

2-(2-Hydroxyphenyl)benzotriazoles. I. Synthesis and their ultraviolet and infrared spectra

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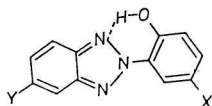
2-(2-Hydroxy-5-X-phenyl)-5-Y-benzotriazoles were prepared by reduction of the corresponding *o*-nitroazo compounds. The shifts of wavenumbers of the stretching vibrations of O—H group forming intramolecular hydrogen bond with nitrogen of the triazole ring were linearly dependent on the Hammett σ_p constants of the substituents X ($\rho = -61$) and Y ($\rho = +45$). The shifts of wavenumbers of the absorption band in the region of 30 200—25 600 cm^{-1} with the σ_R constants of the groups X ($\rho = +5.1$) fulfilled this correlation, too. Also the logarithm of molar absorptivity of the absorption band at about 300 nm was nearly linearly dependent on the σ_R constants of the groups Y as well as that of the band in the region of 330—390 nm on the σ_R constants of the groups X.

2-Phenylbenzotriazoles and especially 2-(2-hydroxyphenyl)benzotriazoles absorb satisfactorily in the near u.v. region [1—3]. For this property, they are frequently used as absorbents of the undesirable u.v. rays for different materials, mainly for high-molecular compounds [4—14]. We studied the effect of substitution on the behaviour of 2-(2-hydroxyphenyl)benzotriazole in the u.v. and i.r. spectra. For this purpose we prepared 2-(2-hydroxy-5-X-phenyl)-5-Y-benzotriazoles I—XXVIII (characterization of these compounds is in Table 1) of the general formula given in Scheme 1.

Compounds I—VIII, XXI—XXIV were prepared by cyclization reduction of the appropriate 5'-substituted 2-nitro-2'-hydroxyazobenzenes and 4-substituted 2-nitro-2'-hydroxy-5'-methylazobenzenes, respectively. These substituted azobenzenes were prepared by copulation of 2-nitrobenzenediazonium ion with phenol suitably substituted in the position 4 and by copulation of 4-substituted 2-nitrobenzenediazonium ion with *p*-cresol, respectively. The reduction was accomplished by sodium dithionite in water at pH 12—14 [17, 18].

Compound IX changed chemically at temperature higher by 20°C than its melting point in spite of the fact that beside chloroformyl group it contained a hydroxyl group. In inert solvents as benzene, toluene, xylene, and dioxan this compound was stable even at its melting point. Similarly as the majority of acyl chlorides, this compound was also a reactive substrate for nucleophiles and so it was possible to prepare compounds X—XVI [19]. Compounds XVIII and XXVIII were prepared by the method of Fries [20].

The absorption band at 3200 cm^{-1} with all substances proved the existence of an intramolecular hydrogen bond between the hydrogen atom of the OH group and nitrogen of the triazole ring (Table 2). The wavenumber of the OH stretching vibration with the associated hydrogen was linearly dependent on the constants σ_p of the substituents X with $\rho = -61$ as well as on that of the substituents Y with $\rho = +45$. The different signs



I	Y = H, X = CH ₃	XI	Y = H, X = COO(CH ₂) ₅ CH ₃
II	(CH ₂) ₃ CH ₃	XII	COOC ₆ H ₄ CH ₃
III	(CH ₂) ₇ CH ₃	XIII	CONH ₂
IV	C(CH ₃) ₃	XIV	CONHCH ₃
V	OCH ₃	XV	CON(C ₂ H ₅) ₂
VI	COOH	XVI	CONHC ₆ H ₅
VII	NH ₂	XVII	NHCOCH ₃
VIII	Br	XVIII	OH
IX	COCl	XIX	I
X	COOCH ₃	XX	H
	XXI	X = H, Y = NH ₂	
	XXII	CH ₃	
	XXIII	Br	
	XXIV	COOH	
	XXV	NHCOCH ₃	
	XXVI	N(COCH ₃) ₂	
	XXVII	NHCH ₃	
	XXVIII	OH	

Scheme 1

of ρ values are understandable when considering that the electron-donating groups in the position X decrease the acidity of the OH bond in phenol while in the position Y increase the electron density on nitrogen of the triazole ring which is a donor of electrons for the intramolecular hydrogen bond.

2-Phenylbenzotriazole shows an absorption at 220 nm besides an intensive one at 307 nm. A large substituent (CH₃, Cl) in *o*-position to nitrogen atom caused a moderate hypsochromic and hypochromic shift of the band at 307 nm due to the changed angle between the planes of the phenyl and triazole rings [1]. When the OH group was in the same position, a further band appeared at 334 nm [2]. According to Heller [3], the OH group, or its hydrogen atom, formed an intramolecular hydrogen bond with nitrogen of the triazole ring. This compensated the steric disadvantage of the planar conformation by its energy contribution so that besides the preferred conformation with screwed planes of the phenyl and triazole rings, also a planar conformer existed absorbing at lower energies. Thus the absorption band at 307 nm corresponded to the nonplanar conformation and the band at 334 nm to the planar one. Some of our experimental results are in accordance with this hypothesis (Table 2). Intensity of the absorption bands F and M expressed as the logarithm of molar absorptivity showed a clear tendency to linear correlation with the constants σ_R of the groups X and Y, respectively (Fig. 1). *E.g.*, the decreased intensity of the absorption band M and the simultaneous increased intensity of the band F due to the electron-donating groups X were in connection with the decreasing energy of intramolecular hydrogen bond due to the decreased acidity of a hydrogen atom in the OH group and corresponded, in accordance with [3], to the decreased concentration of the planar conformation and increased concentration of the nonplanar

Table 1

The prepared 2-(2-hydroxy-5-X-phenyl)-5-Y-benzotriazoles

Compound	Formula	M	Calculated/found				Yield [%]	M.p. [°C] (Solvent)
			% C	% H	% N	% Hal		
<i>III</i>	C ₂₀ H ₂₅ N ₃ O	323.44	74.27	7.79	12.99	—	75	104
<i>V</i>	C ₁₃ H ₁₁ N ₃ O ₂	241.31	74.42	7.87	12.83	—	65	(Ethanol)
			64.53	4.48	17.63	—		126
<i>VI</i>	C ₁₃ H ₉ N ₃ O ₃	255.18	61.19	3.56	16.47	—	60	(Benzene)
			61.41	3.80	16.08	—		304—306
<i>VII</i>	C ₁₃ H ₁₀ N ₄ O	226.24	—	—	24.27	—	50	186—187 ^a
<i>VIII</i>	C ₁₂ H ₈ N ₃ OBr	290.13	—	—	14.48	27.55	62	(Toluene)
					14.64	27.10		147—148
<i>IX</i>	C ₁₃ H ₈ N ₃ O ₂ Cl	273.68	—	—	15.36	12.96	70	(Ethanol)
					15.37	12.99		172—173
<i>X</i>	C ₁₄ H ₁₁ N ₃ O ₃	269.26	—	—	15.61	—	98	(Benzene)
					15.46	—		215—216
<i>XI</i>	C ₁₉ H ₂₁ N ₃ O ₃	339.40	—	—	12.38	—	96	(Methanol)
					12.48	—		83—84
<i>XII</i>	C ₂₀ H ₁₅ N ₃ O ₃	345.41	—	—	12.17	—	87	(<i>n</i> -Hexane)
					12.08	—		193—194
<i>XIII</i>	C ₁₃ H ₁₀ N ₄ O ₂	254.32	—	—	22.03	—	97	(Acetic acid)
					21.94	—		296—297
<i>XIV</i>	C ₁₄ H ₁₃ N ₄ O ₂	268.28	—	—	20.89	—	95	(Acetic acid)
					20.55	—		288—289
<i>XV</i>	C ₁₇ H ₁₈ N ₄ O ₂	310.42	—	—	18.05	—	98	(Ethanol)
					18.03	—		108—109
<i>XVI</i>	C ₁₉ H ₁₄ N ₄ O ₂	330.35	—	—	16.96	—	87	(Ethanol)
					16.90	—		296—297
<i>XVII</i>	C ₁₄ H ₁₂ N ₄ O ₂	268.28	—	—	20.89	—	94	(<i>p</i> -Xylene)
					20.81	—		276
<i>XVIII</i>	C ₁₂ H ₉ N ₃ O ₂	227.23	—	—	18.49	—	80	(Acetic acid)
					18.33	—		239
<i>XIX</i>	C ₁₂ H ₉ N ₃ OI	337.13	—	—	12.47	37.64	40	(Ethanol)
					12.58	36.13		170—172
<i>XXI</i>	C ₁₃ H ₁₂ N ₄ O	240.27	64.93	5.03	23.32	—	30	(Ethanol)
			64.66	4.55	23.22	—		203—204
<i>XXII</i>	C ₁₄ H ₁₃ N ₃ O	239.28	—	—	17.56	—	64	(Toluene)
					17.74	—		97—98
<i>XXIII</i>	C ₁₃ H ₁₁ N ₃ OBr	304.16	—	—	13.82	26.27	50	(Ethanol)
					14.02	25.81		95—96
<i>XXIV</i>	C ₁₄ H ₁₁ N ₃ O ₃	269.26	—	—	15.61	—	74	(Ethanol)
					15.46	—		263—264
<i>XXV</i>	C ₁₅ H ₁₄ N ₄ O ₂	282.31	—	—	19.85	—	74	(Acetic acid)
					19.72	—		207—208
<i>XXVI</i>	C ₁₇ H ₁₄ N ₄ O ₃	324.35	—	—	17.28	—	85	(Ethanol)
					17.55	—		163
<i>XXVII</i>	C ₁₄ H ₁₄ N ₄ O	254.29	—	—	22.03	—	95	(Ethanol)
					21.76	—		210
<i>XXVIII</i>	C ₁₃ H ₁₁ N ₃ O ₂	241.25	—	—	17.42	—	60	(Ethanol)
					17.20	—		220—221

^a) Compound of m.p. 282°C described in [22] is not *VII* but its isomer 2-(2-amino-5-hydroxyphenyl)benzotriazole.

Table 2

Absorption in the u.v. region and in the region of OH stretching vibration

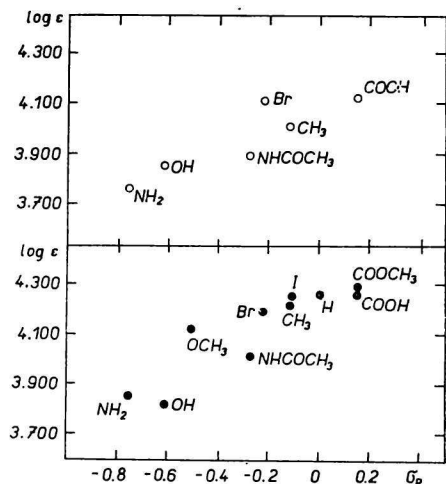
Com- pound	A		B		C		D		E		F		G		M		log ϵ	$\bar{\nu}$ (O-H) [cm ⁻¹]
	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	log ϵ	λ_{\max} [nm]	$\bar{\nu}$ [cm ⁻¹]		
I	224	4.160	*240	4.020	244	4.030	—	—	—	—	299	4.160	—	—	343	29.154	4.225	3210
V	226	4.220	*238	4.055	*245	4.000	288	3.660	—	—	300	4.205	—	—	360	27.777	4.120	3230
VI	232	4.420	*240	4.370	251	4.265	259	4.180	*294	4.080	298	4.130	*327	4.260	332	30.120	4.270	—
VII	234	4.280	—	—	—	—	—	—	*286	4.080	308	4.270	—	—	391	25.575	3.850	—
VIII	228	4.280	*240	4.140	—	—	—	—	—	—	299	4.140	—	—	341	29.325	4.205	3175
X	232	4.430	*240	4.380	250	4.280	261	4.230	*292	4.080	298	4.150	*326	4.275	331	30.211	4.290	3130
XVII	241	4.400	—	—	—	—	266	4.060	—	—	302	4.250	—	—	359	27.855	4.060	—
XVIII	237	4.290	—	—	—	—	—	—	*287	4.090	309	4.230	—	—	385	25.974	3.810	—
XIX	228	4.453	—	—	—	—	—	—	—	—	300	4.271	—	—	340	29.411	4.259	3170
XX	238	4.045	*241	4.030	—	—	—	—	—	—	299	4.105	—	—	333	30.033	4.265	3180
XXI	237	4.154	—	—	*258	4.034	—	—	*290	3.680	300	3.768	—	—	372	—	4.121	3190
XXII	241	4.060	—	—	—	—	—	—	—	—	305	4.080	—	—	340	—	4.251	3205
XXIII	240	4.002	—	—	—	—	—	—	—	—	300	4.125	—	—	341	—	4.197	3230
XXIV	250	3.984	—	—	—	—	—	—	—	—	305	4.120	—	—	350	—	4.197	—
XXV	244	4.204	—	—	—	—	—	—	—	—	305	3.894	—	—	354	—	4.176	3215
XXVI	255	4.251	—	—	—	—	—	—	—	—	314	4.038	—	—	360	—	4.315	3225
XXVII	236	4.053	—	—	*256	4.195	—	—	*290	3.651	300	3.790	—	—	372	—	4.153	3190
XXVIII	248	3.965	—	—	—	—	—	—	—	—	299	3.857	—	—	352	—	4.222	—

* Insignificant absorption band.

conformation. The electron-donating groups Y increasing the electron density on the nitrogen atom (donor of electrons for the formation of the intramolecular hydrogen bond) showed the reversed effect.

Fig. 1. Logarithm of molar extinction coefficient in dependence on the constants σ_R .

- absorption band F;
● absorption band M.



The relationship between electron effects of the groups X and the absorption energy was expressed by a fairly linear dependence of wavenumbers of the band M (the highest wavenumber) on the σ_R constants of the groups X with $\rho + 5.1$. *E.g.*, the electron-donating groups X, though decreased the concentration of the planar conformer (hypochromic effect), caused a bathochromic shift of the band M. This was in connection with the energy of electron transfer affected by conjugation of the molecule, *i.e.* by the degree of planarity of the phenyl and triazole rings influenced by the groups X. The constant σ_p 0.566 of the 2-benzotriazolyl group indicated an electron-accepting effect [21]. Supposing that the phenyl and the triazole rings were conjugated (in case of a certain degree of planarity of both rings), the electron-donating groups X promoted the natural course of conjugation between both rings and decreased the energy of the appropriate electron transfer, *i.e.* the absorption energy. The electron-accepting groups X showed a reversed effect. The groups Y, regardless of the course of conjugation, always caused a bathochromic shift.

It will be possible to bring more detailed interpretation of the electronic spectra only by using quantum chemical data.

Experimental

Melting points (Kofler), elemental analyses, and yields of the synthesized compounds are given in Table 1.

Infrared spectra were measured on a Zeiss Jena UR-10 apparatus in 1-cm quartz cells using carbon tetrachloride as solvent.

Ultraviolet spectra of the compounds I–XX (10⁻⁴ M in tetrahydrofuran) were measured on a UNICAM SP 700 apparatus and those of the compounds XXI–XXVIII (6.0 × 10⁻⁵ M in ethanol) on an Optica Milano apparatus.

Elemental analyses were accomplished at the Department of Organic Chemistry, Faculty of Natural Sciences, J. E. Purkyně University and at the Research Institute of Pure Chemicals (analytical laboratory), Lachema, Brno.

2-(2-Hydroxyphenyl)benzotriazole (XX) was prepared from VII according to [16].

Derivatives I—VI, VIII, XXI—XXIV

A solution of diazonium salt (from 0.05 mole of 2-nitro- and 2,4-dinitroaniline, respectively) [15] was added dropwise to a solution of substituted phenol (0.05 mole), sodium hydroxide (2.0 g), and anhydrous sodium carbonate (15 g) in water (150 ml) under vigorous stirring at 10–15°C. The formed suspension of the dye was allowed to stay for about 1 hour at laboratory temperature under occasional stirring. The substituted azobenzene was filtered at reduced pressure and washed with cold water to neutral reaction. The humid filtration cake was suspended in 5% sodium hydroxide (800 ml) and crystalline sodium dithionite (40 g) was added during one hour at laboratory temperature under stirring. The reaction mixture was boiled for one hour. From the yellow solution, cooled to laboratory temperature, cream-coloured plates were precipitated with carbon dioxide.

2-(2-Hydroxy-5-aminophenyl)benzotriazole (VII)

Copulation of the diazonium salt prepared from *o*-nitroaniline (0.05 mole; 6.9 g) [15] with *p*-hydroxyacetanilide (0.05 mole; 7.55 g) was carried out in the mixture of pyridine (200 ml) and water (100 ml) at 10–15°C. The cyclization reduction was accomplished similarly as with compound I.

2-(2-Hydroxy-5-chloroformylphenyl)benzotriazole (IX)

A mixture of compound VI (10 g) and thionyl chloride (50 ml) was heated at 65–70°C for 2 hours. After the unaltered thionyl chloride was distilled off, cream-coloured needles were obtained.

2-(2-Hydroxy-5-alkoxycarbonylphenyl)benzotriazoles (X—XII)

A mixture of compound IX (10 g) and the appropriate alcohol (200 ml) was boiled for 15 minutes. Then the alcohol (100 ml) was distilled off giving white needles of the product.

2-(2-Hydroxy-5-carbamidophenyl)benzotriazole (XIII) and its N-derivatives (XIV—XVI)

A mixture of compound IX (10 g) and concentrated aqueous solution of ammonia and amine (100 ml), respectively, was boiled for 10 minutes. The reaction mixture was adjusted to pH about 7 with diluted hydrochloric acid. The white crystals were sucked off and washed with water.

N-Acetyl derivatives (XVII, XXV, and XXVI)

To a solution of compound VII and XXI (3 g), respectively, in glacial acetic acid (60 ml), acetic anhydride (12 ml) was added and boiled for 10 minutes. After cooling the mixture to the room temperature, yellowish needles were precipitated.

Dihydroxy derivatives (XVIII and XXVIII)

A mixture of compound VII and XXI (4 g), respectively, 2 N sulfuric acid (40 ml), and boric acid (0.8 g) was heated at 200°C for 4 hours. After cooling the mixture to the room temperature, yellowish crystals were formed.

2-(2-Hydroxy-5-iodophenyl)benzotriazole (XIX)

To a mixture of compound VII (3.4 g), sulfuric acid (2 g), and water (70 ml), a solution of sodium nitrite (1.1 g) in water (10 ml) was added dropwise at a temperature lower than 10°C under stirring. After 30 minutes, potassium iodide (5 g) was added under vigorous stirring and cooling. After two-hour stirring at room temperature, the reaction mixture was boiled for a short time and allowed to stay overnight. The formed precipitate was sucked off and washed with water.

2-(2-Hydroxy-5-methylphenyl)-5-methylaminobenzotriazole (XXVII)

To a solution of compound XXI (10 g) in chloroform (200 ml), dimethyl sulfate (6 g) was added at laboratory temperature. On heating the solution to about 60°C, a yellowish product precipitated.

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