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Synthesis and Crystal Structure of N,N-*Bis*[(4-aminophenoxy)ethyl]benzene Sulfonamide

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The reaction of diethanol amine and benzene sulfonyl chloride produced the benzene sulfonate intermediates, then it was nucleophilicly substituted by 4-nitrophenol and subsequently reduced by hydrazine hydrate in the presence of activated carbon and iron(III) chloride. A new binary aromatic amine, N,N-*bis*[(4-aminophenoxy)ethyl]benzene sulfonamide was prepared. The intermediates and the final product were structurally characterized by the means of IR, ^{1}H NMR and single crystal X-ray diffraction analysis.

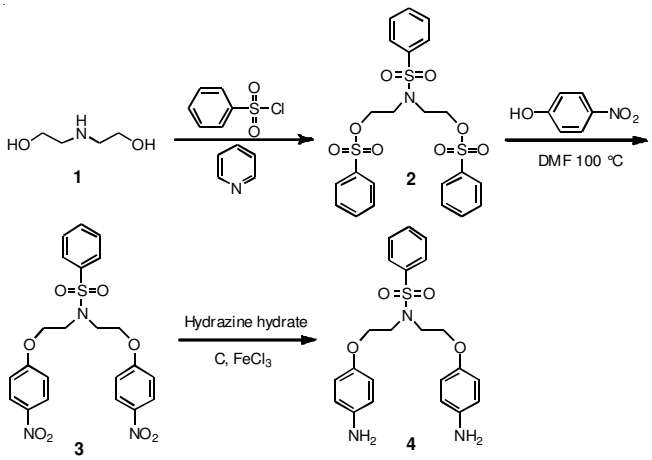
Keywords: Benzene sulfonamide, Aromatic amine, Crystal structure.

INTRODUCTION

The aromatic amines are important intermediates in the synthesis of organic functional materials such as dyes, pigments and bioactive compounds[1-3]. It is well known that the aromatic amines are prepared mainly depending on the condensation of amino-containing compounds and the reduction of the nitro compounds[4,5]. Since the amino-containing compounds condensation reactions need to be added an amino-protecting group and their lower yields, so it is generally difficult to synthesize a specific aromatic amine. Now, the reduction of the nitro compounds to the corresponding amino compound has become a commonly used method in the preparation of fine chemical productions. Among the reduction process, methods of catalytic hydrogenation, metal reduction, hydration hydrazine reduction, electrochemical reduction are widely used[6-9]. In this paper, low cost and available diethanol amine was adopted as raw material, a new binary aromatic amine, N,N-*bis*[(4-aminophenoxy)ethyl]benzene sulfonamide, was synthesized. The final product was structurally characterized by the methods of IR, ^{1}H NMR and single crystal X-ray diffraction analysis.

EXPERIMENTAL

All the reagents and solvents were used as commercial sources without further purification. The IR spectra were recorded on a Bio-Rad spectrophotometer using KBr discs in the 4000-400 cm^{-1} region. The ^{1}H NMR spectra of the compound was recorded on a JEOL ECX 500 MHz spectrometer. Crystal structure was determinated on a Bruker Apex 2 diffractometer. The synthesis route of N,N-*bis*[(4-aminophenoxy)ethyl]benzene sulfonamide is illustrated in **Scheme-I**.



Scheme-I: Synthetic route of N,N-*bis*[(4-aminophenoxy)ethyl]benzene sulfonamide

Synthesis of the compound (2): Benzene sulfonyl chloride (80 mL, 630 mmol) was added dropwise to a stirred mixture of diethanolamine (20.0 mL, 208.5 mmol) and pyridine (105 mL) in a three-necked flask with the temperature lower than 35 ºC. The mixture was stirred for 2.5 h, subsequently stirred for 1 h in a water bath of 40 ºC. After cooling to room temperature, concentrated hydrochloric acid (20 mL) was added, white solid was precipitated, then filtrated and washed three times with distilled water. The precipitate was further crystallized from ethanol solvent, yielding 74.3 % white solid: m.p.

116-117 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.42 (t, 4H, *J* = 5.8 Hz, -N-CH_2), 4.15 (t, 4H, *J* = 6.3Hz, -O-CH_2), 7.26-7.89 (m, 15H, Ar-H) ; IR (KBr, ν_{max}, cm^{-1}): 3436(s), 3067(w), 2998(w), 2892(w), 1447(s), 1403(m), 1361(s), 757(s).

Synthesis of the compound (3): Compound **2** (5.26 g, 10 mmol) dissolved in DMF (30 mL) was added dropwise to a solution of anhydrous potassium carbonate (2.76 g, 20 mmol) and 4-nitrophenol (2.78 g, 20 mmol) in DMF (40 mL) at 60 ºC for 2 h. The mixture was stirred at 100 ºC for 24 h, after cooling to room temperature, 1 mol/L NaOH solution (100 mL) was added, pale yellow solid was precipitated. The precipitate was filtrated and washed with distilled water, yielding 55.4 % solid of **3**: m.p. 153-154 ºC; IR (KBr, ν_{max}, cm^{-1}): 3436(s), 2928(w), 1594(s), 1511(vs), 1336(vs), 1264(s), 1161(m), 1111(m), 851(w), 580(w).

Synthesis of the compound (4): Compound **3** (4.87g, 10 mmol) and actived carbon (0.6 g, 50 mmol) and $FeCl_3$ (3.25 g, 20 mmol) were suspended in ethanol solvent (50 mL), with continuously stirred and heated to reflux, 80 % hydrazine hydrate (10 mL) was added dropwise, refluxed for 24 h and separated by filtration, the filtrate was kept at room temperature for slow evaporation. Colourless crystals were obtained after a few days in a yield of 43.3 %. m.p. 106-107 ºC; ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 3.52 (t, 4H, *J* = 6.3Hz, -N-CH_2), 3.96 (t, 4H, *J* = 5.8 Hz, -O-CH_2), 4.62 (s, 4H, -NH_2), 6.47-6.56 (m, 8H, Ar-H) , 7.60-7.87 (m, 5H, Ar-H); IR (KBr, ν_{max}, cm^{-1}): 3425(m), 3202(w), 1627(s), 1514(vs), 1443(s), 1295(w), 1283(w), 826(s).

Crystal structure determination: The X-ray data were collected on a Bruker Apex-II CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 293 (2) K with crystal size 0.11 mm × 0.14 mm × 0.15 mm. A total of 7757 (R_{int} = 0.0816) independent reflections were collected by ö and ù scans technique in the range of 0.909 ≤ θ ≤ 26.04º from which 5198 [I > 2σ(I)] reflection were corrected for Lorentz and polarization factors. The structure was solved by direct method and refined using a full-matrix least-squares procedure on F^2 in SHELXS-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model.

RESULTS AND DISCUSSION

The synthesis of benzene sulfonate is sensitive to the reaction temperature, it should be strictly controlled in an ice bath blew 35 ºC, when the reaction was performed at ambient temperature, reaction temperature raised quickly and no white solid was precipitated out. The nitro compound of **3** exhibits poor solubility in common organic solvents, only IR spectrum data can be obtained for it. In the process of reduction, hydrazine hydrate should be added slowly and tracked by TLC, 24 h is needed for the reduction reaction.

X-Ray diffraction analysis reveals there are two crystallographically independent molecules in the asymmetric unit. The molecular structure of compound **4** (Fig. 1) shows it crystallized in the monoclinic system, P 21/n space group, with the crystal cell parameters a = 13.599 (6), b = 16.852 (7), c = 19.928 (9) Å, β = 109.046 (5)º, V = 4317 (3) $Å^3$, Z = 8, D_c = 1.316 g/cm^3, $F_{(000)}$ = 1808.0, M_r = 427.52, R_1 = 0.0503, wR_2 = 0.1117. The selected bond lengths and bond angles are listed in Table-1, the hydrogen bondings parameters are given in Table-2.

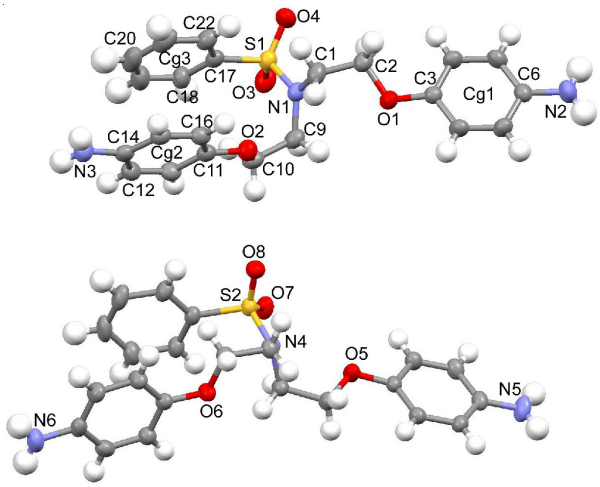


Fig. 1. Molecular structure of compound **4**

TABLE-1
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

S(1)-N(1)	1.626(2)	C(10)-O(2)	1.434(3)	N(1)- S(1)-C(17)	108.19(11)
C(1)-N(1)	1.483(3)	C(3)-O(1)	1.389(3)	N(1)- S(1)-O(3)	107.03(11)
C(9)-N(1)	1.473(3)	C(11)-O(2)	1.386(3)	N(1)- S(1)-O(4)	107.20(11)
S(1)-O(3)	1.4344(19)	C(6)-N(2)	1.400(4)	C(2)- O(1)-C(3)	116.79(19)
S(1)-O(4)	1.436(2)	C(14)-N(3)	1.405(4)	C(10)-O(2)-C(11)	117.90(19)
C(2)-O(1)	1.428(3)	C(1)-C(2)	1.503(4)	N(1)-C(1)-C(2)	112.4(2)

TABLE-2
HYDROGEN BOND DISTANCES (Å) AND ANGLES (º)

Type (D-H···A)	d (D-H)	d (H···A)	∠(DHA)	d (D···A)	Symmetry codes
N(2)-H(2D)···N(3)	0.8600	2.3900	168.00	3.240(4)	x, 1 + y, z
N(3)-H(3B)···O(3)	0.8600	2.2700	172.00	3.124(3)	3/2-x, -1/2 + y, 1/2-z
N(5)-H(5B)···N(6)	0.8600	2.3600	161.00	3.187(4)	x, 1 + y, z
N(6)-H(6A)···O(8)	0.8600	2.3400	159.00	3.160(3)	1/2-x, -1/2 + y, 1/2-z
C(9)-H(9B)···O(3)	0.9700	2.5400	102.00	2.905(4)	x, y, z
C(18)-H(18)···O(3)	0.9300	2.4900	106.00	2.886(4)	x, y, z
C(23)-H(23A)···O(7)	0.9700	2.4500	108.00	2.903(3)	x, y, z
C(23)-H(23B)···O(6)	0.9700	2.4700	121.00	3.086(3)	x, y, z
C(44)-H(44)···O(8)	0.9300	2.5200	105.00	2.896(3)	x, y, z

In compound **4**, the three phenyl rings possess different orientations, with the bond angles of N(1)-S(1)-C(17), N(1)-C(1)-C(2), N(1)-C(9)-C(10) are 108.19 (11), 112.4 (2), 115.4 (2)º, respectively. Five intramolecular C-H···O hydrogen bondings and few intermolecular N-H···N as well as N-H···O hydrogen bondings are involved in the structure to stabilize the crystal. Furthermore, intramolecular π-π stacking interactions have been found in the structure, with the distance of Cg2···Cg3 is 3.956 (3) Å, where Cg is the corresponding phenyl ring defined by C(11)-C(16) and C(17)-C(22) atoms.

Conclusion

A new binary aromatic amine, N,N-*bis*[(4-aminophenoxy)-ethyl]benzene sulfonamide, has been prepared by the method of hydration hydrazine reduction and characterized by the means of IR, ^{1}H NMR and single crystal X-ray diffraction analysis. Intramolecular and intermolecular hydrogen bondings as well as π-π stacking interactions are involved in the structure to stabilize the crystal. The new compound not only enriches the family members of aromatic amines, but also has promising applications in chemical industries.

Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 936538.

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