

**Functional Polymers. XXI\*\*:**

**Synthesis of Compounds with More than One Benzotriazole Group in the Molecule**

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Several 2(2-hydroxyphenyl)2*H*-benzotriazoles with more than one benzotriazole group substituted on di- and trihydroxybenzenes were synthesized by azo coupling of *o*-nitrobenzenediazonium chloride with resorcinol or phloroglucinol followed by reductive cyclization with zinc powder and sodium hydroxide. By careful diazonium coupling with *o*-nitrobenzenediazonium chloride, the monobenzotriazolyl compound, 4(2*H*-benzotriazole-2-yl)-1,3-dihydroxybenzene [2(2,4-dihydroxyphenyl)2*H*-benzotriazole] was obtained. All compounds have unusual spectral characteristics with high extinction coefficients, cut off of the absorption below 400 nm and are excellent candidates for ultraviolet stabilizers.

[*Keywords: Benzotriazolization of phenols; 2(2-Hydroxyphenyl)2H-benzotriazole; Ultraviolet absorbers; Ultraviolet stabilizers*]

*Funktionalisierte Polymere, 21. Mitt.: Synthese von Verbindungen mit mehr als einer Benzotriazol-Gruppe im Molekül*

Es wurden einige 2(2-Hydroxyphenyl)2*H*-benzotriazole mit mehr als einer Benzotriazolgruppe am Di- bzw. Trihydroxybenzol mittels Azokupplung von *o*-Nitrobenzoldiazoniumchlorid mit Resorcin bzw. Phloroglucin und nachfolgender reduktiver Cyclisierung mit Zn-Pulver/NaOH hergestellt. Durch sorgfältige Kupplung mit *o*-Nitrobenzoldiazoniumchlorid konnte die Monobenzotriazolylverbindung hergestellt werden: 4(2*H*-benzotriazol-2-yl)-1,3-dihydroxybenzol [2(2,4-Dihydroxyphenyl)2*H*-benzotriazol]. Alle Verbindungen haben unge-

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wöhnliche UV-VIS-spektroskopische Eigenschaften mit sehr hohen Extinktionskoeffizienten und einem starken Abfall der Adsorption bei 400 nm; es sollte sich um ausgezeichnete UV-Stabilisatoren handeln.

### Introduction

2(2-Hydroxyphenyl)2*H*-benzotriazoles with various substituents in the benzotriazole or phenyl rings have been known for over 20 years as ultraviolet stabilizers<sup>1-3</sup> and have been used in the last 5 years extensively to stabilize polymers from the detrimental influence of ultraviolet and sun radiation<sup>4,5</sup>. In numerous patents the advantages of 2(2-hydroxyphenyl)2*H*-benzotriazoles have been described and a series of materials are now commercially available<sup>6,7</sup>.

In recent years the importance of permanence in stabilizers, particularly UV stabilizers of the ultraviolet screen category, has resulted in an intensive study for more compatible, polymerizable and polymer-bound stabilizers<sup>8-15</sup>. In the last few years a number of papers describing the polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazoles have been published and their effectiveness in certain applications described<sup>16,17</sup>. At the same time photophysical studies of the 2(2-hydroxyphenyl)2*H*-benzotriazole family have been investigated<sup>18,19</sup>.

In the search for new compounds with possibly more effective ultraviolet characteristics and capabilities of acting as effective UV stabilizers, work has been undertaken to introduce more than one benzotriazole unit into the molecule. It was expected that this could be done by benzotriazolization of polyhydroxylated aromatic compounds such as resorcinol and phloroglucinol.

Investigation of the earlier work on the preparation of benzotriazoles revealed that condensation of *o*-nitrobenzenediazonium chloride with phenol (unsubstituted in the *para* position) gave the expected *para*-substitution and after zinc and sodium hydroxide reduction, 2(4-hydroxyphenyl)2*H*-benzotriazoles<sup>20,21</sup>. *Elbs*<sup>20,21</sup> described condensations of *o*-nitrobenzenediazonium chloride with *para*-substituted phenols and obtained, after reductive cyclization, 2(2-hydroxyphenyl)2*H*-benzotriazoles. The same authors already described the condensation of *o*-nitrobenzenediazonium chloride with resorcinol which, after reductive cyclization with zinc and sodium hydroxide, gave a compound with a m.p. of 188 °C and with the correct nitrogen analysis for C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>N<sub>3</sub><sup>22-24</sup>. A compound with apparently two benzotriazole rings in the molecule, C<sub>18</sub>H<sub>12</sub>O<sub>2</sub>N<sub>6</sub> and a m.p. of 196 to 198 °C was also obtained<sup>22,24</sup> in low yield. The authors<sup>22</sup> described the compound as 2,4[di(2*H*-benzotriazole-2-yl)]1,5-dihydroxybenzene.

It was the objective of this work to prepare 2(2-hydroxyphenyl)2*H*-benzotriazoles with more than one benzotriazole unit in the molecule, to characterize them by chemical and spectroscopic means; the study of the photophysical behavior will be described in more detail in a subsequent paper.

### Results and Discussion

Four benzotriazolyl substituted dihydroxy- and trihydroxybenzenes have been prepared. 2,4[Di(2*H*-benzotriazole-2-yl)]1,3-dihydroxybenzene (*DBDH*) and 4(2*H*-benzotriazole-2-yl)1,3-dihydroxybenzene (*BDH*) have been synthesized and characterized\*.

The two compounds have been made previously but their purification and proper characterization have not yet been described<sup>22</sup>. Two new compounds, 2,4[Di(2*H*-benzotriazole-2-yl)]1,3,5-trihydroxybenzene (*DBTH*) and 2,4,6[tri(2*H*-benzotriazole-2-yl)]1,3,5-trihydroxybenzene (*TBTH*), have been synthesized and their chemical and spectral characterization was carried out.

*BDH* and *DBDH* were synthesized by condensing *o*-nitrobenzenediazonium chloride with resorcinol followed by reduction of the corresponding azo dyes with zinc and sodium hydroxide to the mono- and dibenzotriazolyl substituted resorcinols. For the synthesis of *BDH* the condensation occurred by adding slowly 0.4 mol of *o*-nitrobenzenediazonium chloride to 0.8 mol of resorcinol; (a mol ratio of diazonium salt to resorcinol of 1:2) sodium bicarbonate was used to buffer the coupling reaction rather than the normal sodium carbonate/sodium hydroxide mixture used in our work for the condensation reaction of *o*-nitrobenzenediazonium chloride with monosubstituted phenols. The condensation was carried out by adding slowly the diazonium salt solution to resorcinol below 10 °C to guarantee always a large excess of resorcinol, in attempts to avoid disubstitution. After the reduction of the azo dye with zinc and sodium hydroxide, the benzotriazolization product was obtained in 80-90% crude yield; it was carefully fractionally crystallized because the initially isolated product consisted of a mixture of

\* The nomenclature of 2(2-hydroxyphenyl)2*H*-benzotriazole can be done by describing the substituent on the 2*H*-benzotriazole part of the molecules as we have done in previous papers<sup>8-15</sup> or, which is sometimes more convenient especially when the higher substitution in the phenol ring is the center of attention, to describe the substitution of the 2*H*-benzotriazolyl group or groups on the polyhydroxylated benzene ring. The two types of nomenclature are given as follows: (A), (B), (C), (D).

(A) 4-(2*H*-Benzotriazole-2-yl)1,3-Dihydroxybenzene (*BDH*)

4-(1,3-Dihydroxyphenyl)2*H*-Benzotriazole.

(B) 2,4-[Di(2*H*-Benzotriazole-2-yl)]1,3-Dihydroxybenzene (*DBDH*)

2,4-(1,3-Dihydroxyphenyl)-Di(2*H*-Benzotriazole).

(C) 2,4-[Di(2*H*-Benzotriazole-2-yl)]1,3,5-Trihydroxybenzene (*DBTH*)

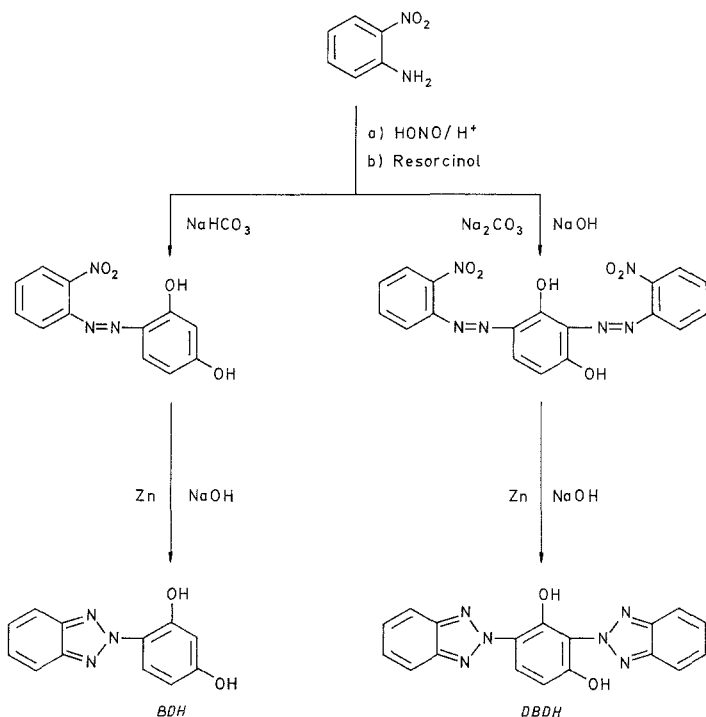
2,4-(1,3,5-Trihydroxyphenyl)-Di(2*H*-Benzotriazole).

(D) 2,4,6-[Tri(2*H*-Benzotriazole-2-yl)]1,3,5-Trihydroxybenzene (*TBTH*)

2,4,6-(1,3,5-Trihydroxyphenyl)-Tri(2*H*-Benzotriazole).

*BDH* and *DBDH*. After purification a 23% yield of *BDH* and a 19% yield of *DBTH* were obtained.

Scheme 1



When the *o*-nitrobenzenediazonium chloride was added rapidly in equal molar quantities to resorcinol, or the resorcinol solution was added to the *o*-nitrobenzenediazonium chloride solution, after reductive cyclization, only *DBDH* with a melting point of 210–212 °C was isolated in 46% yield.

*BDH* was apparently prepared the first time by *Elbs*<sup>22</sup>. It was described as white needles, m.p. 188 °C. Later it was described as pale brown crystals with a m.p. of 191 °C<sup>24</sup>.

*DBDH* was also described previously<sup>22</sup> as being obtained in 30–40% yield as small, yellowish white needles, m.p. 196–198 °C<sup>23</sup> obtained in 79% yield, melting at 200 °C<sup>22</sup> when recrystallized from benzene or from ethanol.

It should also be pointed out that *DBDH* can have two structural isomers but was described in Ref.<sup>22</sup> as the 2,4-[di(2*H*-benzotriazole-2-

Table 1. Reaction conditions and results of benzotriazolization reactions of resorcinol and phloroglucinol. Reactants: *o*-Nitroaniline: 55 g (0.4 mol). Coupling temperature: 0 to 10°C

Starting Compound	g	(mol)	Mode of Addition <sup>a</sup>	Reaction		m.p.
				Product after Cyclization <sup>b</sup>	yield g (%) <sup>b</sup>	
Resorcinol	88	(0.80)	(1) → (2)	<i>BDH</i>	21 (23)	199-200
				<i>DBDH</i>	6 (19)	210-212
Phloroglucinol	44	(0.40)	(1) → (2)	<i>DBDH</i>	30 (46)	210-212
	65	(0.40)	(1) → (3)	<i>DBTH</i>	25 (35)	240-242
	32	(0.20)	(3) → (1)	<i>TBTH</i>	13.3 (21)	317-318

<sup>a</sup> (1) *o*-Nitroaniline, (2) Resorcinol, (3) Phloroglucinol.

<sup>b</sup> Yield based on *o*-nitroaniline.

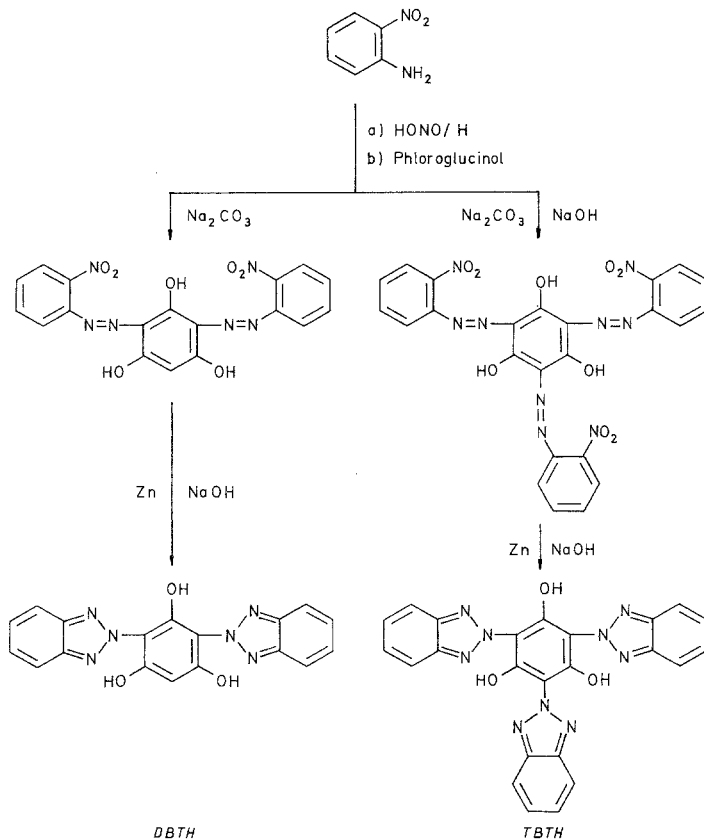
yl)]1,5-dihydroxybenzene isomer. Although two *para* positions are open in resorcinol for condensation, one would expect that this isomer would be obtained predominantly. It was not completely out of the question that the isomeric 2,4[di(2*H*-benzotriazole-2-yl)]1,3-dihydroxybenzene could have been obtained because the substitution of the second diazonium coupling reaction on the initial mono-azo reaction product in 4-position could conceivably changed the direction of substitution of the monosubstituted resorcinol from the normally expected 4,6 position (one *para*, one *ortho*-directing —OH substituent) to the 2,4 position (two *ortho* directing —OH substituents).

Discrepancies in the yield of crude products, and possible error in the assignment of the isomeric structure made it necessary to repeat the earlier work carefully in order to see if a difference in reaction condition could have caused the substantially different results of the condensation reaction. The synthesis of the monosubstituted benzotriazolyl resorcinol (*BDH*) was carried out as closely as possible to the earlier Ref.<sup>22</sup>. The main difference between the early procedure and ours was that after the diazotization of *o*-nitroaniline was completed the diazonium salt solution was diluted with cold water to three times its original volume and the aqueous diazonium salt was added dropwise to the sodium hydroxide solution of resorcinol under vigorous stirring, between —1 and —5°C.

The reduction was carried out with 2*N* NaOH and Zn and required 40 h. A seemingly important difference was found in the description of the filtration step; the literature reference required the suspension after the reduction to be filtered into a suction flask which contained dilute sulfuric acid and a small amount of sodium bisulfite. After neutralization the crude mixture containing *BDH* precipitated, the suspension was filtered, the compound was washed, dried and gave an 82% yield of dried crude product which was found to be quite impure. This yield compares to a 90% crude yield described in the literature<sup>22</sup>.

After careful crystallization four times from ethanol/water, pure *BDH* was obtained in 18% yield and *DBDH* was isolated in 17% yield for a total yield of pure compounds of 35%. The yield of 82% of crude product was calculated based on a yield of a product consisting entirely of *BDH*.

Scheme 2



The synthesis of *DBDH* was also carried out as closely as possible to the earlier literature Ref.<sup>22</sup>. Again, the coupling was carried out with sodium carbonate as the buffer; the *o*-nitrobenzenediazonium chloride was added dropwise into a sodium carbonate solution of resorcinol under vigorous stirring at 5–10 °C. The reduction was carried out in 2 *N* NaOH solutions for a period of 48 h at 40–45 °C. After the reductive cyclization, the suspension was filtered into a filter flask which contained dilute sulfuric acid and a small amount of sodium bisulfite. The washed and dried product was obtained in 55% yield if calculated for pure *DBDH* and had a melting point of 130 °C. Pure *DBDH* was obtained after several recrystallizations from benzene or ethanol in 8% yield with a m.p. of 210–212 °C. The literature describes the compound as having been obtained in

30-40% yield with a m.p. 196-198 °C<sup>22</sup>. Importantly, the authors describe the compound as decomposing during the melting process. Another author<sup>23</sup> described a melting point of 200-201.5 °C for the compound of the structure of *DBDH*.

We also found it interesting to study the possible benzotriazolization of hydroquinone, the 1,4-dihydroxybenzene where both hydroxyl groups might be *ortho*-directing, but *meta*-deactivating. Although the coupling was carried out in two ways with the sodium hydroxide solution of hydroquinone and *o*-nitrobenzenediazonium chloride; only a small amount of a yellow powder was obtained rather than the nearly quantitative yield of the normal red powder of the azo coupling products when condensing resorcinol or *para* substituted phenols; a large amount of gas was released at the same time. The failure of this reaction is not surprising since the order of coupling of phenols is known to be phloroglucinol > resorcinol > *m*-cresol > phenol > hydroquinone > *o*-nitrophenol, as described earlier<sup>25</sup>. It is also known that hydroquinone reacts very slowly with *p*-nitrobenzene diazo hydrate<sup>26</sup>. It is further known that hydroquinone is quite inactive, in general, for such coupling reactions. Diazonium salts form readily, as does *o*-nitrobenzenediazonium chloride, in near neutral or basic solution, the aryl diazohydroxide which, when the condensation is slow, decomposes readily to nitrogen and phenol. Furthermore, hydroquinone is a strong reducing agent; in our case, the *o*-nitrobenzenediazonium chloride could be reduced with hydroquinone to nitrobenzene with the elimination of gaseous nitrogen while being oxidized to benzoquinone.

It should be pointed out that one of the papers for the preparation of 2-(2-hydroxyphenyl)2*H*-benzotriazole<sup>3</sup> describes the reaction of a *para*-substituted phenol similar to hydroquinone, namely, the condensation product of *p*-aminophenol, followed by reduction to the corresponding 2(2-hydroxy-5-aminophenyl)2*H*-benzotriazole, a monosubstituted benzotriazole derivative; in this particular case the azo coupling and subsequent reductive cyclization seem to have worked satisfactorily.

The reaction of phloroglucinol with *o*-nitrobenzenediazonium chloride took a not completely expected direction and always gave di- or tribenzotriazolized products; no monobenzotriazolized compound was obtained under all conditions tried up to this time. When *o*-nitrobenzenediazonium chloride was added slowly to phloroglucinol (1:1 final ratio), *DBTH* was obtained in 35% yield after the original reaction product was purified. If, however, phloroglucinol was added slowly to the diazonium compound, having ultimately a 2:1 excess, *TBTH* was the only product obtained after purification in 21% (Table 1).

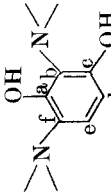
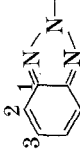
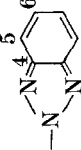
Table 2.  $^1\text{H-NMR}$  Chemical shift data for various benzotriazole derivatives

Group Assignment	Chemical Shift Assignment	BDH <sup>a</sup>	DBDH	DBTH	TBTH
a	(OH)	10.4	(OH)	(OH)	(OH)
b	(H)	6.7	(s)	(b)	(s)
c	(OH)	10.4	(b)	(OH)	(OH)
d	(H)	6.6	(d)	(H)	(s)
e	(H)	c	(H)	(OH)	(OH)
f					
Benzotriazole Group					
2	8.0	(m)	8.0	8.1	8.1
3	7.5	(m)	7.4	7.6	7.5

<sup>a</sup> For abbreviations see Experimental Part and Formulas.<sup>b</sup> : broad.<sup>c</sup> Obscured by benzotriazole protons.



Table 3.  $^{13}\text{C}$ -NMR Chemical shift data for several 2H-benzotriazole substituted di- and triphenols

Group Assignment	BDH			DBDH			DBTH			TBTH		
	Obs	CS <sup>a</sup>	Calc	Obs	CS	Calc	Obs	CS	Calc	Obs	CS	Calc
	151.8	151.8	153.0	148.1	148.1	148.6	151.5	151.5	152.4	152.0	152.0	155.4
	103.8	103.8	103.7	118.9	118.9	119.6	111.4	111.4	111.0	112.1	112.1	113.0
	159.8	159.8	159.8	155.9	155.9	156.5	156.3	156.3	159.2	152.0	152.0	155.4
	107.5	107.5	107.6	107.8	107.8	108.2	94.2	94.2	95.9	112.1	112.1	113.0
	125.4	125.4	124.6	125.4	125.4	129.0	156.3	156.3	159.2	152.0	152.0	155.4
	119.7	119.7	119.7	119.4	119.4	120.4	111.4	111.4	111.0	112.1	112.1	113.0
	144.6	144.6	144.3 <sup>b</sup>	144.4	144.4	144.5	144.6	144.6	144.6	144.5	144.5	144.6
	117.6	117.6	117.5 <sup>b</sup>	118.4	118.4	118.3	118.5	118.5	117.6	118.2	118.2	117.6
	126.9	126.9	125.9 <sup>b</sup>	126.9	126.9	126.8	126.9	126.9	126.9	126.8	126.8	126.9
	—	—	—	143.0	143.0	144.6	—	—	—	—	—	—
	—	—	—	117.6	117.6	117.6	—	—	—	—	—	—
	—	—	—	127.5	127.5	126.9	—	—	—	—	—	—

<sup>a</sup> CS: Chemical shift values (ppm, TMS) in  $\text{DMSO-}d_6$ .<sup>b</sup> Calc. according to Ref.<sup>27</sup>.

The study of the infrared spectrum of the four compounds *BDH*, *DBDH*, *DBTH* and *TBTH*, showed them to have the typical infrared absorptions of benzotriazolized polyhydroxybenzenes, the complicated spectra reflecting the functional groups in addition to the aromatic rings.

It has been established that tetrasubstituted benzene rings absorb in the 800-900  $\text{cm}^{-1}$  region. 1,2,4,5-Tetrasubstitution on the benzene ring shows IR absorption bands between 850-870  $\text{cm}^{-1}$  while 1,2,3,4-tetrasubstituted benzene rings show peaks at 800-810  $\text{cm}^{-1}$ . In the infrared spectrum of *DBDH* it shows peaks at 855  $\text{cm}^{-1}$  and at 800  $\text{cm}^{-1}$ . On the basis of the IR spectrum alone, the compound *DBDH* cannot be unequivocally assigned to one of the two kinds of isomers with the benzotriazole group substituted in 2,4 position of the 1,2,4,5 isomer of 2,4 position of the 1,2,3,4 isomer. It should be recalled that *Elbs* proposed earlier for his *DBDH* compound for which we found a m.p. of 210-212 °C, the structure of the 1,2,4,5 isomer.

The  $^{13}\text{C}$ NMR chemical shift data of all four compounds *BDH*, *DBDH*, *DBTH* and *TBTH* are shown in Table 3. The  $^{13}\text{C}$ NMR chemical shift data for *BDH* show the individual carbon atoms of the phenol ring clearly separated; the values agree well with the calculated values with the exception of the carbon atom number a. This difference indicates that steric crowding occurs which seems to cause an angular change of the position of the benzotriazole ring.

Based on IR,  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectroscopy data, we have concluded that *DBDH* prepared by us is the 1,2,3,4 isomer, rather than the 1,2,4,5 isomer.

The ultraviolet spectra of various benzotriazole derivatives are shown in Table 4 and Figs. 1, 2. *BDH* has a  $\lambda_{\text{max}}$  of 251 nm with an extinction coefficient of about  $8 \cdot 10^3$  and a  $\lambda_{\text{max}}$  of 343 nm and an  $\epsilon$  of  $23.6 \cdot 10^3$ . *DBTH* has a  $\lambda_{\text{max}}$  of 238 nm with an  $\epsilon$  of  $16 \cdot 10^3$  and a  $\lambda_{\text{max}}$  at 325 nm and an  $\epsilon$  of  $36.2 \cdot 10^3$ . As substitution increases as in the case of *DBTH*, a  $\lambda_{\text{max}}$  of 239 nm and an  $\epsilon$  of  $13.6 \cdot 10^3$  was found and a  $\lambda_{\text{max}}$  at 340 nm and an  $\epsilon$  of  $40 \cdot 10^3$ . *TBTH* has a single broad absorption peak with a  $\lambda_{\text{max}}$  at 337 nm and an extinction coefficient of  $41.6 \cdot 10^3$ . Shoulders are noticed at 265 nm and 300 nm. *2H5P* [2(2-hydroxy-5-isopropenyl)2*H*-benzotriazole] which is used here for comparison, has a  $\lambda_{\text{max}}$  at 241 nm and an extinction coefficient of  $18.1 \cdot 10^3$ , a  $\lambda_{\text{max}}$  of 270 nm and an  $\epsilon$  of  $15.3 \cdot 10^3$ , a  $\lambda_{\text{max}}$  at 303 nm, an  $\epsilon$  of  $17.1 \cdot 10^3$  and finally a  $\lambda_{\text{max}}$  of 346 nm with an  $\epsilon$  of  $13.3 \cdot 10^3$ . Table 4 shows the extinction coefficient of *BDH*, *DBTH* and *2H5P*; as a second benzotriazole ring is added to the molecule and each of the rings can hydrogen bond with a phenolic *ortho*-hydroxyl group, the ultraviolet absorption peaks become broad, have high extinction coefficients and much of the structure of the absorption band disappears.

The extinction coefficient of *DBTH* and *TBTH* is nearly the same except that *TBTH* has strong shoulders into the lower wavelength region and consequently a broad spectrum from 250 nm all the way to 380 nm.

In conclusion, several highly substituted polyhydroxybenzenes substituted with benzotriazole rings have been prepared, characterized by their IR,  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra and their ultraviolet characteristics have been evaluated. As the substitution increased, the extinction coefficient of the molecule increased dramatically and, in addition,

Table 4. Ultraviolet absorption of various benzotriazole derivatives in  $\text{CHCl}_3$  ( $c = 2 \cdot 10^{-5}$  mol/l)

Compound	$\lambda_{\text{max}}$	$\epsilon \cdot 10^{-3}$	$\lambda_{\text{max}}$	$\epsilon \cdot 10^{-3}$	$\lambda_{\text{max}}$	$\epsilon \cdot 10^{-3}$	$\lambda_{\text{max}}$	$\epsilon \cdot 10^{-3}$
<i>BDH</i>	251	7.87					343	23.6
<i>DBDH</i>	238	16.2					325	36.2
<i>DBTH</i>	239	13.6					340	40.0
<i>TBTH</i>	265	(shoulder)	300	(shoulder)			337	41.6
<i>2H5P</i>	241	18.1	270	15.3	303	17.1	346	13.3

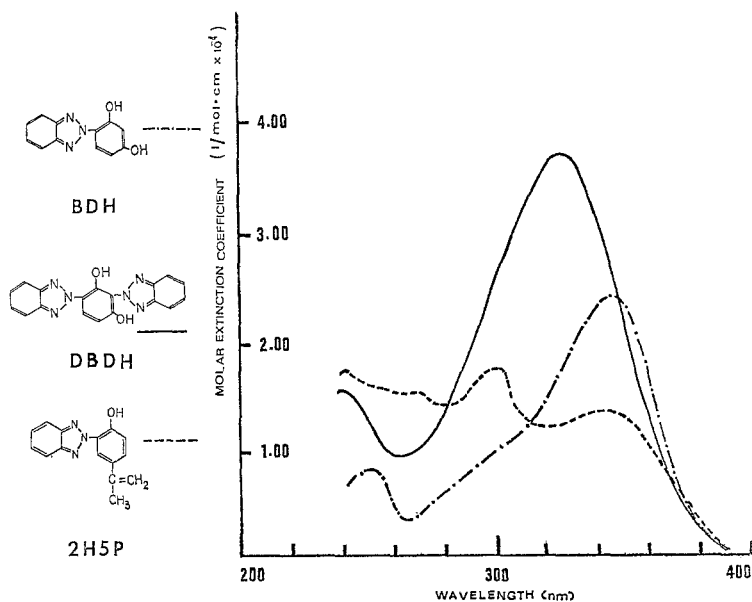


Fig. 1. Ultraviolet Absorption Spectra of 4(2*H*-Benzotriazole-2-yl)1,3-Dihydroxybenzene (*BDH*), 2,4[Di(2*H*-Benzotriazole-2-yl)]1,3-Dihydroxybenzene (*DBDH*), and 2(2-Hydroxy-5-Isopropenylphenyl)2*H*-Benzotriazole (*2H5P*)

a strong broadening of the single absorption peak was noted with the loss of some structure of the absorption peak. This absorption peak covers the important ultraviolet range nearly into the visible region. A detailed spectroscopic investigation of this class of compounds is underway and its relationship to the photo-physical behavior will be reported in the near future.

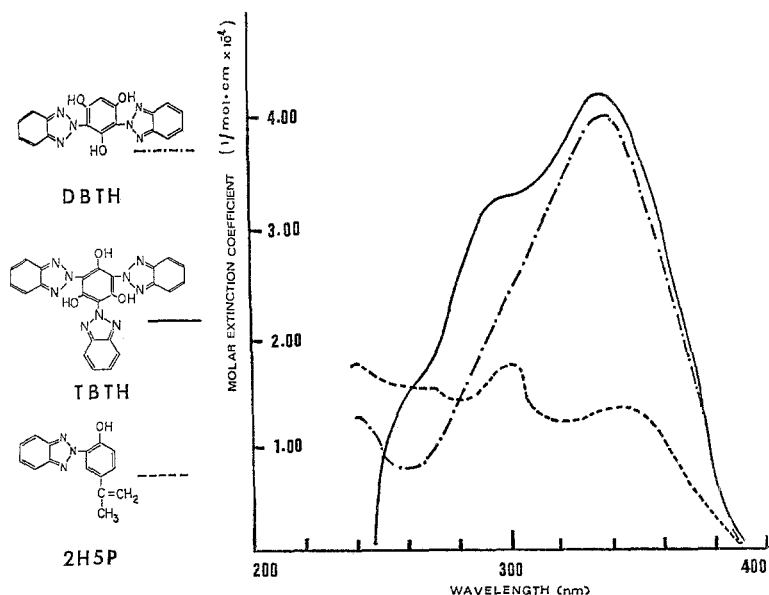


Fig. 2. Ultraviolet Spectrum of 2,4[Di(2*H*-Benzotriazole-2-yl)]1,3,5-Trihydroxybenzene (*DBTH*), 2,4,6[Tri-(2*H*-Benzotriazole-2-yl)]1,3,5-Trihydroxybenzene (*TBTH*), and 2(2-Hydroxy-5-Isopropenylphenyl)2*H*-Benzotriazole (*2H5P*)

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### Experimental Part

**Materials:** *o*-Nitroaniline (Aldrich Chemical Co.), resorcinol (MCB Manufacturing Chemists, Inc.), phloroglucinol (J. T. Baker Chemical Co.) and most solvents such as benzene, chloroform, methanol and ethanol were used as received. Dimethyl sulfoxide-*d*<sub>6</sub> (99.9% D) was obtained from Aldrich Chemical Co.

**Measurements:** Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer, Model 283. Solid samples were measured in the form of potassium bromide pellets. <sup>1</sup>H NMR spectra were recorded on a Varian A-60 spectrometer and <sup>13</sup>C NMR spectra on a Varian CTF-20 spectrometer with complete proton

decoupling; *TMS* was used as the internal standard. The compounds were measured in deuterated *DMSO* in 15% or saturated solutions. Conditions for acquiring the spectra were as follows: spectral width 4000 Hz, number of transients > 6000, acquisition time 1.023 s, pulse width 19 sec, pulse delay 1.0 s, data points 8184. Ultraviolet absorptions were measured in chloroform solution (Spectrograde, Fisher Scientific Co.) with a Beckman MVI spectrometer in a double beam servo mode (1.0 cm optical path length). Melting points were determined on a MELT-TEMP Capillary melting point apparatus at a heating rate of 2 °C/min and are uncorrected. Microanalyses were carried out at the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

*2,4[Di(2 H-Benzotriazole-2-yl)]1,3-Dihydroxybenzene (DBDH)*

A solution of *o*-nitroaniline (55 g, 0.4 mol) in concentrated hydrochloric acid (150 ml) was diazotized at 0 °C, with a solution of sodium nitrite (28 g, 0.40 mol) in water (100 ml). The cold solution of *o*-nitrobenzenediazonium chloride was added over a period of 1 h with stirring to a solution of resorcinol (44 g, 0.4 mol), sodium carbonate (120 g, 1.13 mol) and sodium hydroxide (32 g, 0.8 mol) in water (600 ml), cooled to 0 °C. The azo compound separated immediately in the form of dark red crystals. After stirring the reaction mixture for 2 h the azo compound was isolated by filtration, washed 3 times with water, and then dissolved in a 2 *N* sodium hydroxide solution (600 ml) in a two liter-beaker. Zinc powder (120 g, 1.84 mol) was added with stirring to the solution of the azo compound over a period of 0.5 h, followed by the addition of a solution of sodium hydroxide (150 ml, 40%) over a period of 1 h with the bath temperature raised to 50 °C. The color of the reaction mixture changed from red to green, indicating that the azo compound had been reduced. After 16 h the suspension was filtered and the residue was extracted twice with aqueous sodium hydroxide (10%); the filtrate was combined with this extract and cooled in an ice bath. While keeping the temperature below 10 °C, the solution was acidified with concentrated hydrochloric acid and crude *DBDH* precipitated. It was isolated by filtration, air-dried and then placed in a Soxhlet extractor. After extracting for 3 days with benzene, 30 g (46% yield) of *DBDH* were isolated from the benzene extract. Recrystallization from chloroform gave pure *DBDH* as white needles, m.p. 210-212 °C.

The ultraviolet absorption data are presented in Table 4. IR (KBr): 3080  $\text{cm}^{-1}$  (O—H stretching).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shift data are presented in Tables 2 and 3.

Anal. Calcd. for  $\text{C}_{18}\text{H}_{12}\text{N}_6\text{O}_2$ : C 62.79, H 3.49, N 24.42. Found: C 62.66, H 3.38, N 24.22.

*4(2 H-Benzotriazole-2-yl)1,3-Dihydroxybenzene (BDH)*

The synthesis of *BDH* followed essentially the same procedure as described for the synthesis of *DBDH*, except that the molar ratio of *o*-nitrobenzenediazonium chloride/resorcinol was 1:2. Resorcinol (88 g, 0.8 mol) and sodium bicarbonate (168 g, 2 mol) was used for the coupling reaction rather than sodium carbonate and sodium hydroxide. Crude *BDH* was extracted for 2 days with ethanol in a Soxhlet apparatus. After diluting the ethanol extract with water,

some material precipitated, which was isolated and identified to be *DBDH* (6 g, 9% yield). After further addition of water to the ethanol extract (ethanol:water = 1:1), 21 g (23% yield) of crude *BDH* precipitated; it was recrystallized from ethanol:water (1:1) and gave white needles, m.p. 199-200 °C.

The ultraviolet absorption data are presented in Table 4. IR (KBr): 3 220  $\text{cm}^{-1}$  (O—H stretching).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shift data are shown in Tables 2 and 3.

Anal. Calcd. for  $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2$ : C 63.43, H 3.99, N 18.49. Found: C 63.17, H 3.92, N 18.49.

#### *2,4,6[Tri(2 H-Benzotriazole-2-yl)]1,3,5-Trihydroxybenzene (TBTH)*

*o*-Nitroaniline (55 g, 0.4 mol) was diazotized as described for the synthesis of *DBDH*. To the stirred solution of *o*-nitrobenzenediazonium chloride, cooled to 0°-5 °C, was added dropwise a solution of phloroglucinol (32 g, 0.2 mol), sodium hydroxide (24 g, 0.6 mol) and sodium carbonate (120 g, 1.13 mol) in water (600 ml). The procedures for work-up, reductive cyclization and isolation of the crude *TBTH* were essentially the same as described for *DBDH*. The crude product was purified by *Soxhlet* extraction with acetone (3 days); the acetone extract yielded 13.3 g (21%) of *TBTH*. Recrystallization from acetone gave yellow needles, m.p. 317-318 °C.

The ultraviolet absorption data are presented in Table 4. IR (KBr): 3 140  $\text{cm}^{-1}$  (O—H stretching).  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift data are presented in Tables 2 and 3.

Anal. Calc. for  $\text{C}_{24}\text{H}_{15}\text{N}_9\text{O}_3$ : C 60.37, H 3.17, N 26.40. Found: C 60.59, H 3.03, N 26.50.

#### *2,4[Di(2 H-Benzotriazole-2-yl)]1,3,5-Trihydroxybenzene (DBTH)*

The synthesis of *DBTH* followed the same procedure as outlined for *BDH*, but with phloroglucinol (65 g, 0.40 mol) as starting material, and sodium carbonate (148 g, 1.4 mol) for the coupling reaction. The *Soxhlet* extraction was carried out for 3 days with acetone as the solvent and yielded 25 g (35%) of *DBTH*. After recrystallization from acetone, pale yellow needles were obtained, m.p. 240-242 °C.

The ultraviolet absorption data are presented in Table 4. IR (KBr): 3 050  $\text{cm}^{-1}$  (O—H stretching).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shift data are presented in Tables 2 and 3.

Anal. Calcd. for  $\text{C}_{18}\text{H}_{12}\text{N}_6\text{O}_3$ : C 60.00, H 3.33, N 23.33. Found: C 60.10, H 3.35, N 22.99.

### References

- 1 Balaban L., Borkovec J., Rysavy D., Czechoslovakian Pat. (1963); C.A. **61**, 3267 h (1964).
- 2 Monte D. D., Mangini A., Passerini R., Zanli C., Gazz. Chim. Ital. **88**, 977 (1958).
- 3 Belusa J., Janousek Z., Knoflickova H., Chem. Zvesti **28**, 673 (1974).
- 4 Bailey D., Vogl O., J. Macromol. Sci., Reviews **C14**, 267 (1976).
- 5 Hardy W. B., Forster W. S., Colemann R. A., U.S. Patent 2,962,533 (1980).
- 6 Karvas M., Holcik J., Chem. Prum. **17**, 543 (1967).
- 7 Milionis J. P., Hardy W. B., Baitinger W. F., U.S. Patent 3,159,646 (1964).

- <sup>8</sup> *Yoshida S., Vogl O.*, Polymer Preprints, ACS Division of Polymer Chemistry **21**, 203 (1980).
- <sup>9</sup> *Vogl O., Yoshida S.*, Preprints, Plenary Lectures, Annual Meeting, Society of Polymer Science, Kyoto, **29**, 648 (1980).
- <sup>10</sup> *Vogl O., Yoshida S.*, Rev. Roum. de Chimie **7**, 1123 (1980).
- <sup>11</sup> *Pradellok W., Gupta A., Vogl O.*, J. Polym. Sci., Polym. Chem. Ed. **19**, 3307 (1981).
- <sup>12</sup> *Yoshida S., Vogl O.*, Makromol. Chem. **183**, 259 (1982).
- <sup>13</sup> *Yoshida S., Lillya C. P., Vogl O.*, Monatsh. Chem. **113**, 603 (1982).
- <sup>14</sup> *Yoshida S., Lillya C. P., Vogl O.*, J. Polym. Sci., Polym. Chem. Ed. **20**, 2215 (1982).
- <sup>15</sup> *Nir Z., Gupta A., Vogl O.*, J. Polym. Sci., Polym. Chem. Ed. **20**, 2735 (1982).
- <sup>16</sup> *Kitayama M., Vogl O.*, Polymer J. (Japan) **14**, 537 (1982).
- <sup>17</sup> *Gupta A., Liang R. H., Vogl O., Pradellok W., Scott G.*, Macromolecules, in press.
- <sup>18</sup> *Gupta A., Scott G., Vogl O.*, Proceedings, IUPAC, 28<sup>th</sup> Macromol. Symposium, 298, Amherst, MA, 1982.
- <sup>19</sup> *Werner T., Woessner G., Kramer H. E. A.*, ACS Symposium Series **151**, 1 (1981).
- <sup>20</sup> *Goldschmidt H., Merz A.*, Ber. **30**, 670 (1897).
- <sup>21</sup> *Elbs K., Keiper W.*, J. Prakt. Chem. [2] **67**, 580 (1905).
- <sup>22</sup> *Elbs K.*, J. Prakt. Chem. **108**, 209 (1924).
- <sup>23</sup> *Fries K., Franke W., Bruns W.*, Ann. Chem. **511**, 241 (1934).
- <sup>24</sup> *Chakrabarty S. N., Dutt S.*, J. Indian Chem. Soc. **5**, 555 (1928).
- <sup>25</sup> *Groggins P. H.*, Unit Processes in Organic Synthesis (Chemical Engineering Series). McGraw-Hill. 1952.
- <sup>26</sup> *Meyer K. H., Irschick A., Schlosser H.*, Ber. **47**, 1741 (1914).
- <sup>27</sup> *Begtrup M., Claramunt R. M., Elgero J.*, J. Chem. Soc., Perkin II **1978**, 99.