum ether-triethylamine (7:7:2). The reaction liquid was sampled with a capillary and dissolved in ethyl acetate.

2.3. Crystal structure determination

White color crystals of **III** suitable for X-ray analysis were grown from methanol. A crystal was put on a glass fiber. The diffraction data were collected on a Nonius CAD4 single-crystal diffractometer equipped with a graphite-monochromated Mo K α radiation (k = 0.71073 Å) by using a x/2h scan mode at 293 K. The crystal structure was solved by the direct method and refined by the full-matrix leastsquares procedure on F^2 using SHELXL-97 program [14]. Positions of hydrogen atoms were located by geometrical calculation (x, y, z and U_{iso} fixed to 1.2 times U_{iso} of the atom they are bound to).

2.4. Computational methods

The DFT calculations at $6-31G^*$ basis set and the Hatree–Fock calculations at $6-31G^*$ basis set were performed with the Gaussian 03 software package [15–17].

3. Results and discussion

3.1. TLC results

The reaction course of I to II was monitored with TLC by measuring the reaction solution as a function of time (Fig. 2). At the beginning of the reaction (0 min), only the raw material



Fig. 2. TLC monitoring the reaction solution.

Table 1

Crystal and structural refinement data of III.

Chemical formula	$C_{24}H_{20}N_4O_8S_2$
CCDC number	292524
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Space group	P21/c (No. 14)
a (Å)	12.231(2)
b (Å)	21.700(4)
<i>c</i> (Å)	10.453(2)
α (°)	90.00
β (°)	114.00(3)
γ(°)	90.00
V (Å ³), Z	2534.5(9), 4
Density (calc) (g cm ⁻³)	1.459
Abs. coeff. (mm^{-1})	0.267
F(000)	1152
θ ranges (data collection)	1.82-25.28
Index ranges	$-14 \leqslant h \leqslant 13$
	$-26 \leqslant k \leqslant 0$
	$0 \leqslant l \leqslant 12$
Reflections collected	4870
R _{int}	0.110
Independent reflections	4601
Refinement method on F^2	Full-matrix least-squares
Goodness-of-fit on F^2	1.000
Final R indices $[I > 2\sigma(I)]$	0.0796
R indices (all data)	0.1979
Residual (e Å ⁻³)	0.249/-0.223

(**I**, R_f = 0.82) was detected. At 20 min, the product (**II**, R_f = 0.27) and an unknown intermediate (**III**, R_f = 0.57) appeared. At 40 min, **I** was almost run out. At 60 min, only **II** was left.

3.2. Identification of III

The intermediate **III** was separated and identified as 3-(3-nitrophenylsulfonyl)aniline, a new compound confirmed by IR, ¹H NMR, and elemental analysis. m.p. 147–148 °C; Elemental analysis: Anal. Calcd for C₁₂H₁₀N₂O₄S: C 51.79, H 3.62, N 10.07; found C 51.66, H 3.63, N 10.04; ¹H NMR (DMSO-d6) δ : 5.73 (s, 2H, NH), 6.81–7.10 (m, 2H, Ar—H), 7.16–7.95 (t, 3H, Ar—H), 8.30–8.54 (m, 3H, Ar—H); IR (KBr, cm⁻¹) ν : 3482.8, 3391 (N—H), 3100 (Ar=C—H), 1629 (N—H), 1602, 1486, 1451 (Ar C=C), 1533, 1357 (Ar N—O), 1319 (Ar—NO2), 1162 (S=O).

3.3. Description of the crystal structure

Crystal data, experimental details, structure determination and refinement of the compound **III** are reported in Table 1, and final coordinates in Table 2. Bond distances are given in Table 3, and a selection of bond and torsion angles in Table 4 and Table 5. The displacement ellipsoid plot with the numbering scheme is shown in Fig. 3 and a perspective view of the crystal packing in the unit cell is shown in Fig. 4.

Crystal structure shows that the molecule **III** has the conformation with the two phenyl rings approximately perpendicular to the C(6)—S—C(7) plane as shown by the values of the wl and w2 parameters used to define the dihedral angles by a linear

 Table 2

 Atomic coordinates of non-hydrogen atoms and their thermal parameters for III.

Atom	x	у	Z	U (eq)
S1	0.27645(13)	0.45331(8)	0.65667(15)	0.0641(4)
S2	0.18293(14)	0.73346(7)	0.04528(16)	0.0591(4)
N1	-0.0233(5)	0.5288(2)	0.1680(5)	0.0691(15)
N2	0.5499(5)	0.3717(2)	0.4310(5)	0.099(2)
N3	0.3572(5)	0.5159(3)	0.1751(6)	0.0749(16)
N4	-0.2307(5)	0.6334(3)	-0.1538(6)	0.146(3)
01	0.0373(4)	0.5773(2)	0.1983(5)	0.1074(17)
02	-0.0997(4)	0.5170(2)	0.0552(4)	0.0913(15)
03	0.3283(3)	0.51334(18)	0.6505(4)	0.0721(12)
04	0.2499(3)	0.4371(2)	0.7735(4)	0.0845(14)
05	0.4077(4)	0.4701(2)	0.1559(5)	0.1067(18)
06	0.3208(4)	0.5163(2)	0.2686(5)	0.1078(18)
07	0.2364(3)	0.78818(16)	0.0175(4)	0.0778(13)
08	0.1806(3)	0.72650(18)	0.1802(4)	0.0767(12)
C1	0.0680(5)	0.3979(3)	0.4875(6)	0.0660(17)
C2	-0.0309(5)	0.3906(2)	0.3693(6)	0.0760(19)
C3	-0.0614(5)	0.4343(3)	0.2627(6)	0.0648(16)
C4	0.0125(4)	0.4825(2)	0.2803(6)	0.0534(14)
C5	0.1150(4)	0.4911(2)	0.3988(5)	0.0526(14)
C6	0.1424(4)	0.4470(2)	0.5011(5)	0.0492(13)
C7	0.3686(4)	0.3955(3)	0.6348(5)	0.0542(14)
C8	0.3798(5)	0.3397(3)	0.7012(6)	0.079(2)
C9	0.4509(6)	0.2952(3)	0.6751(7)	0.089(2)
C10	0.5053(6)	0.3062(3)	0.5866(7)	0.085(2)
C11	0.4950(5)	0.3627(3)	0.5228(6)	0.0669(17)
C12	0.4238(4)	0.4070(2)	0.5452(5)	0.0515(14)
C13	0.3048(4)	0.6696(2)	-0.0820(5)	0.0461(13)
C14	0.3675(5)	0.6198(3)	-0.0962(6)	0.0602(15)
C15	0.3831(5)	0.5695(3)	-0.0134(6)	0.0619(16)
C16	0.3399(4)	0.5698(3)	0.0873(5)	0.0529(14)
C17	0.2785(4)	0.6191(2)	0.1084(5)	0.0505(13)
C18	0.2598(4)	0.6682(2)	0.0204(5)	0.0439(12)
C19	0.0361(4)	0.7266(2)	-0.0823(5)	0.0474(13)
C20	-0.0059(6)	0.7680(3)	-0.1924(7)	0.0716(18)
C21	-0.1203(7)	0.7620(3)	-0.2892(7)	0.089(2)
C22	-0.1945(6)	0.7172(3)	-0.2771(6)	0.0767(19)
C23	-0.1529(5)	0.6760(3)	-0.1644(6)	0.0742(19)
C24	-0.0346(5)	0.6817(2)	-0.0674(6)	0.0672(17)

Table 3

A selection of bond lengths (Å) of III with esds in parentheses.

Parameters	X-ray	HF/6-31G*	B3LYP/6-31G*
S1-04	1.429(4)	1.4353	1.4712
S1-03	1.462(4)	1.4351	1.4711
S1-C7	1.762(5)	1.7752	1.8001
S1-C6	1.784(5)	1.7789	1.8112
N1-02	1.197(5)	1.1933	1.2299
N1-01	1.251(5)	1.1924	1.2292
N1-C4	1.470(6)	1.4587	1.4751
N2-C11	1.391(6)	1.3907	1.3906
C1-C2	1.341(7)	1.3854	1.3965
S2-08	1.430(3)	1.4351	1.4711
S2-07	1.441(4)	1.4353	1.4712
S2-C19	1.754(5)	1.7752	1.8001
S2-C18	1.776(5)	1.7789	1.8112
05–N3	1.228(6)	1.1933	1.2299
06–N3	1.227(6)	1.1924	1.2292
N3-C16	1.447(6)	1.4587	1.4751
N4-C23	1.364(7)	1.3907	1.3906

Table 4				
A selection of bond	angles (°)	of III wit	th esds in	parentheses.

Parameters	X-ray	HF/6-31G*	B3LYP/6-31G*
04-S1-03	120.7(3)	121.1653	121.9887
04-S1-C7	108.4(3)	107.9946	107.9661
03-S1-C7	108.5(3)	107.9573	107.9192
04-S1-C6	108.4(2)	106.7587	106.5018
03-S1-C6	106.4(2)	106.9509	106.7143
C7-S1-C6	103.1(2)	104.8925	104.438
02-N1-01	125.1(6)	124.9407	124.9489
02-N1-C4	120.0(5)	117.4808	117.4859
01-N1-C4	114.7(5)	117.5781	117.5648
C2-C1-C6	119.9(5)	119.7359	119.4184
C3-C4-N1	117.2(5)	118.9641	118.9262
C5-C4-N1	119.7(5)	118.7277	118.6928
C5-C6-S1	120.1(4)	119.2376	119.0752
C1-C6-S1	118.6(4)	119.6327	119.419
C8-C7-S1	120.0(5)	119.2003	119.0945
C12-C7-S1	118.3(4)	118.5564	118.3209
C10-C11-N2	119.0(6)	120.7481	120.8679
C12-C11-N2	122.3(6)	120.6465	120.6319
08—S2—07	118.6(2)	121.1653	121.9887
08-S2-C19	108.4(2)	107.9573	107.9192
07—S2—C19	109.0(3)	107.9946	107.9661
08-S2-C18	106.5(2)	106.9509	106.7143
07—S2—C18	108.5(2)	106.7587	106.5018
C19-S2-C18	105.1(2)	104.8925	104.438
06-N3-05	120.3(6)	124.9407	124.9489
06-N3-C16	119.5(6)	117.5781	117.5648
05-N3-C16	120.2(6)	117.4808	117.4859
C15-C16-N3	119.1(6)	118.9641	118.9262
C17-C16-N3	118.4(5)	118.7277	118.6928
C17-C18-S2	118.5(4)	119.2376	119.0752
C13-C18-S2	119.6(4)	119.6327	119.419
C24-C19-S2	118.6(4)	118.5564	118.3209
C20-C19-S2	119.7(5)	119.2003	119.0945
N4-C23-C24	123.6(6)	120.6465	120.6319
N4-C23-C22	118.3(6)	120.7481	120.8679

Table 5	
A selection of torsion angles (°) of III	with esds in parentheses.

C7—S1—C6—C5	T1	-107.1(5)
C7-S1-C6-C1	T2	73.5(5)
C6-S1-C7-C8	T3	-100.0(5)
C6-S1-C7-C12	T4	77.2(5)
(T1 + T2 + 180)/2	w1	73.2
(T3 + T4 + 180)/2	w2	78.6



Fig. 3. X-ray structure of III (ellipsoids are shown at the 50% probability level) and the computed structure.



Fig. 4. A packing diagram of III. Hydrogen bonds are shown as dashed lines.

combination of torsion angles (Table 5). In such a way the molecule is seen to adopt a typical arrangement intermediate between 'but-terfly' and 'propeller' conformations (Fig. 3).

In the crystal, there are two crystallographically independent molecules, A and B. Each NH₂ in A or B donates two hydrogen bonds, one to NO₂ oxygen located on B or A to form an intramolecular hydrogen bond (N2–H2 \cdots O5 or N4–H4 \cdots O2), and the other to SO₂ oxygen located on different molecules to form an intermolecular hydrogen bond (N–H \cdots O=S=O) (Figs. 3 and 4, Table 6).

In the resonant chain indicated by the shading (Fig. 5, above), the resonance generates partial charges to strengthen the hydrogen bonds (Fig. 5, below). It has been reported that more efficient hydrogen bonds can be established whenever the donor and acceptor groups are connected by a π -conjugated system (RAHB = resonance assisted hydrogen bond) [18,19]. In spite of the resonance, the N—H···O=S=O hydrogen bond in **III** appears to be intrinsically rather weak. The N···O distance on the shortest hydrogen bond of **III** is 3.043(7) Å (Table 6), while the average value on intermolecular N—H···O hydrogen bonds is reported [20] to be 2.892(3) Å. The m-aminophenylsulfonyl group in **III** mimics m-nitroanilines, because the average N···O distance for 29 such compounds amounts to 3.06(9) Å [21].

The formation of N–H···O=S=O hydrogen bonds can be drawn from the values of the IR frequencies of the NH₂ group (Table 7). The values of the NH₂ group for compound III (v_a = 3482 and v_s = 3390 cm⁻¹) are slightly smaller than the values of v_a = 3550–3500 and v_s = 3450–3400 cm⁻¹ in the absence of interactions [21].

The $d(C-NH_2)$ value in III [1.391(6)Å] is shorter than the commonly accepted value for a single $C(sp^2)-N(sp^3)$ bond of 1.44–1.45 [18].

The S–C distance at the side of aniline ring [on average 1.758(5) Å; (S1-C7 = 1.762(5) Å, S2-C19 = 1.754(5) Å] is shorter than the accepted value of 1.763 [18,22] for the C(aromatic)–SO₂ bond and shorter than the other S–C distance at the side of nitrophenyl ring [on average 1.780(5) Å; (S1-C6 = 1.784(5) Å, S2-C18 = 1.776(5) Å].

3.4. Quantum chemical calculations

Over the past couple of decades, many methods have been developed for the purpose of crystal structure prediction. Computational methods can be used not only to predict how a molecule will crystallize (i.e. unit cell, space group and all atomic positions), even prior to the synthesis of the given molecule, leading to crystallize with desired structural and physical properties, but also can help to assess the undiscovered polymorphism, for a molecule with a known crystal structure [23]. Recently, quantum-chemical calculation methods have become available to provide a powerful approach for crystal structure prediction [24–26].

3.4.1. Molecular geometry of III

DFT-B3LYP/6-31G^{*} and HF/6-31G^{*} calculations were performed on **III**, respectively. The optimized structures were characterized to the relative energy minimum of the potential surface by frequency calculation. The optimized structure by HF/6-31G^{*} is shown in

Table 7

Table 6Hydrogen bonds (Å and °) of III.

D−H···A	<i>d</i> (D–H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	<(DHA)
N2-H2A···07#1	0.86	2.28	3.043(7)	149.00
N2-H2B···O3#2	0.86	2.48	3.194(7)	141.00
N2-H2B···O5	0.86	2.71	3.433(7)	142.00
C12-H12A06	0.93	2.70	3.551(6)	152.00
N4-H4B····O2	0.86	2.49	3.297(8)	156.00
C5-H5A···O3	0.93	2.52	2.894(6)	105.00
C8—H8A···O4	0.93	2.57	2.922(8)	103.00
C17-H17A08	0.93	2.49	2.857(6)	104.00
C20–H20A···07	0.93	2.54	2.915(8)	105.00
C24–H24A…01	0.9300	2.4900	3.411(7)	169.00

Symmetry transformations used to generate equivalent atoms: #1 1 - x, -1/2 + y, 1/2 - z; #2 1 - x, 1 - y, 1 - z.



Fig. 5. The system of resonant chain (above) and the partial charges generated (below).

Fig. 3. Some optimized geometric parameters are listed in Tables 3 and 4. Comparisons of the experimental bond lengths with the calculated values show that for B3LYP method, the biggest bond difference is 0.0548 Å for C(1)-C(2) bond, and that for HF method is 0.0591 Å for N(1)—O(1) bond (Table 3), which suggest that both methods can predict well the bond length of the system studied here. On the contrary, in view of the bond angles difference between the experimental and calculated values, both methods give biggest difference for O(6)-N(3)-O(5) bond angle (B3LYP 4.5889° and HF 4.5807°, Table 4). Because of the hydrogen bonds (Figs. 3 and 4, Tables 3 and 4), the theoretical value of the angle related to the nitro group is some different from the crystal data. In spite of these differences, both the methods give satisfactory precision, which shows that both the optimized geometries calculated by B3LYP/6-31G* and HF/6-31G* methods can well reproduce the crystal structure of III.

3.4.2. Electronic properties

The frontier orbitals, HOMO and LUMO, determine the way a molecule interacts with other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. Small frontier orbital gap makes a molecule more polarisable and is generally associated with a high-chemical reactivity and low-kinetic stability [27]. The frontier orbital gap of **III** (0.364 a.u.) is lower than that of **I** (0.417 a.u.), indicating that replacing a nitro group with an amino group causes a higher chemical activity.

The 3D plots of the atomic frontier orbitals are shown in Fig. 6. It can be seen that the HOMO of **III** is distributed uniformly almost over the aniline ring and shows considerable antibonding character. The LUMO of **III** is found to be spread over the nitrophenyl ring. The nodes of HOMO and LUMO are placed almost symmetrically.

The electrostatic potential isosurface map simultaneously displays molecular shape, size and electrostatic potential values. This mapping is very useful in the investigation of the molecular

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2925 1629 1637 1625 ν (Ar C= 1602 1618 1533 1534 δ (Ar-N0	—H)
1629 1637 1625 v (Ar C= 1602 1618 1533 1534 δ (Ar-N0	
1602 1618 1533 1534 δ (Ar-N0	C)
1533 1534 δ (Ar—No	
	J ₂)
1486 1466 v (Ar C=	C)
1451 1449	
1356 1352 1352 v (Ar–No	J ₂)
1319 1317	
1162 1160 1155 v (S=O)	
1126 1138 1123	
1083 1081 1076 δ (Ar =C	—H)
991 991	
899 890 907	
875 855 875	
783 776 791 δ (Ar =C	—H)
761 760 765	
733 730	
698 691 δ (Ar =C	—H)
663 662 671	
612 622	
584 578 586	
524 521 516	

Comparison of experimental IR spectrum of III with theoretical spectra (ν cm⁻¹).



Fig. 6. The frontier molecular orbitals and the electrostatic potential isosurfaces of III.

structure with its physiochemical property relationships [17]. The electrostatic potential isosurface map of **III** (Fig. 6) shows clearly that the two major negative potential regions characterized by yellowish red color around the nitro group and the sulfonyl group, and the amino group exert a positive potential, whereas the two benzene rings seem to have a potential halfway between the two extremes, red and dark blue color. This mapping can be used to explain the intra-charge transfer path.

3.4.3. Vibrational frequency of III

The experimental and the simulated infrared spectra are shown in Fig. 7, where the calculated intensity is plotted against the



Fig. 7. FTIR spectra of I, III, and the predicted spectra of III by B3LYP/6-31G* and HF/6-31G*.

harmonic vibrational frequencies. Some primary calculated harmonic frequencies calculated at B3LYP/6-31G^{*} and HF/6-31G^{*} levels of theory are listed in Table 7 and compared with the experimental data. The descriptions concerning the assignment have also been indicated in the Table 7.

Seen from Fig. 7 and Table 7, by using the HF/6-31G^{*} method, predicted vibrational frequencies are in good agreement with experimental values except that some experimental vibrational bands, such as Ar—NO₂, cannot be predicted. On the other hand, by using the B3LYP/6-31G^{*} method, the experimental vibrational bands of Ar C=C and Ar—NH₂ cannot be predicted. Above comparison shows that HF/6-31G^{*} method is superior to B3LYP/ $6-31G^*$ method to predict the vibrational frequencies for the system studied here.

4. Conclusions

3-(3-nitrophenylsulfonyl)aniline (III) was first found during the catalytic transfer hydrogenation of 3,3'-dinitrodiphenyl sulfone (I)

to 3,3'-diaminodiphenyl sulfone (II). III was identified and characterized by elemental analysis, IR, ¹H NMR, and X-ray single crystal diffraction. The optimized geometries of III calculated by DFT-B3LYP/6-31G* and HF/6-31G* closely resemble the crystal structure. The frontier orbital gap and the electrostatic potential isosurface map of III were calculated and compared with those of I. The comparisons between the calculated results and the experimental data indicate HF/6-31G* method is better than B3LYP/6-31G* method to predict the vibrational frequencies for III. The present study of III, in general, may lead to the better understanding of the mechanisms and intermediates of the reduction of polynitro aromatic compounds, especially the nitro groups at the different aromatic rings, and may also help in designing and synthesizing new partial reduction products for technological applications.

Supplementary material

CCDC-292524 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at

http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax:+44 (0)1222 336033; e-mail: deposit@ccdc.cam.ac.uk].

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