

2-(2-Amino-5-X-phenyl)benzotriazoles

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*Dedicated to Professor RNDr. Jaromír Hadáček,
in honour of his 70th birthday*

2-(2-Amino-5-X-phenyl)benzotriazoles were prepared by cyclization reduction of the corresponding 2-amino-5-X-2'-nitroazo compounds and their electronic spectra were investigated. In the preparation of the azo compounds, protection of the amino group in *p*-substituted anilines was examined by converting them to aminomethanesulfonates, prior the copulation with *o*-nitrobenzenediazonium chloride. It was observed that besides the quoted azo compounds, new, so far not described derivatives, alkaline 1-(2-nitrophenyl)-3-(4-X-phenyl)triazene-3-methanesulfonates, were formed.

Были синтезированы замещенные 2-(2-амино-5-X-фенил)бензотриазолы восстановительным замыканием круга соответствующих 2-амино-5-X-2'-нитроазосоединений и исследованы их электронные спектры. Была испытана защита аминной группы в *p*-замещенных анилинах переводом их в аминометансульфонаты перед азосочетанием с *o*-нитробензолдиазонийхлоридом. Оказалось, что помимо указанных азосоединений образуются новые, до сих пор неописанные вещества, щелочные 1-(2-нитрофенил)-3-(4-X-фенил)триазен-3-метансульфонаты.

2-(2-Hydroxy-5-X-phenyl)benzotriazoles exhibiting suitable absorption in the ultraviolet spectral region were earlier synthesized in our laboratory [1]. Because of this property they are potential light stabilizers of plastics. In the present paper we compare the properties of the above 2-hydroxy derivatives and 2-amino derivatives. Due to a possibility of hydrogen bridge formation between a hydrogen of the amino group and nitrogen of the triazole ring, the compounds could also have desired absorption properties.

The cyclization reduction of 2-nitroazobenzenes represents a convenient route to preparation of 2-phenylbenzotriazoles in high yields [2—4]. For this purpose we directed our attention to synthesis of 5-substituted 2-amino-2'-nitroazobenzenes by copulation reaction of *o*-nitrobenzenediazonium chloride with *p*-substituted

anilines. It is known that the copulation leads to the formation of C or N copulation products or mixtures of both, depending on structure and pH of the reaction medium. While in neutral and slightly acidic medium triazenes are formed preferentially, proportion of azo compounds increases with rising acidity. In strongly acidic medium, however, the concentration of the nonprotonized amine remains so low that the copulation almost does not take place. Tendency of anilines having a free amino group to form the C copulation products, *i.e.* azo dyes, increases with higher basicity of the aromatic system due to a suitable electron-donating substituent. While unsubstituted aniline gives almost exclusively triazene, 3-methyl-, 3-methoxy, and 3-hydroxyanilines with occupied *p*-position afford almost exclusively 2-aminoazobenzenes [5]. Similarly, 1,3-phenylenediamines give C copulation products [6]. 1,4-Phenylenediamines, however, almost do not react [7].

Experimental

Elemental analyses were done with an automatic elemental analyzer CHN C. Erba, Milan, Model 1102. Melting points were determined on a Kofler stage. pH was measured with a Radelkis OP 205 pH-meter. Electronic spectra were recorded with a UNICAM SP 1800 spectrophotometer in ethanolic solutions. ¹H-N.m.r. spectra were measured on a Tesla 487 C spectrometer in DMSO. Homogeneity of compounds and course of reactions were followed by thin-layer chromatography on Silufol UV 254 plates (Kavalier, Votice). Colourless compounds were visualized using a Fluotest Universal Quarzlampe apparatus (Hanau). Dyes were chromatographed in solvent system ethyl acetate: methanol (3.5: 1).

All synthesized compounds and their characteristics are summarized in Table 1.

Sodium 4-X-anilinmethanesulfonates (I—XII)

A mixture of *p*-X-aniline (0.5 mol), formaldehyde bisulfite (0.5 mol) [11], and 50% ethanol (100 ml) was stirred for 5 h at room temperature. Separated amorphous material was collected by filtration, washed with ether and recrystallized from water to give white glossy crystals.

Sodium 2'-nitro-5-X-azobenzene-2-aminomethanesulfonates (XIII—XVIII)

To a solution of sodium 4-X-anilinmethanesulfonate (0.05 mol) and sodium acetate (25 g) in water (200 ml), *o*-nitrobenzenediazonium chloride (0.05 mol) was added dropwise under cooling (0—5°C) and then stirred for 5 h at room temperature. The formed dye was salted out with sodium chloride, sucked off, washed with ether and recrystallized from dimethylformamide to give red crystals.

Table 1

Characteristics of the synthesized compounds

Substance	M	Calculated/found			M.p., °C
		% C	% H	% N	
III	306.12	27.47	2.96	4.58	
		27.24	2.98	4.36	
V	296.26	40.15	4.49	5.20	
		40.15	4.58	5.26	
VII	293.22	32.77	4.00	4.78	
		32.32	4.17	4.65	
VIII	285.20	37.90	4.24	4.91	
		38.24	4.31	4.86	
IX	376.24	25.52	3.72	7.45	
		26.31	3.86	7.34	
XI	298.32	44.29	6.42	9.39	
		44.64	6.32	9.24	
XII	300.25	36.00	4.36	9.33	
		36.19	4.48	9.52	
XIII	390.34	43.08	3.87	14.35	
		41.98	3.78	14.63	
XIV	410.76	38.01	2.95	13.64	
		39.23	3.04	13.72	
XVI	418.36	43.07	3.61	13.39	
		43.16	3.65	13.86	
XVII	478.25	32.62	2.53	11.72	
		32.83	2.58	11.85	
XVIII	442.32	38.02	2.74	12.67	
		37.94	2.68	12.76	
XXI	390.34	43.08	3.87	14.35	204
		42.87	3.74	14.65	
XXII	410.76	38.01	2.95	13.64	208
		38.34	2.78	13.72	
XXIII	224.27	69.62	5.39	24.98	128—129
		69.55	5.48	25.12	
XXIV	244.69	59.06	3.71	22.96	152—153
		58.92	3.69	22.56	
XXV	240.27	64.99	5.03	23.32	121—123
		64.85	4.95	23.35	
XXVI	290.30	49.65	3.47	19.30	89—91
		48.86	3.38	19.28	
XXVII	226.39	63.71	4.46	24.77	284
		63.56	4.57	25.08	

1-(2-Nitrophenyl)-3-(4-X-phenyl)triazenes (XIX and XX)

A copulation mixture leading to preparation of substance *XIII* or *XIV* was diluted with water (500 ml) and left to stand at room temperature for 24 h. The formed precipitate was sucked off, washed with water and recrystallized from ethanol to give orange crystalline product.

Sodium 1-(2-nitrophenyl)-3-(4-X-phenyl)triazene-3-methanesulfonates (XXI and XXII)

The substances were isolated from the reaction mixtures leading to substances *XIII* and *XIV*, respectively, by column chromatography.

¹H-N.m.r.: *XXI* 7.10—7.90 (m, 8 H, CH_{arom})
5.20 (s, 2 H, CH₂)
2.25 (s, 3 H, CH₃)

Structure of substances XXI and XXII

Substance *XXI* or *XXII* (0.5 g) was gradually dissolved under cooling in concentrated hydrochloric acid (20 ml). After 5 min a solution of 2-naphthol (0.4 g) and sodium hydroxide (0.5 g) in water (100 ml) was added dropwise under cooling with 50 g of crushed ice. After mild acidification with hydrochloric acid a precipitate was formed which was sucked off, washed with water and recrystallized from acetic acid. In both cases the same product was obtained, red crystals of 1-(2-nitrophenylazo)-2-naphthol, m.p. 208°C.

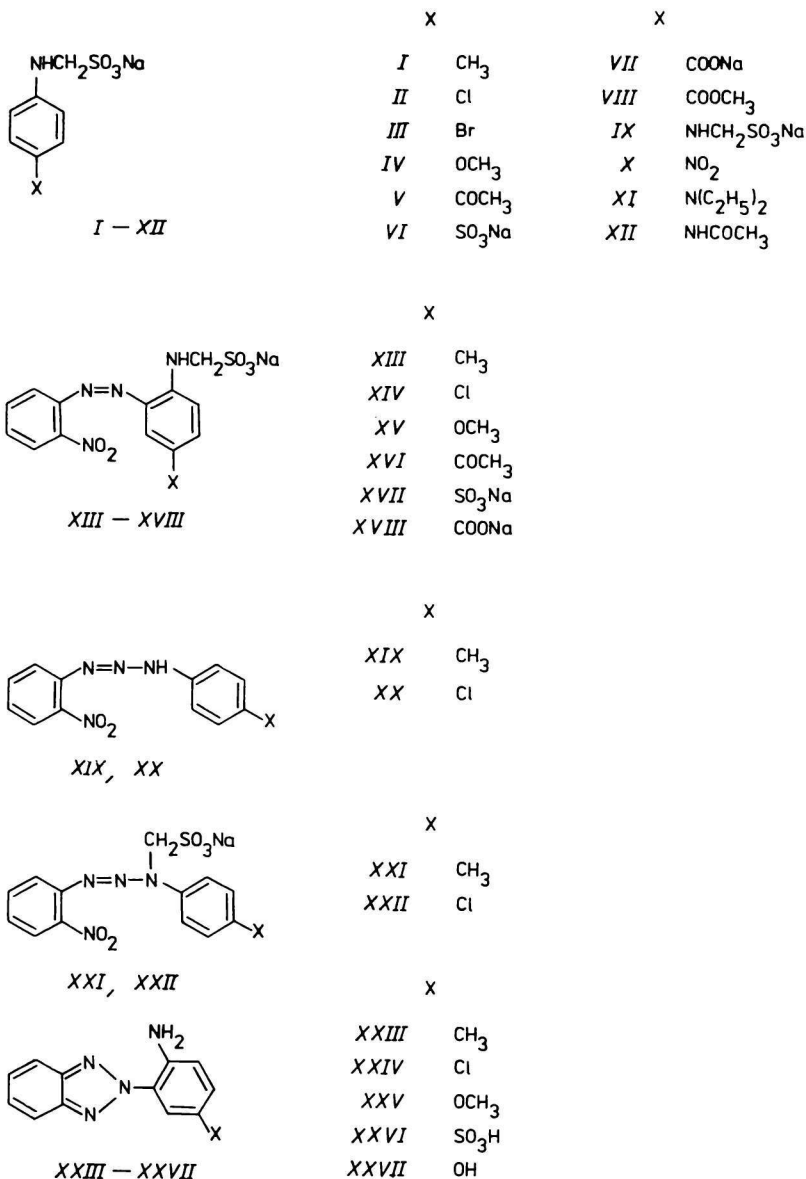
2-(2-Amino-5-X-phenyl)benzotriazoles (XXIII—XXVII)

Azo compound *XIII* or *XIV—XVIII* (0.02 mol) was suspended in 5% solution of sodium hydroxide (18 g; 0.45 mol). In the course of 30 min sodium dithionite (17.4 g; 0.1 mol) was added in portions slowly at room temperature. The mixture was stirred for 30 min, then heated to boiling and refluxed for 2 h. The solution was filtered under heating, cooled and saturated with carbon dioxide. The formed crystals were sucked off, washed with water and recrystallized from acetic acid.

Results and discussion

Preparation of 5-substituted 2-amino-2'-nitroazobenzenes by copulation reaction of *o*-nitrobenzenediazonium chloride with *p*-substituted anilines meets with the requirement of the protection of the amino group against the electrophilic attack and, simultaneously, an increment of the electron density on the aromatic ring. Such a protection is achieved by *N*-alkylation or acylation, or by conversion to *N*-sulfonates and *N*-methanesulfonates. While *N*-acylanilines show relatively low reactivity [8], *N*-alkylanilines copulate very well, almost without a possibility to

convert the resulting azo compound to primary amine. For these reasons the use of *N*-sulfonates or *N*-methanesulfonates is advantageous in several aspects, such as their easy preparation, excellent solubility in water and simple conversion to free amine upon acid or alkaline hydrolysis [9].



Scheme 1

p-Substituted sodium anilinethanesulfonates afford the corresponding 2-aminoazo compounds in good yields in mild acidic or neutral medium particularly when they have electron-donating substituents in the position 3 [10]. A series of 4,5-disubstituted 2-amino-2'-nitroazobenzenes was prepared in this way.

To obtain the required 2-amino-2'-nitroazo compounds, copulation reaction of *o*-nitrobenzenediazonium chloride with suitable anilinethanesulfonates was selected. Twelve derivatives of 4-substituted anilinethanesulfonates *I*–*XII* were synthesized (Scheme 1) by reaction of 4-substituted anilines with a formaldehyde bisulfite compound. The derivatives *III*, *V*, *VII*, *VIII*, *XI*, and *XII* have not been described yet. Their purity was proved chromatographically and structure by ¹H-n.m.r. spectroscopy (Table 2). The substances are thermolabile without distinct melting points and form hydrates with one molecule of water.

The anilinethanesulfonates were further used in the copulation reaction. Chromatographic analysis of the copulation products showed that, contrary to literature data, they do not represent a single compound, but a mixture of three components, two of which have close *R_f* values.

Besides the anticipated azo compounds *XIII*–*XVIII* we have succeeded in the identification of triazenes, of which substances *XIX* and *XX* were isolated.

The formation of a small amount of triazene can be ascribed to the fact that a part of aminomethanesulfonate may undergo hydrolysis in strongly acidic solution of diazonium salt even at a relatively low reaction temperature (0–5°C). The nonpolar character of triazenes allows their easy isolation.

Table 2
¹H-N.m.r. spectral characteristics

Substance	δ, p.p.m.				Other
	CH ₂ ^a	NH ^b	CH ₂ ^a	CH ₂ ^a	
<i>I</i>	3.88	5.68	6.55	6.78	CH ₃ 2.09
<i>II</i>	3.90	6.26	6.69	7.00	
<i>III</i>	4.14	5.90	6.92	7.41	
<i>IV</i>	3.89	5.50	6.68	6.68	CH ₃ 3.61
<i>V</i>	4.20	7.30	6.98	7.93	CH ₃ 2.64
<i>VI</i>	3.91	6.21	6.60	7.30	
<i>VII</i>	4.19	6.99	6.98	7.90	
<i>VIII</i>	4.56	7.26	6.71	7.70	CH ₃ 3.73
<i>IX</i>	4.61	6.97	6.65 ^c		
<i>X</i>	4.05	5.98	6.98	8.11	
<i>XII</i>	4.09	6.00	6.80	7.41	CH ₃ 2.13 NH ^c 9.76

a) Doublet; b) triplet; c) singlet.

Substances *XXI* and *XXII* were isolated as further components of the reaction mixtures and identified as triazene-3-methanesulfonates. Their structure was established by $^1\text{H-n.m.r.}$ spectroscopy (the triplet of the NH group proton was absent in the spectra and the signal of the methylene group was not split) and confirmed by a chemical evidence based on decomposition of the triazenes in acidic medium containing sodium 2-naphtholate. This treatment resulted in the isolation of the anticipated compound, 1-(2-nitrophenylazo)-2-naphthol in the case of both substances *XXI* and *XXII*.

The fact that the copulation of anilinmethanesulfonates is accompanied by formation of about 40% of 1-(2-nitrophenyl)-3-(4-X-phenyl)triazene-3-methanesulfonates, so far not reported, pointed out that, contrary to published data [9], the group $-\text{CH}_2\text{SO}_3\text{Na}$ is unable to protect sufficiently the amino group against the electrophilic attack on the nitrogen atom by *o*-nitrobenzenediazonium ion, a strong electrophile.

The formation of triazene-3-methanesulfonate derivatives which are difficult to separate, is an undesired fact complicating the subsequent preparative step, the cyclization reduction of azo dyes. Further attention was therefore devoted to the effect of medium pH on the yield of azo compound and, eventually, on reduction or prevention of triazene formation in the reaction of *o*-nitrobenzenediazonium chloride with substance *I*. In accordance with literature data it was observed that the copulation proceeds at the best in neutral or slightly acidic medium. However, in this pH region the formation of triazene also increases. In acidic medium (pH 3—5) both processes are strongly inhibited, but the relative proportion of azo dye increases. In spite of that, the percentage of triazene remains still higher than that of azo compound. From this one may infer that pH does not have the decisive effect on the direction of electrophilic attack, but this is determined first of all by electron relations on the ring influenced by the structure of the substrate.

Regarding the above given facts, all further azo dyes were prepared in slightly acidic medium. The yields varied in the range 10—15%. Anilinmethanesulfonate *X* did not react with the diazonium salt and substances *III*, *IX*, *XI*, and *XII* afforded resinous products. The azo dyes having the aminomethanesulfonate group crystallize again with one molecule of water and are thermolabile without distinct melting points.

For these reasons the azo dyes were not isolated before subsequent synthesis and were reduced with sodium dithionite directly in the crude reaction mixture after alkalization. The side products (triazenes) are namely split under these conditions and do not interfere with the isolation. 2-(2-Amino-5-X-phenyl)benzotriazoles *XXIII*—*XXVII* were prepared in this way.

Further triazoles which were prepared were identified on the basis of their electronic spectra in ethereal extracts because of low content of azo dyes *XVI* and

Table 3

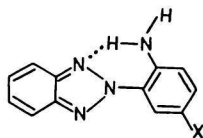
Electronic spectra of 2-(2-amino-5-X-phenyl)-benzotriazoles

Substance	Band					
	A		B		C	
	λ/nm	$\epsilon \cdot 10^{-4}$	λ/nm	$\epsilon \cdot 10^{-4}$	λ/nm	$\epsilon \cdot 10^{-4}$
XXIII	231	1.92	296	1.20	364	0.823
XXIV	230	1.76	297	0.941	358	0.742
XXV	228	2.02	300	1.17	378	0.725
XXVI	331	2.05	296	1.23	346	0.753
XXVII	232	2.44	300	1.28	375	0.712

 ϵ in $\text{l mol}^{-1} \text{cm}^{-1}$.

XVIII in the crude copulation mixtures. The corresponding triazoles were not isolated in solid state.

Ultraviolet spectra of the synthesized triazoles pointed out that the substitution of the phenyl chromophore at the position 5 only slightly affects the position of the bands A and B (Table 3). The position of the band C, however, is influenced by electron relations more expressively. Greater electron-accepting effects of the substituents at the position 5 enhance acidity of hydrogens of the amino group. This leads to a strengthening of the hydrogen bond with the nitrogen atom of the



triazole ring and therefore to a decrease of the energy of the free n -orbital of the nitrogen atom. This situation is reflected in the spectra in a hypsochromic shift of the band C, because the energy of the $n \rightarrow \pi^*$ transition is thus enhanced. In comparison with the spectra of the corresponding hydroxy derivatives [1] the position of the bands A and B is essentially the same with both series of compounds. 2-Amino derivatives, however, exhibit a bathochromic shift of the longest wave band C by about 20 nm. In regard of the character of spectra, 2-aminobenzotriazoles therefore represent suitable stabilizers, but the complicated way of their preparation does not make their practical applications possible.

References

1. Běluša, J., Janoušek, Z., and Knofličková, H., *Chem. Zvesti* 28, 673 (1974).
2. Běluša, J., Borkovec, J., and Brokl, M., *Czech.* 119333; *Chem. Abstr.* 67, 64405 (1967).
3. Běluša, J. and Potáček, M., *Tetrahedron Lett.* 10, 1167 (1968).
4. Běluša, J. and Janoušek, Z., *Czech.* 128667; *Chem. Abstr.* 70, 115164 (1970).
5. Mehner, H., *J. Prakt. Chem.* 65, 401, 421 (1902).
6. Hoffmann, A. W., *Ber.* 10, 213, 388 (1877).
7. Venkataraman, K., *The Chemistry of Synthetic Dyes*, p. 1417. Academic Press, New York, 1952.
8. König, W., *Ber.* 54, 981 (1921).
9. Gaetani, E., Moiso, W., and Papa, S., *Chim. Ind.* 44, 127 (1962); *Chem. Abstr.* 57, 12357 (1962).
10. Mohr, R. and Hertel, H., *Ger.* 1088060; *Chem. Abstr.* 56, 1446 (1962).
11. Tishchenko, D. and Kylitsin, A., *Zh. Prikl. Khim.* 34, 1612 (1961).

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