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Synthesis and Properties of Aminoarylsulphonanilide-3′,5′-dicarboxylic Acids

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ABSTRACT

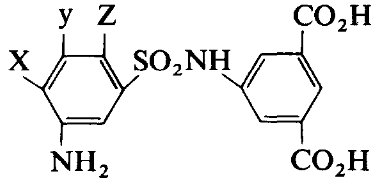
The synthesis of six new nitro- and amino-arylsulphonanilide-3′,5′-dicarboxylic acids is described. The structures of the products were confirmed by elemental analysis, IR and ^1H*-NMR spectra. Aminoarylsulphonanilide-3′,5′-dicarboxylic acids are useful diazo components for the synthesis of acid dyes.*

1 INTRODUCTION

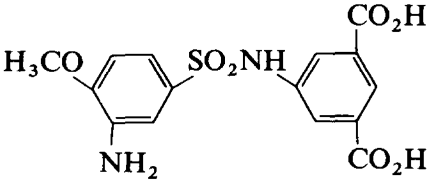
On the basis of preliminary investigations, it was found that useful components for the synthesis of various dyes were aminoarylsulphonanilidecarboxylic acids. In cases where only one carboxylic group is present in the anilide radical of the diazo component, the coupling components used should have a sulphonic group to increase the water solubility of the derived dyes. On the other hand, very useful diazo components were the acids containing two carboxylic groups in the anilide portion (viz. derivatives of 5-aminoisophthalic acid). In this case, for the synthesis of acid dyes, it is possible to use coupling components with or without water-solubilizing groups.

The monoazo acid dyes prepared from derivatives of amino-arylsulphonanilide-3′,5′-dicarboxylic acid are characterized by very good application and performance properties. They have good water solubility, bright hue and high wet- and light-fastness. Dyes of this type are suitable for dyeing polyamide fibres from a slightly acidic dyebath.

This present study is concerned with the synthesis of the aminoarylsulphonanilide-3′,5′-dicarboxylic acids shown in formulae **A-1** to **A-2**, and **A-6**.



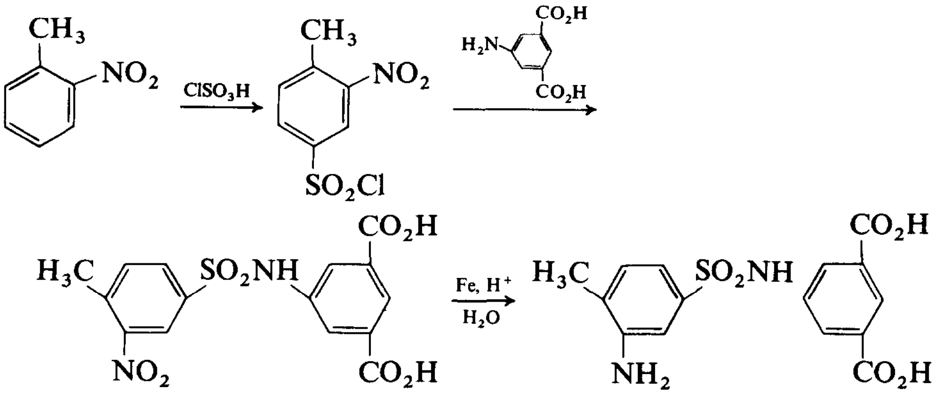
A-1: X = H, y = H, Z = H
A-2: X = CH_3, y = H, Z = H
A-3: X = H, y = H, Z = CH_3
A-4: X = Cl, y = H, Z = H
A-5: X = CH_3, y = Cl, Z = H



A-6

2 EXPERIMENTAL

The acids **A-1** to **A-5** were prepared according to the general scheme below, using *o*-nitrotoluene as representative starting material.



Acid **A-6** was obtained by chlorosulphonation of acetyl-*o*-anisidine followed by condensation of the resultant sulphochloride with 5-aminoisophthalic acid and hydrolysis of the acetyl group with 15% hydrochloric acid.

TABLE 1
Some Parameters of the Reaction Condensation and Characterization Data of the Nitroarylsulphonanilide-3′,5′-dicarboxylic Acids

Nitro compound[a]	*Time of reaction (h)*	*Yield (%)*	*Melting point (°C)*	*Elemental analysis data (%) Calcd/Found*					*IR absorption bands (cm^{-1})*				
				C	*H*	*N*	*S*	*Cl*	*$NHSO_2$*	*C NO_2*	*COOH*	*CH_3*	*CONH*
N-1	6·0	90·0	302·5–303	45·9	2·75	7·65	8·75		3 250, 1 350, 1 170	1 540, 1 360, 890	1 720		
				45·8	2·7	7·5	8·7						
N-2	6·0	93·7	297–298	47·4	3·2	7·4	8·4		3 200, 1 350, 1 170	1 540, 1 360, 900	1 720	2 930, 2 870	
				47·5	3·2	7·3	8·4						
N-3	6·0	90·3	296–297	47·4	3·2	7·4	8·4		3 250, 1 350, 1 180	1 540, 1 360, 880	1 720	2 930, 2 870	
				47·4	3·2	7·4	8·4						
N-4	5·5	94·2	302–304	42·0	2·3	7·0	8·0	8·85	3 200, 1 350, 1 180	1 540, 1 360, 890	1 720		
				41·9	2·3	7·0	8·0	8·9					
N-5	6·5	89·5	312–314	43·4	2·7	6·75	7·7	8·55	3 250, 1 350, 1 180	1 550, 1 360, 900	1 730	2 930, 2 870	
				43·5	2·6	6·7	7·8	8·6					
Ac-6	6·0	88·4	266–268	50·1	3·7	6·9	7·9		3 200, 1 350, 1 170		1 720		1 700, 1 540, 730, 670
				50·2	3·7	6·85	7·2						

[a] Number of nitro compound corresponds to number of amine, e.g. **N-1** corresponds to **A-1**.

TABLE 2

Characterization Data for Aminoarylsulphonanilide-3′,5′-dicarboxylic Acids

Amine	*Yield of reaction (%)*	*Melting point (°C)*	*Elemental analysis (%)*										*IR absorption (cm^{-1})*		
			C		*H*		*N*		*S*		*Cl*		*NH$_2$*	*NHSO$_2$*	*COOH*
			Calcd	*Found*	*Calcd*	*Found*	*Calcd*	*Found*	*Calcd*	*Found*	*Calcd*	*Found*			
A-1	93·7	274–276	50·0	49·9	3·6	3·6	8·3	8·2	9·5	9·5			3 550, 3 450, 1 620	3 250, 1 350, 1 170	1 710
A-2	95·1	303–304·5	51·4	51·5	4·0	4·05	8·0	8·2	9·15	9·1			3 550, 3 450, 1 620	3 250, 1 350, 1 170	1 720
A-3	94·7	262–263·5	51·4	51·4	4·0	4·1	8·0	8·0	9·15	9·1			3 550, 3 450, 1 625	3 250, 1 350, 1 170	1 710 1 720
A-4	96·1	288–290	45·35	45·3	3·0	3·0	7·6	7·6	8·65	8·7	9·6	9·4	3 550, 3 450, 1 620	3 250, 1 360, 1 170	1 705 1 715
A-5	96·3	325–326·5	46·8	47·0	3·4	3·7	7·3	7·2	8·3	8·3	9·2	9·1	3 550, 3 450, 1 620	3 250, 1 360, 1 170	1 710 1 740
A-6	89·3	227–230	49·2	49·1	3·85	3·8	7·65	7·6	8·75	8·5			3 550, 3 450, 1 620	3 250, 1 350, 1 170	1 720

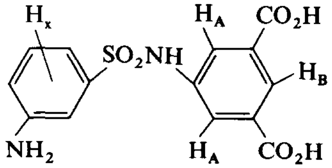
The following substances were used for the syntheses: nitrobenzene, *o*- and *p*-nitrotoluenes (standard pure; POCh, Poland), 6-chloro-2-nitrotoluene (a commercial product from Hoechst, purified by crystallization from 70% ethanol). 5-Aminoisophthalic acid was prepared by nitration of pure isophthalic acid with a nitrating mixture at 80°C.[1] 5-Nitroisophthalic acid was reduced with iron filings dust in an aqueous system at the boil in the presence of ammonium chloride. The sodium salt of 5-aminoisophthalic acid was purified by crystallization from water. 3-Nitrobenzenesulphochloride, 2-nitrotoluene-4-sulphochloride, 4-nitrotoluene-2-sulphochloride, 2-nitrochlorobenzene-4-sulphochloride, 2-nitro-6-chlorotoluene-4-sulphochloride and 2-methoxyacetanilide-5-sulphochloride were prepared according to methods described in the literature.[2-5]

The sulphochlorides were used for the condensation with 5-aminoisophthalic acid directly after their separation from the reaction mixture and quantitative determination. The condensations of these arylsulphochlorides with 5-aminoisophthalic acid (sodium salts) were carried out in aqueous systems within the pH range 6·5–7·0 at temperatures of 25–50°C (at the end of the process). Nitroarylsulphonanilidedicarboxylic acids were separated from the reaction mixture in the form of sodium salts. For elemental analysis, melting points and spectroscopic examination, the compounds were converted to the free carboxylic acids by acidifying with hydrochloric acid and crystallization from 80% ethanol.

Some of the reaction parameters, melting points of the nitroarylsulphonanilide-3'-5'-dicarboxylic acids, elemental analyses and IR spectra data are given in Table 1.

TABLE 3

^{1}H-NMR Spectra of the Aminoarylsulphonanilide-3',5'-dicarboxylic Acids (ppm)



Amine	*CH_3*	*Number of H_x*	*H_x^**	*Number of H_A*	*H_A^**	*Number of H_B*	*H_B^**
A-1		4	6·96–7·73	2	8·32	1	8·52
A-2	2·08	3	6·90–7·30	2	8·03	1	8·20
A-3	2·10	3	7·47–7·97	2	8·37	1	8·58
A-4		3	7·00–7·73	2	8·18	1	8·42
A-5	2·23	2	7·13	2	8·13	1	8·32
A-6	1·38	3	7·08–7·60	2	8·13	1	8·28

H_x^*, multiplet; H_A^*, doublet ($J = 2$ Hz); H_B^*, doublet ($J = 2$ Hz).

Reduction of the nitroarylsulphonanilide-3′,5′dicarboxylic acids was carried out in water or in 40% aqueous *N,N*-dimethylformamide by the method of Bechamp. After reduction in *N,N*-dimethylformamide, the amines were separated from the reaction mixture after filtering off iron oxides by adding water and acidifying with hydrochloric acid to obtain a weak acidic reaction with Congo Red paper. For elemental analyses and spectroscopic examinations, the amines obtained were crystallized from ethanol. The structures of the amines were confirmed by elemental analysis, IR spectroscopy (using a Specord IR-71; Carl Zeiss, Jena) and ^{1}H-NMR studies,[6] (using a Tesla BS 467; CSSR). Melting points were measured with a Boetius without correction. The results and some of the reaction parameters are given in Tables 2 and 3.

3 EXAMPLES OF THE SYNTHESES

3.1 Synthesis of 2-nitrotoluene-4-sulphonanilide-3′,5′-dicarboxylic acid (N-2)

To 90 g (0·4 mol) of the sodium salt of 5-aminoisophthalic acid dissolved in 500 cm^3 of water, 94·2 g (0·4 mol) of 2-nitrotoluene-4-sulphochloride was added at 25°C over 1 h with vigorous stirring. The pH was controlled within the range 6·5–7·0 with a 10% solution of sodium hydroxide added dropwise. After 4 h (precipitate deposition) the reaction mixture was heated for 1 h to 50°C. After a further 2 h, no change in the pH was observed and tests for 5-aminoisophthalic acid did not show any further decrease in the quantity present (two subsequent measurements were made over 30 min). There remained 0·0188 mol of unreacted 5-aminoisophthalic acid.

The mixture was heated over 30 min to 60°C and maintained at this temperature for a further 1 h. The mixture was then acidified with 30% hydrochloric acid to pH 5·5 and salted out with 50 g of sodium chloride (about 10% by vol.). After cooling to ambient temperature, a crystalline precipitate was filtered off, washed with a 10% brine solution and dried at 70–75°C (160 g, 89% product content). The nitro compound content was determined by reduction with zinc powder and diazotization with a standard solution of sodium nitrite.

The other nitroarylsulphonalide-3′,5′-dicarboxylic acids were prepared by the same procedure.

3.2 Synthesis of 2-toluidine-4-sulphonanilide-3′,5′-dicarboxylic acid (A-2)

A mixture of 600 cm^3 of water, 55 g of iron powder and 15 g of ammonium chloride was heated to 98°C and 114·1 g (129 g of 89% product = 0·3 mol) of the sodium salts of 2-nitrotoluene-4-sulphonanilide-3′,5′-dicarboxylic acid was added over 1·5 h, maintaining a temperature of 55–90°C. After addition of the nitro compound, 15 g of iron powder and 5 g of ammonium chloride were added and stirring was continued at 98°C for a further 2 h. The mixture was then cooled to 70°C and 3 g of sodium sulphite and 10 cm^3 of 30% sodium hydroxide were added to obtain an alkaline reaction with Brilliant Yellow paper, and to precipitate the iron salt (tested with Na_2S). The mass was then heated to boiling point and the iron oxides filtered off and washed twice with 100 cm^3 of hot water. The filtrate was cooled to ambient temperature and acidified with 30% hydrochloric acid (70 cm^3) to obtain a weak acidic reaction with Congo Red paper. After filtering and drying at 70°C, 103 g of product containing 97·1% 2-toluidine-4-sulphonanilide-3′,5′-dicarboxylic acid was contained. The amine content in the product was determined by diazotization with a standard solution of sodium nitrite.

The other nitroarylsulphonanilide-3′,5′-dicarboxylic acids were reduced in the same way.

3.3 Synthesis of 2-anisidine-4-sulphonanilide-3′,5′-dicarboxylic acid (A-6)

To 90 g (0·4 mol) of the sodium salts of 5-aminoisophthalic acid dissolved in 500 cm^3 of water, 105·4 g (0·4 mol) of 2-methoxyacetanilide-5-sulphochloride was added with vigorous stirring at 25–30°C over 1 h, maintaining a pH of 6·5–7·0 by dropwise addition of 40% sodium acetate solution. After 2 h, the temperature was raised to 35°C and maintained for a further 2 h. The test for 5-aminoisophthalic acid did not show any further decrease in its amount (0·023 mol remained). The mixture was then heated to 60°C and maintained at that temperature for a further 1 h. After condensation at 60°C, 300 cm^3 of 30% hydrochloric acid was added dropwise and the mixture was heated to boiling point for 3 h (during this period, precipitate deposition was observed). The mass was then cooled to ambient temperature and the precipitate was filtered off. After drying at 70°C, 143 g of product, containing 91·5% 2-anisidine-4-sulphonanilide-3′,5′-dicarboxylic acid, was obtained.

4 DISCUSSION OF RESULTS

It was found that 5-aminoisophthalic acid reacted readily with all the nitroarylsulphochlorides under the same conditions. The structure of the sulphochloride had no apparent effect on the process. In all the cases, reaction yields were high and the products obtained had good purity. The optimum pH and temperature were found to be 6·5–7·0 and 20–50°C, respectively.

Reduction of the sodium salts of nitroarylsulphonanilide-3′,5′-dicarboxylic acid in water by the Bechamp method in the presence of ammonium chloride proceeded very readily. The process is suitable for use on a large scale.

The reduction of nitroarylsulphonanilide-3′,5′-dicarboxylic acids can be carried out also by the Bechamp method in 40% *N*,*N*-dimethylformamide. In this case, the aminoarylsulphonanilide-3′,5′-dicarboxylic acids are separated from the reaction liquor by dilution and acidifying.

The aminoarylsulphonanilide-3′,5′-dicarboxylic acids were used for the synthesis of acid dyes.

REFERENCES

1. Kimura, M. & Thoma, M., *Yakugaku Zasshi*, **78** (1958) 1401–3; *Chem. Abstr.*, **53** (1959) 8056.
2. BIOS Report No. 1153, pp. 40–1.
3. BIOS Report No. 1153, pp. 42–3.
4. BIOS Report No. 1153, pp. 217–18.
5. BIOS Report No. 1153, pp. 38–9.
6. Silverstein, R. M. & Bassler, G. G., *Spectrometric Identification of Organic Compounds*. John Wiley and Sons, New York, 1967.