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Synthesis and Properties of Aminoarylsulphonanilidesulphonic Acids

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SUMMARY

Several isomeric nitro- and amino-arylsulphonanilidesulphonic acids were synthesized. The structures of the compounds were confirmed by elemental analysis and IR spectroscopy. Water solubilities of the nitroarylsulphonanilidesulphonic acids were measured and the values of $\mathrm{p}K_{a1}$ *of the sulphonic group and* $\mathrm{p}K_{a2}$ *of the sulphonamide group were determined. Their measurements can be utilized in selecting suitable coupling components for the synthesis of acid dyes where solubility factors are of great importance in their application or in the fastness of their dyeings. The amines synthesized were used in the preparation of acid dyes.*

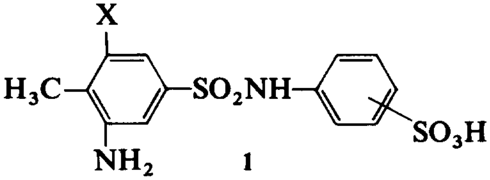
1 INTRODUCTION

Among the acid dyes having good dyeing fastness properties and brightness of hue, there is a group of monoazo dyes containing in the dye molecule one sulphonic group and an arylsulphonanilide radical.[1–5] Such dyes are useful for the coloration of polyamide fibres, silk and wool; the sulphonic group in the dyes is mainly present in the coupling component and the sulphonanilide radical in the diazo component. Such a structural arrangement of these groups in the dye molecule imposes certain restrictions on the possible synthesis of a wide colouristic range of dyes of this type.

On the basis of preliminary investigations and from literature reports, it was found that useful components for the synthesis of these dyes were aminoarylsulphonanilidesulphonic acids in which the sulphonic group can be present in various positions of the anilide radical of the diazo component.

The use of such compounds as diazo components allows the utilization as coupling components of compounds without sulphonic or carboxylic groups, e.g. naphtholates, derivatives of 1-phenyl-3-methylpyrazolone-5, pyridone, acetylacetic anilides and tertiary amines.

We describe here the synthesis of some aminoarylanilidesulphonic acids represented by structures **1**, **2** and **3**, and in which X = H or Cl and Y = H, CH_3 or OCH_3.



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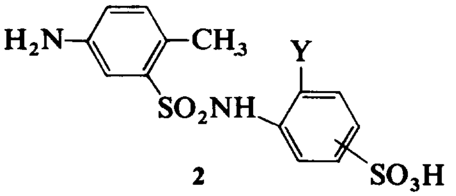

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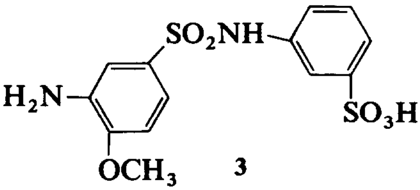

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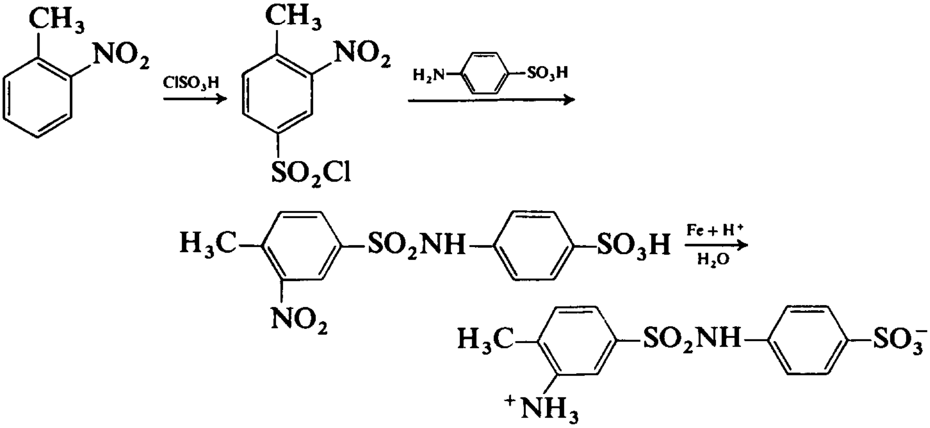
Some properties of these compounds were also examined on the basis that they may affect the fastness properties of dyes synthesized from them.

2 EXPERIMENTAL

2.1 General

The acids **A-1** to **A-9** (Table 3) of general formula **1** and **2** were prepared according to the accompanying general reaction scheme (Scheme 1), starting from *o*-nitrotoluene and sulphanilic acid:



Scheme 1

Acid **A-10** (formula **3**) was prepared by chlorosulphonation of acetyl-*o*-anisidine, condensation of the resultant sulphochloride with metanilic acid and hydrolysis of the acetyl group with hydrochloric acid. The following parent substances were used for the syntheses: *o*- and *p*-nitrotoluenes (standard-pure, POCh-Poland), 6-chloro-2-nitrotoluene (a commercial product, Hoechst, purified by crystallization from 70% ethanol). Metanilic and orthanilic acids were commercial products purified by crystallization from water. 2-Toluidine-4-sulphonic acid, 2-anisidine-4-sulphonic acid, 2-nitrotoluene-4-sulphochloride (**4**), 4-nitrotoluene-2-sulphochloride (**5**), 2-nitro-6-chlorotoluene-4-sulphochloride (**6**) and 2-methoxyacetanilide-5-sulphochloride (**7**) were prepared according to methods described in the literature.[6,7]

The condensation of these arylsulphochlorides with suitable anilidesulphonic acids (sodium salts) were carried out in aqueous systems within the pH range 6·5–7·2 at temperatures of 35–50°C. Nitroarylsulphonanilidesulphonic acids were separated from the reaction medium in the form of sodium salts. For the elemental analysis and melting point measurements, these compounds were converted to the free sulphonic acids by treating aqueous solutions of the sodium salts with sulphuric acid. Reduction of the nitro compounds was carried out by the method of Bechamp. The structures of the nitro compounds and the amines were confirmed by elemental analysis and IR spectroscopy, using a Specord IR-71 apparatus (Carl Zeiss, Jena). Melting points were measured with a Boetius apparatus without correction. The results and some of the reaction parameters are listed in Tables 1, 2 and 3.

Water solubilities of the sodium salts of nitroarylsulphonanilidesulphonic acids were determined at constant temperatures of 20 and 100°C (± 5°C). The pK_a values of the sulphonic acid and sulphonanilide groups in the compounds were determined by the potentiometric method. All compounds

TABLE 1
The Structure of Nitroarylsulphonanilides and Some Reaction Parameters

Nitro compound	*Formula*	*Substituents*		*Position of sulphonic group*	*Temperature of reaction (°C)*	*Time of reaction (h)*	*Extent of reaction (%)*	*Yield of reaction (%)*	*Melting point (°C)*
		X	*Y*						
N-1	**1**	H	—	2′	35–40	11·5	89·3	86·0	351–352
N-2	**1**	H	—	3′	35–40	4·0	96·3	78·1	271–272
N-3	**1**	H	—	4′	35–40	5·5	94·8	84·8	289–290
N-4	**1**	Cl	—	3′	45–50	5·0	93·5	82·5	260–262
N-5	**2**	—	H	2′	35–45	10·0	90·8	90·1	331–332·5
N-6	**2**	—	H	3′	35–40	3·5	97·5	75·3	175–177
N-7	**2**	—	H	4′	35–40	5·0	96·3	78·2	269–271·5
N-8	**2**	—	CH_3	3′	35–40	4·5	96·6	88·5	180–181·5
N-9	**2**	—	OCH_3	3′	35–40	3·5	98·2	88·9	193–195
Ac-10	**3**	—	—	3′	45–50	4·0	94·5	—	

TABLE 2

Elemental Analysis Data for the Sodium Salts of the Nitroarylsulphonanilidesulphonic Acids and Their Specific Absorption Bands in the Infrared Spectra

Nitro compound	Elemental analysis (%)								Specific IR absorption (cm^{-1})				
	C		H		N		Cl		NH—SO_2	C—NO_2	CH_3	SO_3^-	Aromatic C—H
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found					
N-1	39·59	39·64	2·81	3·00	7·10	7·18			3 240, 1 360, 1 170	1 540, 1 370, 890	2 960, 2 870	1 190, 1 030	760, 820, 880
N-2	39·59	39·55	2·81	2·95	7·10	7·07			3 240, 1 360, 1 170	1 540, 1 360, 890	2 960, 2 870	1 190, 1 040	690, 800, 820, 860, 880
N-3	39·59	39·48	2·81	2·90	7·10	7·21			3 250, 1 350, 1 170	1 540, 1 360, 890	2 960, 2 970	1 190, 1 050	830, 850, 880
N-4	36·41	36·40	2·35	2·42	6·53	6·69	8·27	8·42	3 220, 1 360, 1 170	1 540, 1 360, 890	2 960, 2 870	1 190, 1 050	690, 800, 860, 900
N-5	39·59	39·60	2·81	2·91	7·10	6·97			3 240, 1 360, 1 170	1 530, 1 370, 890	2 950, 2 870	1 190, 1 030	760, 820, 880
N-6	39·59	39·43	2·81	2·78	7·10	6·94			3 250, 1 350, 1 180	1 540, 1 360, 890	2 950, 2 870	1 200, 1 040	695, 810, 820, 860, 880
N-7	39·59	39·72	2·81	2·87	7·10	7·13			3 280, 1 360, 1 170	1 530, 1 370, 890	2 950, 2 870	1 190, 1 040	820, 850, 880
N-8	41·18	41·22	3·21	3·30	6·86	6·78			3 270, 1 350, 1 170	1 540, 1 370, 900	2 960, 2 870	1 200, 1 050	820, 880
N-9	39·62	39·72	3·09	3·18	6·60	6·68			3 270, 1 360, 1 170	1 540, 1 370, 900	2 950, 2 870	1 200, 1 040	820, 880

TABLE 3

Some Properties of Aminoarylsulphonanilidesulphonic Acids, Elemental Analysis Data and Specific Absorption Bands in the Infrared Spectra

Amine[a]	Yield of reaction (%)	Melting point (°C)	Elemental analysis (%)										Specific IR absorption (cm^{-1})			
			C		H		N		S		Cl		NH_3^+	$NHSO_2$	SO_3^-	Aromatic C—H
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found				
A-1	96·6	224–225	45·60	45·64	4·12	4·14	8·18	8·09	18·73	18·75			2 600–3 600 1 900–2 000	3 250 1 340, 1 170	1 190 1 030	760, 820 880
A-2	82·7	318·5–320	45·60	45·60	4·12	4·14	8·18	8·20	18·73	18·87			2 600–3 600 2 000–2 100	3 300 1 350, 1 170	1 190 1 040	630, 800, 820 860, 880
A-3	90·1	325–328	45·60	45·72	4·12	4·23	8·18	8·13	18·73	18·51			2 600–3 600 1 900–2 000	3 200 1 340, 1 170	1 190 1 040	830, 850, 880
A-4	92·0	244–245	41·44	41·50	3·48	3·48	7·43	7·23	17·02	16·81	9·41	9·19	2 600–3 600 1 900–2 000	3 250 1 340, 1 170	1 190 1 040	690, 860, 900
A-5	97·3	228–230	45·60	45·77	4·12	4·19	8·18	8·14	18·73	18·43			2 600–3 600 1 900–2 000	3 250 1 340, 1 170	1 180 1 020	760, 810, 880
A-6	80·1	254–256	45·60	45·76	4·12	4·29	8·18	8·02	18·73	18·79			2 600–3 600 1 900–2 000	3 250 1 360, 1 170	1 190 1 040	700, 810, 830 960, 880
A-7	88·0	328–330	45·60	45·36	4·12	4·01	8·18	8·28	18·73	18·62			2 600–3 600 1 900–2 000	3 200 1 340, 1 170	1 190 1 030	820, 850, 880
A-8	91·0	274–276	47·18	47·20	4·53	4·55	7·86	7·92	17·99	18·08			2 600–3 600 1 900–2 000	3 300 1 330, 1 160	1 190 1 030	820, 880
A-9	87·3	245–247	45·15	45·20	4·33	4·15	7·52	7·61	17·22	17·08			2 600–3 600 1 900–2 000	3 250 1 340, 1 170	1 190 1 030	820, 880
A-10	74·1	310–312	43·57	43·60	3·94	3·87	7·82	7·85	17·89	17·70			2 600–3 600 1 900–2 000	3 200 1 340, 1 160	1 190 1 040	695, 810, 820 860, 880

[a] Number of amine corresponds to number of nitro compound.

TABLE 4
pK_a of Nitroarylsulphonanilidesulphonic Acids and Their Solubilities in Water at 20 and 100°C

Nitro compound	pK_{a1} (—SO_3H)	pK_{a2} (SO_2–H)	*Solubilities in water (g dm^{-3})*	
			20°C	*100°C*
N-1	2·56	8·19	25	220
N-2	2·64	7·28	280	910
N-3	2·60	7·03	120	630
N-4	2·52	6·90		
N-5	2·48	8·13	25	350
N-6	2·54	7·13	375	1 025
N-7	2·51	6·85	210	780
N-8	3·23	7·38	100	520
N-9	3·30	7·57	115	750

used in these determinations were purified by crystallization from water and 50% ethanol. The results are listed in Table 4.

2.2 Preparation of 2-nitrotoluene-4-sulphonanilide-4′-sulphonic acid (N-3)

To 69·2 g (0·4 mol) of sulphanilic acid dissolved in 400 cm^3 of water and 40 cm^3 of 30% NaOH, 94·2 g (0·4 mol) of 2-nitrotoluene-4-sulphochloride was added at 35–40°C for 1 h with vigorous stirring. The pH was controlled within the range 6·5–7·2 with a saturated solution of sodium acetate or sodium hydroxide. After 4·5 h, tests for sulphanilic acid did not show any further decrease in the quantity present (three subsequent measurements were made at 15-min intervals). There remained 0·0208 mol of unreacted sulphanilic acid.

The mixture was heated over 30 min to 60°C and maintained at this temperature for a further 2 h. The mixture was then acidified with 30% hydrochloric acid to pH 5·0 and salted out with 50 g sodium chloride (about 10% by vol). After cooling to ambient temperature, a crystalline precipitate was filtered, washed with a 10% brine solution and dried at 70–75°C (155·2 g, 86·6% product content). The nitro compound content was determined by reduction with zinc powder and diazotization with a standard solution of sodium nitrite.

The other nitroarylsulphonanilidesulphonic acids were prepared by the same procedure.

2.3 Preparation of 2-toluidine-4-sulphonanilide-4′-sulphonic acid (A-3)

A mixture of 300 cm^3 of water, 5 cm^3 of 30% hydrochloric acid and 60 g iron powder was heated to 95°C and during 1 h 118·3 g (137·8 g of 86·6%

product ≡ 0·3 mol) of the sodium salt of 2-nitrotoluene-4-sulphonanilide-4′-sulphonic acid was added, maintaining a temperature of 95–98°C. After addition of the nitro compound, stirring was continued at the boiling point for a further 1·5 h. The mixture was cooled to 70°C and 10 cm^3 of 30% sodium hydroxide was added to obtain an alkaline reaction with Brilliant Yellow paper, and to precipitate the iron salt (tested with Na_2S); 0·5 g Na_2SO_3 was also added. The mass was then heated to boiling point and the iron oxides filtered off and washed with 50 cm^3 of hot water. The filtrate was cooled to ambient temperature and acidified with 20% sulphuric acid (40 cm^3) to obtain a strong acidic reaction with Congo Red paper. After filtering and drying, 95·7 g of product, having 96·6% product content, was obtained. The amine content in the product was determined by diazotization with a standard solution of sodium nitrite.

The other nitroarylsulphonanilidesulphonic acids were reduced in the same way.

2.4 Preparation of 2-anisidine-4-sulphonanilide-3′-sulphonic acid (A-10)

To 69·2 g (0·4 mol) of metanilic acid dissolved in 300 cm^3 of water and 40 cm^3 of 30% sodium hydroxide, 105·4 g (0·4 mol) of 2-methoxyacetanilide-5-sulphochloride was added with vigorous stirring at 45–50°C over 1 h, maintaining a pH of 6·5–7·2 by addition of saturated sodium acetate solution. After 3 h, the solution was clear and the test for metanilic acid did not show any further decrease in its amount. There remained 0·022 mol of unreacted metanilic acid. The mixture was heated over 30 min to 60°C and maintained at that temperature for a further 60 min; 300 cm^3 of 30% hydrochloric acid was then added at 60°C and the mixture heated to boiling for 1 h. After cooling to 60°C, 70 g of sodium chloride was added (about 10% by vol). After cooling to ambient temperature, the mixture was filtered and the product washed with 10% brine and dried at 70°C, giving 117·3 g of product (90·5% product content).

3 DISCUSSION OF RESULTS

It was found that the condensation of the nitrotoluenesulphochlorides with anilinesulphonic acids was best effected at temperatures between 35 and 50°C. Test condensations of nitrotoluenesulphochlorides with metanilic acid carried out at 12–15°C showed that the reaction required 15 h for completion. However, the extent of reaction of the metanilic acid was only 78·9%, over 20% of the sulphochloride being hydrolysed. However, at 35–40°C, the process was complete within 4 h and the extent of reaction was 96·3%. The same relations were found for the other sulphochlorides and anilinesulphonic acids. At temperatures above 50°C, a distinct increase in the hydrolysis rate of sulphochloride to sulphonic acid was observed. The necessity to carry out the condensation process at elevated temperatures is brought about by the decrease in the nucleophilicity of the amine group after introduction of the electron-accepting sulphonic group into the aniline molecule.

Another important parameter is the pH value of the reaction medium. At low pH, anilinesulphonic acids are precipitated in the form of internal salts which hardly react with sulphochloride. At pH above 8, however, as was shown by the pK_{a2} measurements for nitroanilinesulphonanilidesulphonic acids, reaction with the second molecule of sulphochloride is possible to form *N,N*-diaryldisulphonanilide. The preferable pH range for the process is 6·5–7·2.

It is concluded from the results of the condensations of nitrotoluenesulphochlorides with orthanilic, metanilic and sulphanilic acids that the highest extent of reaction is obtained with metanilic acid (above 96%), a similar one with sulphanilic acid and the lowest with orthanilic acid (about 90%). On the other hand, the yield of product separation from the reaction medium is highest for orthanilic acid and lowest for metanilic acid, due to its high water solubility, despite higher salting out (15% of salt by vol).

As was shown by the water solubility determinations for nitroarylsulphonanilidesulphonic acids, the position of the sulphonic acid group has a marked influence. Derivatives of metanilic acid show considerably higher solubility than those of orthanilic acid derivatives. There are also great differences in solubilities at 20 and 100°C. The solubility of orthanilic acid derivatives at 100°C is 10 times higher than that at 20°C, and the corresponding increase for metanilic acid derivatives is about 300%. The results of the solubility measurements may be utilized in selecting coupling components for the synthesis of dyes, where solubility is of importance in the application process or in the fastness of the dyeings.

The position of the sulphonic group shows a clear effect on the pK_{a2} of the sulphonamide group. The highest pK_{a2} values are observed in orthanilic acid derivatives and the lowest in sulphanilic acid derivatives, differences being greater than 1. Since both the groups are in positions conjugated to the amine group, this would explain their similar effect on the electronic state of the nitrogen atom. The large differences in pK_{a2} values also indicate that in the orthanilic acid derivatives intermolecular hydrogen bonding occurs between the amide hydrogen and the sulphonic group in the *ortho* position, with consequent effect on the pK_{a2} value of this group.

The reduction of nitroarylsulphonanilidesulphonic acid by the method proceeds very readily. The separation of the aminoarylsulphonanilidesulphonic acids from the post-reduction solution by acidification and salting out is almost quantitative, a factor of importance from both the technological and ecological points of view. Thus, the sodium salts of the nitroarylsulphonanilidesulphonic acids, after completion of the condensation, may be used without separation for the reduction process, giving the aminoarylsulphonanilidesulphonic acids of similar purity and in considerably increased yield. The internal salts of aminoarylsulphonanilidesulphonic acids are separated more readily than those of anilinesulphonic acids.

As previously noted, the structures of the nitro- and amino-arylsulphonanilidesulphonic acids were confirmed by elemental analysis and IR spectroscopy.[8] The spectra confirmed the presence of all the functional groups and positions of their substitution. Appropriate IR spectral data are given in Tables 2 and 3.

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