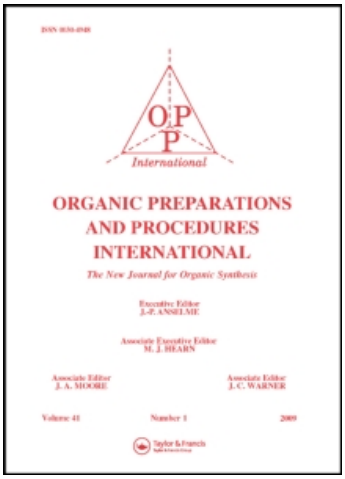

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SYNTHESIS OF NOVEL 4,4'-BENZIDINE DERIVATIVES WITH SULFONIC ACID GROUPS

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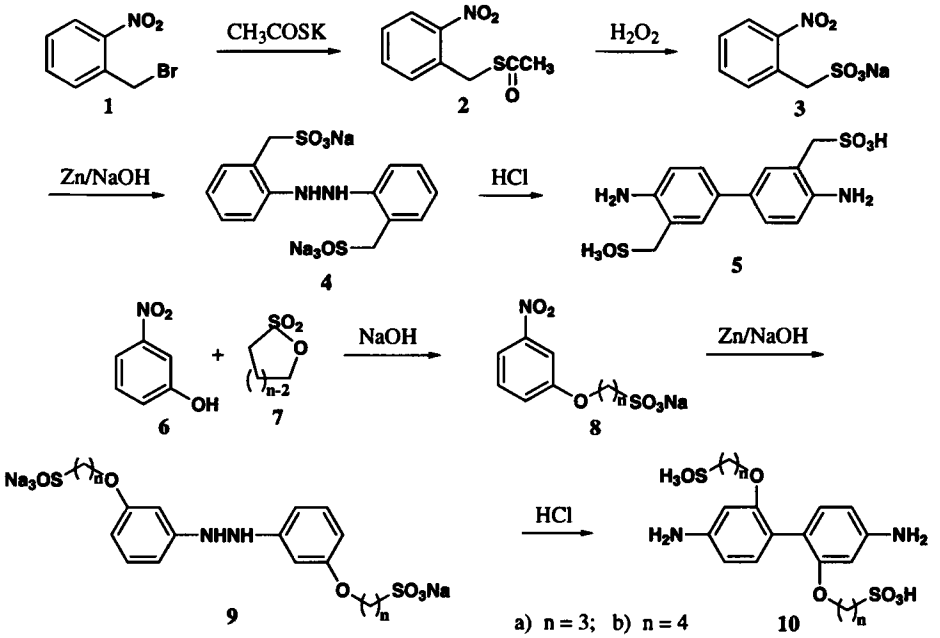
Benzidines substituted in the side-chain have been utilized as diamine components of dye intermediates[1] and of aromatic polyimide monomers.[2] Recently 4,4'-benzidine derivatives, with sulfonate groups, have been of great interest as key monomers of the polyimide-electrolyte film in fuel cell systems.[3] These benzidines with 3,3'-*bis*(sulfoalkoxy) groups have been synthesized by alkylation of commercial 3,3'-dihydroxy-4,4'-benzidine with propane- or butanesultones.[4] However, there is no report on a synthetic method for the 2,2'-substituted or alkylsulfonated ones. We report here a route to 3,3'-*bis*(sulfomethyl)- and 2,2'-*bis* (sulfoalkoxy)-4,4'-benzidine *via* the benzidine rearrangement.



2-Nitrobenzylsulfonic acid (**3**) was synthesized by thioacetylation of 2-nitrobenzyl bromide with potassium thioacetate, followed by oxidation of the thioester with hydrogen

peroxide.[5] 3-Nitrophenoxyalkanesulfonic acids (**8**) were prepared by alkylation of *m*-nitrophenol with alkanesultones (**7**).[4] Reductive coupling to hydrazobenzenes was carried out with zinc powder since hydrazo intermediates dissolve in an aqueous alkaline solution. The benzidine rearrangement of hydrazobenzenes with long alkoxy side-chains produces 2,2'-benzidine as by-product, presumably due to steric hindrance.[6] The content of the desired 4,4'-benzidine was calculated from a CH_2 integrated value by ^{1}H-NMR-spectrometry (75% for **10a**; 55% for **10b**). The product could be isolated in pure form after several recrystallizations from water and aqueous methanol.

EXPERIMENTAL SECTION

The infrared and ^{1}H-NMR spectra were recorded on HORIBA FT-IR-720 and Bruker 400 MHz spectrometers. Elemental analyses were conducted with Carbo Elba EA-1108. Melting points were measured in a capillary tube and are uncorrected. Materials of a reagent grade were used as supplied and solvents were of highest purity commercially available.

Sodium 2-Nitrobenzylsulfonate (**3**).- A mixture of 2-nitrobenzyl bromide (5.0 g, 23.1 mmol) and potassium thioacetate (4.8 g, 41.7 mmol) in anhydrous DMSO (28 mL) was stirred at room temperature for 24 h. The resulting solution was diluted with ethyl acetate (150 mL), washed with water, and then dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue (**2** : IR, C=O, 1691 cm^{-1}) was dissolved in acetic acid (30 mL), and then mixed with 15 mL of 30% hydrogen peroxide (CAUTION). The reaction mixture was stirred for 2 h at room temperature and allowed to stand overnight without stirring. The reaction mixture was concentrated under reduced pressure below 20°C and the residual oil was dissolved in ethanol (20 mL) and basified to pH 10 with 3% sodium hydroxide/90% ethanol solution. The solution was cooled in a refrigerator and the resulting precipitate was collected, washed with ethanol, and then dried *in vacuo* to yield 4.64 g (84%) of white crystal (**3**), mp. 212-214°C. IR (KBr): 1531, 1346 (NO_2); 1214, 1053 (SO_2) cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 4.58 (s. 2H, CH_2); 7.48, 7.59, 7.90 (4H, ArH). *Anal.* Calcd for $C_7H_6NNaO_5S$: C, 35.14; H, 2.53; N, 5.86. Found: C, 35.02; H, 2.82; N, 5.63.

Sodium 3-Nitrophenoxybutanesulfonate (**8b**).- A solution of 1,4-butanesultone (12.5 g, 92 mmol) in methanol (10 mL) was added dropwise to a mixture of *m*-nitrophenol (11.6 g, 83.5 mmol) and sodium hydroxide (3.7 g, 87.7 mmol) in methanol (50 mL). The reaction mixture was refluxed for 12 h with stirring, and then cooled in an ice bath. The resulting orange precipitate was collected, and then recrystallized from methanol to yield 19.9 g (80%) of pale orange solid (**8b**), mp. 90-92°C, IR (KBr): 1527, 1351 (NO_2); 1203, 1054 (SO_2) cm^{-1}. ^{1}H-NMR (D_2O): δ 1.84 (s, 4H, -CH_2CH_2-), 2.91 (t, 2H, -CH_2S), 4.05 (s, 2H, OCH_2-), 7.26, 7.41, 7.68, 7.76 (s, 4H, ArH). *Anal.* Calcd for $C_{10}H_{12}NNaO_6S$: C, 40.40; H, 4.08; N, 4.71. Found: C, 40.20; H, 4.35; N, 4.52. Sodium 3-Nitrophenoxypropanesulfonate[7] (**8a**): yield 76%; mp 202-205°C [*lit.*[7] 230°C (DSC)].

Benzidine-3,3'-*bis*(methanesulfonic Acid) (**5**).- 2-Nitrobenzylsulfonic acid sodium salt (**3**, 3.6 g, 15 mmol) was dissolved in 15 mL of water containing 1.8 g of sodium hydroxide (42 mmol), and

the solution was warmed to 60°C. Zinc powder (90%, 5.1 g, 70 mmol) was added in small portions to the reaction mixture with stirring. The temperature of the mixture rose quickly to and was kept at 90°C until a sample spotted on filter-paper was colorless. The reaction mixture was cooled to 60°C, and the zinc salts were filtered off on a sintered glass funnel, washed with hot 80% aqueous ethanol. The filtrate and washing were cooled in an ice bath, and then added dropwise to a cooled conc. hydrochloric acid/ethanol solution (3 mol/L, 30 mL) below 5°C, while the pH of the reaction mixture was maintained at approximately pH 1 by simultaneous addition of conc. hydrochloric acid solution (6 mol/L). The reaction mixture was stirred in an ice bath for 3 h and allowed to stand in a refrigerator overnight. The resulting precipitate was collected and recrystallized from water to yield 4.35 g (78%) of white solid (**5**), mp. 290°C (dec.), IR (KBr): 3470, 2600 (NH_3^+), 1207, 1035 (SO_2) cm^{-1}. ^{1}H-NMR(D_2O): δ 4.11 (s, 4H, CH_2), 6.88, 7.38 (6H, ArH).

Anal. Calcd for $C_{14}H_{16}N_2O_6S_2$: C, 45.14; H, 4.34; N, 7.52. Found: C, 45.01; H, 4.62; N, 7.37.

Benzidine-2,2'-*bis*(oxybutanesulfonic Acid) (10b).- 3-Nitrophenoxybutanesulfonic acid sodium salt (**8b**, 5.0 g, 16.8 mmol) was dissolved in 20 mL of water containing 2.2 g of sodium hydroxide (53.2 mmol), and the solution was warmed to 60°C. Zinc powder (90%, 6.1 g, 84.8 mmol) was added in small portions to the reaction mixture with stirring. The temperature of the mixture was kept at 90°C until the solution turned colorless. While hot, the mixture was filtered into ethanol (30 mL) on a sintered glass funnel and the zinc salts were thoroughly washed with hot 90% ethanol. The filtrate and washing, which was approximately 80% ethanol, was cooled in a freezer overnight; the resulting pale orange precipitate was collected and washed with cold 80% ethanol. The hydrazobenzene thus obtained was added portionwise to a cooled conc. hydrochloric acid-methanol solution (1 mol/L, 30 mL) below –10°C with vigorous stirring and simultaneous addition of conc. hydrochloric acid-methanol solution (4 mol/L) so as to keep the pH of the reaction mixture at approximately pH 1. The reaction mixture was stirred in an ice bath for 5 h; the resulting pale violet precipitate was collected to give 2.1 g of the crude benzidine. The reaction product consisted of about 55% of 4,4'-benzidine and 45% of isomeric product(s) by proton NMR spectroscopy. Pure 4,4'-benzidine (**10b**) was obtained by recrystallizations from water and from 70% methanol to yield 0.97 g (24%) as white crystals, mp. 290°C (dec.). IR (KBr): 2921, 2875 (-CH_2-); 2618 (OH), 1180, 1039 (SO_2) cm^{-1}. ^{1}H-NMR(D_2O): δ 1.52, 1.62 (m, 8H, - CH_2CH_2-), 2.53 (m, 4H, -CH_2S), 3.95 (m, 4H, OCH_2-), 6.95 (m, 4H, 3,6-Ar-H), 7.24 (m, 2H, 5-Ar-H).

Anal. Calcd for $C_{20}H_{28}N_2O_8S_2$: C, 49.16; H, 5.79; N, 5.75. Found: C, 48.95; H, 5.98; N, 5.61.

Benzidine-2,2'-*bis*(oxypropanesulfonic acid) (**10a**): mp. 260°C (dec.), [*lit.*[7] 341°C (DSC)] ^{1}H-NMR (D_2O): δ 1.96 (m, 4H, -CH_2-), 2.67 (t, 4H, -CH_2S), 4.06 (t, 4H, OCH_2-), 6.97 (t, 4H, 3,6-Ar-H), 7.28 (t, 2H, 5-Ar-H).

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TEMPERATURE DEPENDENT MIGRATION OF THE NITRO GROUP OF POTASSIUM 4-AMINO-3,5-DINITROBENZENESULFONATE VS DESULFONATION

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Electrophilic sulfonations of aromatic compounds such as naphthalene, performed under kinetic control, give products different from those carried out under thermodynamically controlled conditions.[1] The possibility of hydrolytic removal of the sulfonic acid group under relatively mild conditions makes it a suitable protecting group, a process which, for example, has been claimed for the preparation of 2,6-dinitroaniline (**5**), starting from chlorobenzene (*Scheme 1*).[2] However, using this procedure[2] we obtained a mixture of 2,6- and 2,4-dinitroanilines from potassium 4-amino-3,5-dinitrobenzenesulfonate (**4**) which contains up to 20% of the second isomer (estimated by integrated intensity from ^{1}H NMR) which is practically impossible to separate from the desired product; 2,4-dinitroaniline has been obtained cleanly by ammonolysis of 2,4-dinitrochlorobenzene.