2-(2-Hydroxyphenyl)benzotriazoles. II. Electrophilic substitution reactions on the molecule of 2-(2-hydroxy--5-methylphenyl)benzotriazole and ultraviolet spectra of the products

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2-(2-Hydroxy-3-Y-5-methylphenyl)benzotriazoles were prepared by electrophilic substitution reactions. Constitutions of the prepared compounds were proved by synthesis and n.m.r. and mass spectrometry. The effect of substituents on the absorption in the near u.v. region was followed regarding the use of these compounds as photostabilizers.

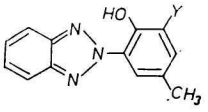
The aromatic nature of 2-(2-hydroxy-5-methylphenyl)benzotriazole and its relatively easy synthesis with a good yield [1, 2] predetermine this compound as substrate for electrophilic substitution enabling to prepare further derivatives of 2-(2-hydroxyphenyl)benzotriazole and continue studying these compounds, above all the effect of substitution on absorption in the near u.v. region. In the patent literature, preparation of 2-(2-hydroxy-3-nitro-5-methylphenyl)benzotriazole by nitration with a nitration mixture [3], preparation of 2-(2-hydroxy-3-allyl-5-methylphenyl)benzotriazole by reaction with propargyl bromide [4], and the reaction of *N*-hydroxymethyl carboxamide with 2-(2-hydroxy-5-methylphenyl)benzotriazole leading to the formation of a derivative containing *N*-acylamidomethyl group on phenyl in the position 3 [5] are described. However, there is no mention of any proof of the constitution of the prepared isomers.

We accomplished some further typical electrophilic substitution reactions on the molecule of 2-(2-hydroxy-5-methylphenyl)benzotriazole and proved the position of the entering substituent. 2-(2-Hydroxy-3-Y-5-methylphenyl)benzotriazoles (characterization in Table 1) were prepared. Their general formula is as shown in Scheme 1.

The positions of the substituents in *III* and *X* were proved by total synthesis. Copulation of *o*-nitrobenzenediazonium ion with 2-bromo-4-methylphenol or 2-acetamido-4--methylphenol and subsequent cyclization reduction gave compounds *III* and *X*.

Compound *X* was also obtained by reduction of *II*. This proved the position of NO_2 group in *II*. The positions of substituents in *VI*—*IX* were proved by reducing the splitting of the azo group. Compound *X* was isolated in a corresponding yield. The position of the substituent in *IV* was not proved regarding the analogous electrophilic substitution reaction. It can be supposed that *IV* was a derivative formed on substituting *I* on phenyl in the position 3.

The constitution of *V* was determined by n.m.r. and mass spectrometry. Its n.m.r. spectrum indicated the presence of methyl protons with δ 2.75, methylene protons with δ 4.5, and aromatic protons in the ratio of 6 : 2 : 12. The main course of fragmentation



Y = H	*I*
NO_2	*II*
Br	*III*
SO_3H	*IV*
$-CH_2-$	*V*
$C_6H_5-N=N$	*VI*
$2\text{-}NO_2C_6H_4-N=N$	*VII*
$4\text{-}NO_2C_6H_4-N=N$	*VIII*
$2,4\text{-}(NO_2)_2C_6H_3-N=N$	*IX*
NH_2	*X*

Scheme 1

of the molecular ions (Fig. 1) in the mass spectrometer was the splitting off of hydrogen atom from methylene group under formation of highly conjugated $(M\text{-}1)^+$ ions with *m/e* 461. The ions with *m/e* 443 and 444 represented the dehydrating products of M^+ and $(M\text{-}1)^+$ ions. The other splitting proceeded in the neighbourhood of the methylene group giving ions with *m/e* 225 and 237. Formation of the discussed ions was proved by the presence of metastable peaks in the mass spectrum ($m^* = 427.0$, $462 \rightarrow 444$; $m^* = 425.5$, $461 \rightarrow 443$; $m^* = 121.6$, $462 \rightarrow 237$; $m^* = 109.6$, $462 \rightarrow 225$).

Because the diazonium ions with different electrophilic power were used to prepare *VI*—*IX* and the reactions proceeded slowly with low yields, the reaction mixtures were

Table 1

Compound	Formula	*M*	Calculated/found					Yield	M.p. [°C]
			% C	% H	% N	% Hal	% S	[%]	(Solvent)
II	$C_{13}H_{10}N_4O_3$	270.23	57.78	3.73	20.73	—	—	83	188—189
			57.35	3.93	20.41	—	—		(Xylene)
III	$C_{13}H_{10}N_3OBr$	304.13	51.33	3.31	13.82	26.28	—	91	205
			51.26	3.24	13.62	25.56	—		(Benzene)
IV	$C_{13}H_{11}N_3O_4S \cdot H_2O$	323.24	48.29	4.05	12.99	—	9.92	72	251—252
			47.96	3.90	13.01	—	9.55		(Acetic acid)
V	$C_{27}H_{22}N_6O_2$	462.49	70.11	4.79	18.17	—	—	90	295
			69.87	5.10	18.04	—	—		(Dimethyl-formamide)
VI	$C_{19}H_{15}N_5O$	329.35	69.58	4.62	21.25	—	—	15.4	196
			69.36	4.67	21.17	—	—		(*n*-Heptane)
VII	$C_{19}H_{14}N_6O_3$	374.35	60.96	3.77	22.45	—	—	13.8	276
			61.80	3.91	22.04	—	—		(Ethanol)
VIII	$C_{19}H_{14}N_6O_3$	374.35	60.96	3.77	22.45	—	—	17.75	276
			60.33	3.73	22.11	—	—		(*n*-Heptane)
IX	$C_{19}H_{13}N_7O_5$	419.34	54.42	3.12	23.38	—	—	4.45	273
			54.38	3.28	23.14	—	—		(*n*-Heptane)
X	$C_{13}H_{12}N_4O$	240.25	64.99	5.03	23.32	—	—	50	228
			64.13	4.92	23.15	—	—		(Toluene)

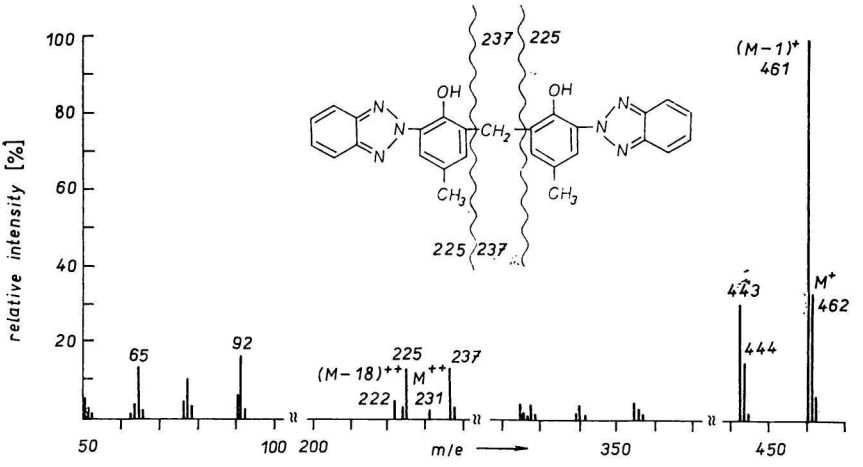


Fig. 1. Mass spectrum of compound *V*.

separated on a preparative loose layer of silica gel and the yields were determined by using u.v. spectrophotometry. For quantitative estimation, pure compounds *VI*—*IX* were used as standards. In addition to the discussed compounds, further two coloured spots with lower R_F values appeared on the chromatogram. These compounds were not identified. Contrary to expectation, the yield of *IX* was low probably because of the bulkiness of the electrophile.

Table 2

Absorption of compounds *I*—*X* in the u.v. region and in the region of OH stretching vibration

Compound	A		B		C		D		E		$\tilde{\nu}$(O—H) [cm^{-1}]
	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε	λ_{max} [nm]	log ε	
I	214	4.41	243	4.03	296	4.17	344	4.23	—	—	3210
II	—	—	238	4.17	306	4.20	338	4.16	—	—	—
III	234	3.86	256	4.77	306	4.12	334	4.12	—	—	—
IV	—	—	241	4.02	300	4.11	332	4.23	—	—	—
V	232	4.30	246	4.09	302	4.40	345	4.43	—	—	3120
VI	—	—	234	4.37	306	4.49	327	4.49	382	4.18	3090
VII	—	—	236	4.29	300	4.35	310	4.35	396	4.08	—
VIII	—	—	233	4.26	300	4.42	326	4.42	402	4.09	—
IX	—	—	236	4.38	302	4.45	324	4.45	414	4.15	—
X	—	—	256	4.12	—	—	326	4.18	—	—	3140, 3240

The stretching vibrations of the associated O—H bond with compounds *II*, *III*, and *IV* were overlapped by those of the aromatic C—H bonds; therefore they were not read.

Low yields of copulation reactions and the fact that sulfonation proceeded only when oleum (5%) was used indicated a decrease in reactivity of the used aromatic system. When *p*-cresol was a reactive substrate for aromatic electrophilic substitution, then 2-benzotriazolyl group acted as a deactivating substituent in accordance with its σ_p 0.566 and σ_m 0.517 [7].

The electronic spectra of *I*—*X* are characterized by the data in Table 2. Substitution on phenyl in the position 3 by NO_2 (*II*), SO_3H (*IV*), and Br (*III*) resulted in a hypsochromic shift of the band M with a highest wavenumber. The intensity of this band with *II* and *III* was lower than that with *I* because of substitution. The SO_3H group in *IV* increased the intensity of the band M probably because the possible interaction of hydrogen of the SO_3H group with oxygen of the OH group increased the acidity of the phenolic hydrogen. Consequently, the energy of the intramolecular hydrogen bond increased and in accordance with the *Heller*'s hypothesis [9], also the concentration of the planar conformation (the energy contribution of intramolecular hydrogen bond is indispensable for its existence) increased.

The position of the band C was influenced only insignificantly by substitution on phenyl in the position 3. However, its intensity reflected the concentration of the nonplanar conformer and changed with the effect of substituents on the energy of the intramolecular hydrogen bond.

Compound *X* absorbed in the u.v. region at 326 nm only. Its i.r. spectrum above 3000 cm^{-1} contained the stretching vibrations of C—H bonds, symmetrical and asymmetrical stretching vibrations of N—H bonds (3360 and 3340 cm^{-1}), and two further absorption bands at 3140 and 3240 cm^{-1} which could be attributed to two unequal intramolecular hydrogen bonds probably with nitrogen of the triazole ring and with nitrogen of the amino group. Thus the wide band at about 326 nm could be taken for the band originally appearing at about 300 nm (compound *I*) bathochromically shifted by conjugation of *n*-electrons of NH_2 group with phenyl overlapped by the absorption band of the highest wavenumber. Compounds *VI*—*IX* acted similarly; the wide band at 300—330 nm showed a tendency to split into two bands C and M separated only by an insignificant minimum. Consequently, it is possible to take the behaviour of the azo group as electron-donor for similar to that of the amino group.

Experimental

The prepared compounds, their melting points (Kofler), and elemental analyses (accomplished in the analytical laboratory at the Research Institute of Pure Chemicals, Lachema) are given in Table 1.

Electronic spectra (Table 2) were recorded with a UNICAM SP 700 and a Zeiss Jena VSU 1 instruments (concentration 3×10^{-5} M in tetrahydrofuran).

Infrared spectra were taken on a Zeiss Jena UR-10 apparatus in KBr pellets (concentration 1%).

Chromatography was carried out on a loose layer of silica gel L 40/100 (Lachema).

Mass spectrum was recorded with an MCh 1306 (USSR) instrument as published earlier [6].

N.m.r. spectrum was measured on a BS 487-A (Tesla, Brno) spectrometer at the working frequency 80 MHz and 27°C (concentration 5% in deuterated concentrated sulfuric acid). HMDS was used as external standard.

2-(2-Hydroxy-5-methylphenyl)benzotriazole (*I*) was prepared according to [1].

2-(2-Hydroxy-3-nitro-5-methylphenyl)benzotriazole (II)

To a mixture of concentrated nitric acid (1 ml) and concentrated sulfuric acid (1.25 ml), a solution of *I* (2.25 g; 0.01 mole) in glacial acetic acid (100 ml) was added dropwise at laboratory temperature under stirring. The reaction mixture was heated in a water bath for 30 minutes. Pouring of the mixture into water resulted in a yellow precipitate.

2-(2-Hydroxy-3-bromo-5-methylphenyl)benzotriazole (III)

a) To a solution of *I* (2.25 g; 0.01 mole) in glacial acetic acid (100 ml), a solution of bromine (1.59 g; 0.01 mole) in glacial acetic acid (5 ml) was added dropwise at laboratory temperature under stirring. The reaction mixture was heated in a water bath for 1 hour. White needles precipitated after pouring the mixture into a multiple amount of cold water.

b) To a solution of 2-bromo-4-methylphenol (3.7 g; 0.02 mole), sodium hydroxide (1 g), and anhydrous sodium carbonate (10 g) in water (100 ml), a solution of diazonium salt prepared from *o*-nitroaniline (2.76 g; 0.02 mole) [8] was added dropwise at 10—15°C under stirring. After 1-hour staying, the red precipitate of 2-nitro-2′-hydroxy-3-bromo-5′-methylazobenzene was sucked off and washed with water to neutral reaction. To the azo compound (5 g) in 5% sodium hydroxide (300 ml), crystalline sodium dithionite (20 g) was added during 30 minutes at laboratory temperature under stirring and then the mixture was boiled for about 1 hour. From the yellow solution a white substance was precipitated by carbon dioxide.

2-(2-Hydroxy-3-sulfo-5-methylphenyl)benzotriazole (IV)

A solution of *I* (2.25 g; 0.01 mole) in 5% oleum (4 ml) was heated for 30 minutes at 70°C under stirring. After pouring the solution onto ice, a pearly-white compound was formed.

2,2′-Dihydroxy-3,3′-di-(2-benzotriazolyl)-5,5′-dimethylphenylmethane (V)

To a solution of *I* (4.5 g; 0.02 mole) in concentrated sulfuric acid (9 ml), 40% solution of formaldehyde (0.01 mole) was added dropwise under continual stirring so that the temperature did not rise above 25°C. The reaction mixture was stirred for 2 hours at laboratory temperature giving a white precipitate. The suspension was poured into ethanol (20 ml), sucked off, and washed with ethanol.

2-[2-Hydroxy-3-(X-phenylazo)-5-methylphenyl]benzotriazole (VI—IX)

To a solution of *I* (2.25 g; 0.01 mole) in 0.5% solution of sodium hydroxide (200 ml), benzenediazonium chloride prepared from aniline and its nitro derivatives (0.01 mole), respectively [8], was added dropwise at laboratory temperature under stirring. The reaction mixture was maintained at pH 9—10. After about 2 hours, pH of the mixture was adjusted to 7. The orange-red product was separated on a loose layer of silica gel. The R_F values of compounds were the following: *VI* 0.41 (benzene—heptane 1 : 1), *VII* 0.63 (chloroform), *VIII* 0.67 (benzene—chloroform 3 : 2), and *IX* 0.58 (benzene—chloroform 1 : 1).

2-(2-Hydroxy-3-amino-5-methylphenyl)benzotriazole (X)

a) It was prepared similarly as *III* by the method b. 2-Acetamido-4-methylphenol was used for copulation. Saponification of acetamido group was achieved under the conditions of cyclization reduction (pH 12).

b) To a solution of *II* (2.7 g; 0.01 mole) in 5% sodium hydroxide (150 ml), crystalline sodium dithionite (7 g) was added. The mixture was boiled for about 30 minutes. From the solution a yellow substance was precipitated by carbon dioxide.

c) A solution of *VI* (3.3 g; 0.01 mole) in 5% sodium hydroxide (150 ml) was heated to about 80—90°C and crystalline sodium dithionite (7 g) was added gradually under stirring. Then the solution was boiled for 30 minutes. From the cooled solution, compound *X* was precipitated by carbon dioxide. The presence of aniline in the crude reaction mixture was proved chromatographically (chloroform as eluent).

A similar splitting was accomplished with *VIII*.

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