

Functional polymers 60. Chemical structure/ ultraviolet spectrum relationship of 2(2-hydroxyphenyl)2H- benzotriazoles: synthesis of novel 2(2-hydroxyphenyl)2H-benzotriazoles*

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The synthesis of several u.v. absorbers of the 2(2-hydroxyphenyl)2H-benzotriazole category is reported. The compounds are of three types: 2(2-hydroxyphenyl)2H-benzotriazoles with one or two substituents located in the benzotriazole moiety of the molecule; 2(2-hydroxyphenyl)2H-benzotriazoles with a substituent in the hydroxy-containing phenyl part of the molecule; and a naphthalene derivative. Syntheses of the 2(2-hydroxyphenyl)2H-benzotriazoles were carried out by the diazotization of a 2-nitroaniline derivative followed by reduction and cyclization, yielding the products in moderate yield. The characterization of the products was carried out by i.r., u.v. and ^{13}C n.m.r. spectroscopy, and included the determination of their molecular weights by elemental analysis and potassium ionization of desorbed species.

(Keywords: u.v.-absorbing polymer; synthesis; characterization)

Introduction

It is widely recognized that sunlight is an important factor in the deteriorative ageing and weathering processes which occur in polymers. Following light absorption, bond dissociation occurs spontaneously with high efficiency to produce free radicals, and these can then start the free-radical photooxidation process via hydrogen atom abstraction¹. Even at low concentrations of chromophoric groups, appreciable quantities of energy may be absorbed. The absorption of energy and its transfer to the bond to be broken may be described as the photophysical aspect of the photodegradation process.

The first chemical step in photodegradation is usually a homolytic bond scission whereby free radicals are formed. If oxygen is present, these free radicals will rapidly react with molecular oxygen to form peroxy radicals which will be very reactive and capable of abstracting a neighbouring hydrogen atom, generating a new free radical and a hydroperoxide. In this way, visible, and specially u.v. radiation, are effective initiators of photooxidation. Such degradation is noticeable in a plastic as a change in colour, such as yellowing, and/or a deterioration of its physical properties.

It is evident that for most polymers, some form of photostabilization is necessary if proper protection against the damaging effects of solar radiation is to be achieved. The photostabilization of light-sensitive polymers involves the retardation or elimination of various photophysical and photochemical processes that take place during photodegradation.

The 2(2-hydroxyphenyl)2H-benzotriazole derivatives are among the most important and widely used stabilizers, because they are excellent u.v. absorbers

and effective photostabilizers for polymeric materials. The stabilizing mechanism of these type of compounds is based on the formation of intramolecular hydrogen bonds between the *o*-hydroxyl group of the phenyl ring and the nitrogen atom of the benzotriazole moiety. For the 2(2-hydroxyphenyl)2H-benzotriazoles, the hydrogen-bonded form provides a facile route for harmlessly deactivating the excited state induced by light absorption. For example, the absorption maximum of 2(2-hydroxy-5-methylphenyl)2H-benzotriazole is found at about 340 nm, with a molar absorptivity coefficient of about $25\,000\text{ l mol}^{-1}\text{ cm}^{-1}$. The capability of intramolecular hydrogen-bond formation was found to be the most important structural element that provides photostability.

Throughout the years, there has been intense activity in the field of synthesis of 2(2-hydroxyphenyl)2H-benzotriazoles, starting with the first description of the synthesis of a 2(2-hydroxyphenyl)2H-benzotriazole by Elbs *et al.*^{2,3}. But it was not realized until the mid 1950s that compounds such as 2(2-hydroxyphenyl)2H-benzotriazole were not only good u.v. absorbers but were very stable compounds in photophysical processes, and were therefore excellent candidates as u.v. stabilizers for polymers⁴. Early synthetic work was carried out in the 1960s^{5–8}.

With increasing demands on the performance of the final moulded plastic product, it is important to prepare polymeric compositions incorporating u.v. absorbers that show a high degree of permanence during the processing steps and afterwards, during the lifetime of the product. Several approaches have been taken towards reaching that goal. One of them is to use molecules that incorporate more than one benzotriazole, specifically, multichromophoric 2(2-hydroxyphenyl)2H-benzotriazoles, with the expectation that one will be able to increase the absorptivity coefficients of the molecule and therefore less of the stabilizer would be needed to stabilize a given polymer, and also, by having a higher

This paper is dedicated to Professor Joachim Klein on the occasion of his 60th birthday with our best wishes

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molecular weight compound, its loss due to volatilization could be reduced.

With that in mind, the synthesis of several compounds of this type has been reported⁹⁻¹³. In one such work⁹, the synthesis and characterization of 2,4[di(2H-benzotriazol-2-yl)]1,3-dihydroxybenzene (DBDH), 2,4[di(2H-benzotriazol-2-yl)]1,3,5-trihydroxybenzene (DBTH) and 2,4,6[tri(2H-benzotriazol-2-yl)]1,3,5-trihydroxybenzene (TBTH) was described. These three compounds have high molecular weights and melting points while showing unusually high absorptivity coefficients of 36 2000, 40 000 and 41 600 l mol⁻¹ cm⁻¹ at wavelength maxima of 325, 340 and 337 nm, respectively. This seems to be in line with an early prediction¹⁴ that the proportion of molecules possessing intramolecular hydrogen-bonded configuration would be increased by (a) the addition of a second hydroxyl group located *ortho* or *para* to the benzotriazole ring, and (b) the presence of bulky alkyl groups located *ortho* to the hydroxyl group.

All of the above multibenzotriazoles are products of the benzotriazolization of polyhydroxylated compounds such as resorcinol and phloroglucinol. In similar work^{11,15}, benzotriazolization of 2,4-dihydroxyacetophenone and 2,4-dihydroxybenzophenone has given the dibenzotriazolized products 3,5[di(2H-benzotriazol-2-yl)]2,4-dihydroxyacetophenone (DBDA) and 3,5[di(2H-benzotriazol-2-yl)]2,4-dihydroxybenzophenone (DBDB). These compounds are effective and useful u.v. stabilizers as they both have the 2(2-hydroxyphenyl)2H-benzotriazole moiety and the 2-hydroxybenzophenone (or acetophenone) moiety in the molecule.

Other multibenzotriazolized 2,4-dihydroxy(acetophenone and benzophenone) molecules with a methoxy substituent in the 4' position of the benzotriazole ring have also been recently prepared¹².

Experimental

Measurements. I.r. spectra were recorded on a Perkin-Elmer model 727, on a Perkin-Elmer 1600 series FTIR or on a Shimadzu IR 435 spectrophotometer. Solid samples of low-molecular-weight compounds were measured in the form of potassium ionization of desorbed species.

¹H n.m.r. spectra were determined on a Varian EM-390 90 MHz spectrometer; the chemical shift values are reported in ppm downfield from tetramethylsilane.

U.v. spectra, unless otherwise specified, were determined in chloroform, on a Varian-Cary 2300 spectrophotometer in a double-beam servo mode.

Melting points were determined in open capillary tubes at a rate of temperature increase of 2°C min⁻¹ on a Mel-Temp melting point apparatus; they are uncorrected.

Column chromatographic separations were carried out on Merck silica-gel 60 (230-400 mesh).

Thin layer chromatography was performed on Analtech Inc. silica-gel GF plates utilizing u.v. and iodine visualization.

Microanalyses were carried out at Microlytics Laboratories, Deerfield, MA (C, H, N, F) or at Schwarzkopf Microanalytical Lab, Woodside, NY (Si).

Molecular-weight determinations (reported in daltons (D)) were obtained from potassium ionization of

desorbed species (K⁺IDS) mass spectrometry and measurements were performed on a modified Finnigan 4615B quadrupole GC/MS system. An electron impact source configuration was used in all experiments. The measurements were carried out in the laboratory of William J. Simonsick Jr at the Marshall R&D Laboratory, E.I. DuPont de Nemours & Co., Philadelphia, PA.

All pertinent spectra are displayed in ref. 16.

Purification of solvents and reagents. For all reactions, the use of Aldrich anhydrous grade solvents (Sure Seal bottles) was found to be adequate. All chemicals, unless otherwise stated, were used as received.

Chloroform spectral grade was used for the absorption spectra and was used as received.

Morpholine was distilled from potassium hydroxide.

The analytical samples were dried over phosphorus pentoxide for 1 day at 50°C and 0.01 mmHg.

Procedures. 1. *Synthesis of 2(2,4-dihydroxyphenyl) 5-fluoro-2H-benzotriazole (FBDH).* A mixture of 4-fluoro-2-nitroaniline (11.7 g, 0.075 mol), concentrated hydrochloric acid (30 ml) and water (90 ml) was cooled to -5°C. Diazotization of what was initially a suspension, was carried out by dropwise addition of a solution of sodium nitrite (5.17 g, 0.075 mol) in water (20 ml) over a 0.5 h period. In the final stage of the addition, the solution became homogeneous. After the addition was completed, the solution was tested for excess unreacted nitrite with starch-iodide paper and a small amount of insoluble material was removed by filtration, while the solution was maintained at low temperature. The clear yellow solution of the diazonium salt was then added through an addition funnel, over a 1 h period, to a solution of resorcinol (16.5 g, 0.15 mol) and hydrochloric acid (30 ml) in water (90 ml) at ambient temperature. The reaction mixture was stirred for 3 h, filtered, and the bright red azocompound which had precipitated was filtered, washed several times with water and dried.

The azocompound was suspended in a 1 N sodium hydroxide solution (325 ml), and Zn powder (19.5 g, 0.3 mol) was added over a period of 0.5 h, while the mixture was stirred. A 40% aqueous solution of sodium hydroxide (70 g) was added over a 1 h period. The mixture was warmed to a temperature of 50-60°C and after a total reaction time of 4 h, the suspension was filtered through a fritted glass filter, the filter cake was washed with 5% sodium hydroxide solution (40 ml) and the combined dark green filtrate was carefully acidified with concentrated hydrochloric acid to a pH of 1. A brownish red precipitate was removed by filtration, the filter cake was washed several times with distilled water (until the washings gave a neutral litmus reaction) and dried. A total of 11.9 g (65%) of crude product was obtained which was purified by recrystallization from ethanol/water. The solid was then dissolved in ethanol, boiled with decolorizing charcoal, filtered, concentrated to near dryness and recrystallized from ethanol; a creamy yellow solid was obtained weighing 9.1 g (49%), m.p. 189.5-190°C. The i.r. spectrum showed a major absorption peak at 3385 cm⁻¹ (phenolic O-H stretch). The u.v. spectrum showed a major absorption band at 341 nm with $\epsilon = 21\,830\text{ l mol}^{-1}\text{ cm}^{-1}$. The ¹H n.m.r. spectrum (DMSO-d₆) showed δ (ppm): 6.5-6.9 and

8.1–8.3 (protons of phenoxy group, 3H), 7.3–7.7 and 7.8–8.1 (protons of benzotriazole group, 3H) and at 10.2 and 10.6 (Ar–OH, 2H, broad doublet). K^+IDS mass spectrum: calcd 245.21 D; found: 245 D.

Elemental analysis for $C_{12}H_8N_3O_2F$: calcd C 58.78%, H 3.29%, N 17.14%; found C 57.91%, H 3.28%, N 16.57%.

2. *2(2,4,6-Trihydroxyphenyl)5-chloro-2H-benzotriazole (CIBTH)*. A mixture of 4-chloro-2-nitroaniline (17.3 g, 0.1 mol), concentrated hydrochloric acid (50 ml) and water (80 ml) was cooled to -5°C . Diazotization was carried out by dropwise addition of a solution of sodium nitrite (6.9 g, 0.1 mol) in water (20 ml) over a 1 h period. The diazotization and the coupling reactions followed procedures described above. The diazonium chloride solution was added to a stirred solution of phloroglucinol (16.2 g, 0.1 mol) in ethanol (60 ml) and water (400 ml) kept at ambient temperature. The reaction was carried out for 3 h; work-up gave 28 g (93%) of the azocompound. For the reduction step, a three-necked round-bottomed flask was charged with the azocompound (21 g, 67.6 mmol) and 1 N sodium hydroxide (500 ml). Zn powder was added portionwise over a 1 h period. The reaction was carried out under a nitrogen atmosphere for 1 day at ambient temperature. The reaction mixture was filtered, the filter cake washed with ethanol, with dichloromethane and again with ethanol; the collected filtrates were acidified with 3 N hydrochloric acid to a pH of *c.* 1 and extracted with dichloromethane. The organic layers were then washed twice with 1 N hydrochloric acid, four times with water and dried over magnesium sulfate. After the solvent was evaporated, a yellow product weighing 12.5 g (67%) was obtained. The product was first recrystallized from ethanol; it was then dissolved in methanol, boiled with decolorizing charcoal, filtered, the solution evaporated to dryness and the residue recrystallized from methanol; pale yellow crystals were obtained, 8.9 g (47%), m.p. $263.5\text{--}265^\circ\text{C}$. The i.r. spectrum showed a peak at 3480 cm^{-1} (phenolic O–H stretch). The u.v. spectrum showed an absorption band at 355 nm with $\epsilon = 25\,560\text{ l mol}^{-1}\text{ cm}^{-1}$. The ^1H n.m.r. spectrum (DMSO- d_6) showed δ (ppm): 6.1 (protons of phenoxy group, 2H, s), 7.5–7.6 and 7.8–8.1 (protons of benzotriazole group, 3H, m) and at 9.9 (Ar–OH, 3H, s). K^+IDS mass spectrum: calcd 277.67 D; found 277 D.

Elemental analysis for $C_{12}H_8N_3O_3Cl$: calcd C 51.91%, H 2.90%, N 15.13%; found C 51.72%, H 3.07%, N 15.03%.

3. *2(2,4-Dihydroxyphenyl)5-chloro-2H-benzotriazole (CIBDH)*. A mixture of 4-chloro-2-nitroaniline (17.3 g, 0.1 mol), concentrated hydrochloric acid (40 ml) and water (100 ml) was cooled to -5°C . Diazotization was carried out by dropwise addition of a solution of sodium nitrite (6.9 g, 0.1 mol) in water (30 ml) over a 0.5 h period. In the final stage of the addition, the solution became homogeneous. The clear yellow filtered solution of the diazonium salt was then added through an addition funnel, over a 1 h period, to a solution of resorcinol (16.5 g, 0.15 mol) and concentrated hydrochloric acid (40 ml) in 150 ml of water. A red azocompound precipitated and the reaction mixture was stirred for 2.5 h, the suspension was filtered and the bright red azocompound was washed several times with water and dried.

A 1 l three-necked round bottomed flask was charged under a nitrogen atmosphere with the azocompound and a 1 N sodium hydroxide solution (500 ml), and Zn powder (33 g, 0.5 mol) was added with stirring over a period of 2 h. Subsequently, a 40% aqueous solution of sodium hydroxide (180 g) was added over a 1 h period. The reaction was carried out at room temperature for 2 days, after which the suspension was filtered through a fritted glass filter, the filter cake washed with 5% sodium hydroxide solution (200 ml) and the combined yellow-green filtrate carefully acidified with concentrated hydrochloric acid to a pH of 5.5–6.0. The suspension containing a light brown precipitate was filtered and the filter cake was washed several times with distilled water until the washings gave a neutral litmus reaction, and was then dried; a crude product weighing 15.3 g (58%) was obtained. The solid was extracted (Soxhlet) for 1 day with a mixture of 5 : 1 acetone : benzene; final purification was carried out by column chromatography using 1 : 3 THF : hexane as eluant; 12.2 g (47%) of CIBDH of m.p. $177\text{--}178^\circ\text{C}$ was obtained. The i.r. spectrum showed a peak at 3220 cm^{-1} (phenolic O–H stretch). The u.v. spectrum showed an absorption band at 346 nm with $\epsilon = 23\,471\text{ l mol}^{-1}\text{ cm}^{-1}$. The ^1H n.m.r. spectrum (DMSO- d_6) showed δ (ppm): 6.5–6.8 and 8.1–8.3 (protons of phenoxy group, 3H), 7.5–7.8 (protons of benzotriazole group) and at 10.4 (Ar–OH, 2H, s). K^+IDS mass spectrum: calcd 261.67 D; found 261 D.

Elemental analysis for $C_{12}H_8N_3O_2Cl$: calcd C 55.08%, H 3.08%, N 16.06%; found C 55.02%, H 3.18%, N 16.02%.

4. *2(2,4-Dihydroxyphenyl)5-morpholino-2H-benzotriazole (MoBDH)*. The synthesis of 5-morpholino-2-nitroaniline (MoA) was carried out following a modified procedure first described by Suhr¹⁷. 5-Chloro-2-nitroaniline was dissolved in DMSO, freshly distilled morpholine was added and the reaction was allowed to proceed at 90°C for 2 days. The reaction mixture was poured into a beaker with water and the solid precipitate was isolated, recrystallized from methanol and gave 18 g (81%) of a very pure yellow solid melting at $184\text{--}186^\circ\text{C}$.

For the preparation of MoBDH, MoA (0.80 g, 3.6 mmol) was suspended in concentrated hydrochloric acid (2.0 ml) and water (5.3 ml) and the suspension cooled to -5°C . Diazotization was carried out by dropwise addition, over a 0.5 h period, of a solution of sodium nitrite (0.25 g, 3.6 mmol) in water (3 ml). In the final stage of the addition, the solution became homogeneous. After the addition was complete, the clear, dark purple solution of the diazonium salt was added through an addition funnel, at room temperature, over a 0.5 h period, to resorcinol (0.55 g, 5 mmol) in a mixture of water (10 ml) and hydrochloric acid (1.0 ml). The bright red azocompound precipitated and the suspension was stirred for 2.5 h, filtered and washed several times with water; the solid was used directly in the next step without further purification. The yield was 1.0 g (81%).

The azocompound was suspended in a 1 N sodium hydroxide solution (30 ml), and Zn powder (1.4 g, 0.021 mol) was added with stirring. A 40% aqueous solution of sodium hydroxide (15 g) was added during a 1 h period, after which the suspension was warmed to 75°C for 6 h (the reduction reaction appears to proceed

sluggishly) and then cooled. The light green suspension was filtered through a fritted glass filter, the filter cake was washed with 5% sodium hydroxide solution (50 ml) and the combined dark green filtrates carefully acidified with concentrated hydrochloric acid to a pH greater than 5. A dark brown precipitate was obtained which was filtered; the filter cake was washed several times with distilled water and then dried, giving 1.8 g of crude product which was extracted for 1 day with ethanol. A very dark solid was recovered after excess solvent was evaporated; yield 0.21 g (19%). Final purification was achieved by column chromatography with a 1:2 THF:hexane solvent mixture; yield 0.07 g (7%); m.p. 237.5–239.5°C. The u.v. spectrum showed a major absorption band at 366 nm with $\epsilon = 21\,520\text{ l mol}^{-1}\text{ cm}^{-1}$ and a molar extinction coefficient of $\epsilon = 51001\text{ mol}^{-1}\text{ cm}^{-1}$ at 400 nm. The ^1H n.m.r. spectrum (DMSO- d_6) showed δ (ppm): 3.0–3.5 (O-CH₂-CH₂-N, 4H, t), 3.5–4.0 (O-CH₂-CH₂-N, 4H, t), 6.5–8.0 (protons of the phenoxy and benzotriazole groups, 6H) and at 10.0 and 10.6 (Ar-OH, 2H, two).

Elemental analysis for C₁₆H₁₆N₄O₃: calcd C 61.53%, H 5.16%, N 17.94%; found C 60.84%, H 5.29%, N 16.59%.

5. 2-(2,4-Dihydroxyphenyl)-5,6-dichloro-2H-benzotriazole (DCIBDH). The diazotization of 4,5-dichloro-2-nitroaniline was carried out following a modified method described in ref. 18. In a 100 ml beaker were placed 40 g of concentrated sulfuric acid, the beaker was cooled in an ice/salt bath and sodium nitrite (3.45 g, 0.05 mol) was added slowly with stirring. The temperature of the mixture was kept below 0°C, and precautions were taken that each portion of sodium nitrite was immediately mixed into the acid (no reddish nitric oxide fumes should form and the solution should not become coloured). Stirring was continued for about 10 min; after all the nitrite had been added, the flask was transferred to a water bath at ambient temperature. When the temperature of the mixture had reached that of the water bath, gentle heating was started and continued until the temperature had reached 70°C. The mixture was stirred at this temperature until all the solid sodium nitrite had dissolved. This step required a total of 2 h. The light yellow, clear solution was then cooled in an ice/water bath to about 20°C, whereby the sulfate of the diazonium salt precipitated. Pulverized 4,5-dichloro-2-nitroaniline (10.8 g, 0.05 mol) was added in small portions with vigorous stirring. A dark red-brown viscous sludge was obtained, which was stirred at room temperature for 1 h. The reaction mixture was then poured into rapidly stirred crushed ice (120 g) and the resultant solution was filtered to remove trace amounts of insoluble material. The diazonium sulfate solution had an orange colour and was used immediately.

Resorcinol (7.7 g, 0.07 mol) was dissolved in water (400 ml) and to this solution was added, over a 30 min period with vigorous mechanical stirring, the diazonium sulfate solution. Almost immediately, a bright red solid separated from the solution. After 2 h stirring, the suspension was filtered, the azocompound was collected by vacuum filtration, washed several times with distilled water and air-dried, giving 17.6 g.

A certain quantity of the azocompound (10.3 g) was suspended in 1 N sodium hydroxide (250 ml), and Zn

powder (10 g) was added in small amounts over a 30 min period. The suspension was warmed to 55°C while a 40% sodium hydroxide solution (50 g) was added slowly. After 1.5 h, the heating was stopped and the reaction was allowed to continue at room temperature for 6 h. The green suspension was filtered, the filter cake washed with two 50 ml portions of 5% sodium hydroxide and the filtrate cooled in an ice/water bath. The solution was slowly acidified with glacial acetic acid to a pH of about 5.5, the dark brown precipitate was collected by vacuum filtration, washed several times with water and dried in a desiccator. A very dark brown impure product was obtained weighing 7.7 g (84%). The product was extracted with benzene (16 h) and with 1:1 ethanol:benzene, recrystallized from 4:1 ethanol:chloroform and from ethanol. It was then passed through a silica-gel-filled chromatographic column using a 1:1 THF:hexane solvent mixture; 3.2 g (35%) of DCIBDH was obtained, m.p. 264–265°C. The i.r. spectrum showed a peak at 3410 cm⁻¹. The u.v. spectrum showed a major absorption band at 338 nm with $\epsilon = 29\,318\text{ l mol}^{-1}\text{ cm}^{-1}$. The ^1H n.m.r. spectrum (DMSO- d_6) showed δ (ppm): 6.5–6.8 and 7.6–7.8 (protons of phenoxy group, 3H, m), 8.6 (protons of benzotriazole group, 2H, s) and 10.2 and 10.5 (Ar-OH, 2H, two singlets). K⁺IDS mass spectrum: calcd 296.11 D; found: 296 D.

Elemental analysis for C₁₂H₇N₃O₂Cl₂: calcd C 48.68%, H 2.38%, N 14.19%; found C 48.39%, H 2.38%, N 13.88%.

6. 2-(2,4-Dihydroxyphenyl)2H-1,3-bis(4-chloro)benzotriazole (CIBBDH). 4-Chloro-2-nitroaniline (35.1 g, 0.2 mol), concentrated hydrochloric acid (100 ml) and water (200 ml) were placed in a 400 ml beaker. The suspension was cooled in an ice/water bath. Diazotization was carried out by dropwise addition of a solution of sodium nitrite (13.8 g, 0.2 mol) in water (50 ml) over a 1 h period, at -5–0°C. The yellow diazonium chloride solution was added dropwise, over a 1 h period, to a stirred solution of resorcinol (11.0 g, 0.1 mol), sodium carbonate (128 g) and sodium hydroxide (40 g) in water (1.0 l). After 6 h, the resulting suspension was filtered and the filter cake was washed with water and dried, giving 37 g (77%) of the azocompound. The azocompound was then suspended in 600 ml of 1 N sodium hydroxide in a 500 ml three-necked round-bottomed flask, and Zn powder (50 g, 0.76 mol) was added in small portions, followed by the addition of a 40% solution of sodium hydroxide (250 g). The reduction was continued under a nitrogen atmosphere and at room temperature for 2 days. The greenish coloured suspension was filtered through a fritted glass filter, the filter cake was washed twice with two 30 ml portions of 5% sodium hydroxide and the dark green filtrate was slowly neutralized (while cooling) with concentrated hydrochloric acid to a pH of about 3.0. A precipitate formed which was collected by filtration, washed several times with water and dried under vacuum. A brown product weighing 13 g (32%) was obtained, which was extracted with benzene and ethanol for 5 days in a Soxhlet extractor. The resulting light brown, still impure solid was recrystallized from 2:1 benzene:ethanol, giving 7.8 g (20%) of yellow powder, m.p. 210–212°C. The u.v. spectrum showed a major absorption band at 341 nm with $\epsilon = 36\,780\text{ l mol}^{-1}\text{ cm}^{-1}$. K⁺IDS mass spectrum: calcd 413.22 D; found: 412 D.

Elemental analysis for $C_{18}H_{10}N_6O_2Cl_2$: calcd C 52.32%, H 2.44%, N 20.34%; found C 52.36%, H 2.40%, N 20.35%.

7. *2-[2-Hydroxy-5-(2-hydroxyethylphenyl)]2H-benzotriazole (HHEPB)*. The following recipe is a modification of a procedure used by Arnold and Renschler¹⁹. In a 500 ml beaker, 2-nitroaniline hydrochloride was prepared by suspending 2-nitroaniline (25 g, 0.18 mol) in concentrated hydrochloric acid (75 ml) and water (200 ml) at a temperature of -5°C . Diazotization was carried out by dropwise addition of a solution of sodium nitrite (12.4 g, 0.18 mol) in water (50 ml) over a 1 h period at $-5-0^{\circ}\text{C}$. In the final stages of addition, the initial suspension became homogeneous. After the addition was completed, a small amount of insoluble material was removed by filtration. The clear orange solution of the diazonium salt was then added through a dropping funnel, over a 2 h period, to a stirred solution of 4-hydroxyphenethyl alcohol (25.0 g, 0.18 mol) in an aqueous (200 ml) solution of sodium carbonate/sodium hydroxide (72 g/14.4 g) kept at room temperature. The reaction mixture was stirred at room temperature for 3 h then filtered, and a dark red azocompound was isolated.

The red solid was placed in a 1 l beaker and 0.6 l of aqueous 1 N sodium hydroxide was added. Zn powder (47 g, 0.72 mol) was added portionwise, over a 0.5 h period, to the mechanically stirred suspension. The temperature of the reaction mixture was then raised to $50-60^{\circ}\text{C}$ and a 40% aqueous solution of sodium hydroxide (100 g) was added over a 1 h period. After a total reaction time of 3.5 h, the suspension was filtered through a fritted glass filter, the filter cake was washed with two 20 ml portions of 5% sodium hydroxide solution, and the combined dark orange filtrate was then carefully acidified with concentrated hydrochloric acid to a pH of 1–2.

The suspension of a light tan precipitate was filtered, and the filter cake was washed with water and then dried; a crude product weighing 26 g (57%) was obtained. Recrystallization from ethanol: water gave 21 g (45%) of a light tan product. The product was again suspended in methanol, boiled with decolorizing charcoal, filtered, evaporated to dryness and recrystallized from methanol, giving 16 g (35%) of a product, m.p. $127-128^{\circ}\text{C}$. The i.r. spectrum showed a peak at 3430 cm^{-1} (phenolic O–H stretching). The u.v. spectrum showed a major absorption band at 345 nm and a smaller band at 300 nm with $\epsilon = 19870$ and $16025\text{ l mol}^{-1}\text{ cm}^{-1}$, respectively. The ^1H n.m.r. spectrum (DMSO- d_6) showed δ (ppm): 2.7–2.9 (Ar-CH₂-CH₂-OH, 2H, t), 3.7–3.9 (Ar-CH₂-CH₂-OH, 2H, t), 7.0–8.1 (protons of phenoxy and benzotriazole groups, 7H). K^+IDS mass spectrum: calcd 255.27 D; found 255 D.

Elemental analysis for $C_{14}H_{13}N_3O_2$: calcd C 65.87%, H 5.13%, N 16.46%; found C 65.65%, H 4.97%, N 16.17%.

8. *3' [5(2H-Benzotriazol-2-yl)4-hydroxyphenyl]propionic acid (BHPA)*. In a 500 ml beaker, 2-nitroaniline hydrochloride was prepared by suspending 2-nitroaniline (41.4 g, 0.3 mol) in concentrated hydrochloric acid (150 ml) and water (300 ml) at -5°C . Diazotization was carried out by dropwise addition of a solution of sodium nitrite (20.7 g, 0.3 mol) in water (70 ml) over a 1 h period while keeping the bath temperature at -5°C . In the final stages of addition, the mixture became homogeneous.

After the addition was complete, a small amount of insoluble material was removed by filtration. The orange coloured solution of the diazonium chloride salt was added through a dropping funnel, over a 1 h period, to a mechanically stirred solution of 3-(4-hydroxyphenyl)propionic acid (51 g, 0.3 mol) and sodium carbonate/sodium hydroxide (192 g/60 g) in water (1.5 l). The reaction mixture was stirred at room temperature for 3.5 h, acidified to a pH of about 1 with concentrated hydrochloric acid, filtered, and the filter cake washed with water (2.5 l). After drying, a dark red powder weighing 87 g (92%) was obtained.

A 2.0 l beaker was charged with 1.0 l of aqueous 1 N sodium hydroxide, the azocompound was suspended, under mechanical stirring, and Zn powder (88 g, 1.35 mol) was added portionwise over a 1 h period followed by a 40% sodium hydroxide solution (300 g) which was added dropwise over a 30 min period. The suspension was stirred for 3 days, filtered through a fritted glass filter, the filter cake was washed twice with 50 ml portions of 5% sodium hydroxide, and the orange coloured filtrate was carefully acidified with concentrated hydrochloric acid to a pH of about 2. A light brown solid was collected by filtration, washed several times with water and dried; 44 g (57%) of crude product was obtained. The solid was extracted with ethanol for 3 days, and recrystallized several times from ethanol; 28 g (33%) of pure BHPA was obtained. The i.r. spectrum showed a broad peak at 3150 cm^{-1} (carboxylic acid O–H stretch) and a peak at 1720 cm^{-1} (carboxylic acid C=O stretch). The u.v. spectrum showed a major absorption band at 340 nm and a smaller band at 300 nm, with $\epsilon = 17480$ and $14290\text{ l mol}^{-1}\text{ cm}^{-1}$, respectively. The ^1H n.m.r. spectrum (DMSO- d_6) showed δ (ppm): 2.5–2.7 (Ar-CH₂-CH₂-C(O)OH, 2H, t), 2.8–3.0 (Ar-CH₂-CH₂-C(O)OH, 2H, t), 7.1–8.2 (protons of the phenoxy and benzotriazole groups, 7H). K^+IDS mass spectrum: calcd 283.29 D; found: 283 D.

Elemental analysis for $C_{15}H_{13}N_3O_3$: calcd C 63.59%, H 4.63%, N 14.83%; found C 63.38%, H 4.44%, N 14.86%.

9. *2(2-Hydroxynaphthalene)2H-benzotriazole (1B2HN)*. A mixture of 2-nitroaniline (13.8 g, 0.1 mol), concentrated hydrochloric acid (40 ml) and water (100 ml) was cooled to -5°C . Diazotization was carried out by dropwise addition of a solution of sodium nitrite (6.9 g, 0.12 mol) in water (20 ml) over a 0.5 h period. In the final stage of the addition, the solution became homogeneous. After the addition was complete, the clear yellow solution of the diazonium salt was added through an addition funnel, over a 1 h period, to 2-hydroxynaphthalene (17.3 g, 0.12 mol) in a solution of water (250 ml) and ethanol (250 ml) at room temperature. The reaction mixture was stirred for 3.5 h, filtered, and the bright red azocompound which precipitated was isolated by filtration; the filter cake was washed several times with water and used directly in the next step.

The azocompound was suspended in a 1 N sodium hydroxide solution (600 ml), and Zn powder (46 g, 0.7 mol) was added with stirring (1 h), followed by the addition of a 40% aqueous solution of sodium hydroxide (80 g) (1 h). The suspension was warmed to $50-60^{\circ}\text{C}$, allowed to proceed for 4 h and then cooled. After an additional 16 h at room temperature, the light green suspension was filtered through a fritted glass filter, the

filter cake was washed with a 5% sodium hydroxide solution (50 ml) and the combined filtrate was carefully acidified with concentrated hydrochloric acid to a pH of about 1. The suspension containing a brown precipitate was filtered; the filter cake was washed several times with distilled water then dried, and gave 23 g (87%) of crude product. Recrystallization from ethanol/water, with a final purification by passing a solution of the compound through a silica-gel-filled column, gave a creamy yellow product with m.p. 145.5–147°C. The i.r. spectrum showed a peak at 3185 cm^{-1} (O–H stretch) and at 1650 cm^{-1} (C=C stretch). The u.v. spectrum showed two absorption bands at 354 and 320 nm, with $\epsilon = 11\,750$ and $11\,290\text{ l mol}^{-1}\text{ cm}^{-1}$, respectively. K^+IDS mass spectrum: calcd 261.28 D; found 261 D.

Elemental analysis for $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}$: calcd C 73.55%, H 4.24%, N 16.08%; found C 72.96%, H 4.52%, N 15.95%.

10. *2(4-Hydroxynaphthalene)2H-benzotriazole (4B1HN)*. A mixture of 2-nitroaniline (13.8 g, 0.1 mol), concentrated hydrochloric acid (40 ml) and water (100 ml) was cooled to -5°C . Diazotization was carried out by dropwise addition of a solution of sodium nitrite (6.9 g, 0.1 mol) in water (20 ml) over a 0.5 h period. The clear yellow solution of the diazonium chloride salt was then added through an addition funnel to a solution of 1-hydroxynaphthalene (21.6 g, 0.15 mol) in a mixture of concentrated hydrochloric acid (40 ml), water (200 ml) and methanol (200 ml) at 10°C . The reaction mixture, a suspension, was stirred for 3 h and filtered; the bright red azocompound was washed several times with water and used directly for the next step.

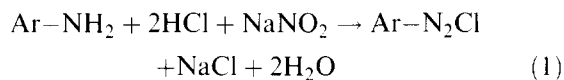
The azocompound was suspended in a 1 N sodium hydroxide solution (600 ml), then Zn powder (26 g, 0.4 mol) was added with stirring over a period of 20 min, followed by the addition, over a 1 h period, of 80 g of a 40 wt% aqueous solution of sodium hydroxide. The suspension was warmed to $50\text{--}60^\circ\text{C}$ and the reaction allowed to proceed for 3 h, then it was cooled to room temperature and the green suspension was filtered through a fritted glass filter. The filter cake was washed with 50 ml of a 5 wt% sodium hydroxide solution, and the combined dark green filtrate was carefully acidified with concentrated hydrochloric acid to a pH of *c.* 1. A purple precipitate was obtained which was filtered; the filter cake was washed several times with water and dried giving 21 g (80%) of crude product. It was purified by dissolving in a 1:1 ethanol:acetone mixture; the solution was added to an excess of water and gave 12.5 g (49%) of a light yellow product, m.p. $200\text{--}202^\circ\text{C}$. The u.v. spectrum showed a major absorption band at 219 nm and a minor band at 316 nm, with $\epsilon = 40\,300$ and close to 3-unit $15\,860\text{ l mol}^{-1}\text{ cm}^{-1}$, respectively. K^+IDS mass spectrum: calcd 261.28 D; found 261 D.

Elemental analysis for $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}$: calcd C 73.55%, H 4.24%, N 10.08%; found C 74.27%, H 4.36%, N 15.63%.

Results and discussion

The synthesis of 2(2-hydroxyphenyl)2H-benzotriazoles involves the diazotization of an *o*-nitroaniline with sodium nitrite in a strongly acidic medium, generating a diazonium salt which is coupled (under either basic or acidic conditions) with a substituted

phenol. This reaction produces an orange to crimson azocompound¹⁸:



According to equation (1), two equivalents of mineral acid are essential for a smooth reaction. In practice, an excess of at least one-half an equivalent of acid is usually added at the beginning.

Coupling reactions of azocompounds have been carried out with a wide variety of substituted phenols. Fierz-David¹⁸ and Zollinger²⁰ have given excellent accounts of the chemistry of azo- and diazocompounds, including the synthesis of the intermediate diazonium salts, the mechanism of their formation and the coupling reaction.

For the synthesis of 2(2-hydroxyphenyl)2H-benzotriazoles, the *o*-hydroxy azocompounds are subsequently reduced with sodium dithionate or Zn powder in a strongly basic medium of aqueous sodium hydroxide. The formation of a green coloured suspension indicates that the reduction–cyclization reaction has taken place. The synthesis of FBDH followed a synthetic scheme which is general to all the rest of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives.

FBDH was prepared from the diazonium salt of 4-fluoro-2-nitroaniline and resorcinol. The initially formed bright red azocompound was reduced in sodium hydroxide solution with zinc powder. A creamy yellow product was isolated in about 50% yield which had a melting point of $189.5\text{--}190^\circ\text{C}$. The u.v. absorption spectrum of FBDH in chloroform showed an absorption band at 341 nm with a molar extinction coefficient of $21\,830\text{ l mol}^{-1}\text{ cm}^{-1}$ and a shoulder at 295 nm, with $\epsilon = 7600\text{ l mol}^{-1}\text{ cm}^{-1}$. The ratio of the intensities of the peak and shoulder, $\text{Abs}(341)/\text{Abs}(295)$, was 2.87.

The i.r. spectrum showed an absorption peak at 3385 cm^{-1} corresponding to the phenolic O–H stretch. The ^1H n.m.r. spectrum of FBDH showed multiple peaks at 6.5–6.9 and 8.1–8.3 due to the phenoxy protons, and at 7.3–8.1 due to the benzotriazole protons. It also showed two broad overlapping peaks at 10.2 and 10.6 ppm, which were assigned to the hydroxyl groups.

K^+IDS is a mass spectrometric technique for molecular weight determination of oligomeric and low-molecular-weight polymeric compounds with minimal molecular fragmentation²¹. The components evolved are detected by electron impact mass spectrometry and the molecular weight is determined by subtracting from the pseudomolecular ion peak ($[\text{M}]\text{K}^+$) the atomic weight of the potassium ion (39.1 D).

For FBDH, the elemental analysis as well as the K^+IDS spectrum were consistent with the proposed structure.

CIBTH was prepared from 4-chloro-2-nitro-aniline and 1,3,5-trihydroxybenzene (phloroglucinol). It was obtained in 67% yield as pale yellow crystals with a melting point of $263.5\text{--}265^\circ\text{C}$.

The u.v. absorption spectrum of CIBTH in chloroform showed a single absorption band at 355 nm with a molar extinction coefficient of $\epsilon = 25\,560\text{ l mol}^{-1}\text{ cm}^{-1}$. The compound showed a significant molar extinction coefficient of $\epsilon = 850\text{ l mol}^{-1}\text{ cm}^{-1}$ at 400 nm.

The i.r. spectrum showed an absorption peak at 3480 cm^{-1} corresponding to the phenolic O–H stretch. The ^1H n.m.r. spectrum of CIBTH showed a sharp peak at 6.1 ppm due to the two protons of the phenoxy group, multiple peaks at 7.5–8.1 due to the three benzotriazole protons, and a singlet at 9.9 ppm due to the three hydroxyl protons. Overall, the ratio of integrated peak areas was consistent with the proposed structure and the K^+IDS spectrum showed the molecular weight of CIBTH to be 277 D.

CIBDH was prepared from 4-chloro-2-nitroaniline and 1,3-dihydroxybenzene (resorcinol) in about 50% yield as a light yellow powder with m.p. $177\text{--}178^\circ\text{C}$.

The u.v. spectrum of CIBDH in chloroform showed an absorption band at 346 nm, with $\epsilon = 23471\text{ l mol}^{-1}\text{ cm}^{-1}$. There is a small shoulder at c. 300 nm with about one-fifth the intensity of the 346 nm band. The compound showed a very small absorption of $130\text{ l mol}^{-1}\text{ cm}^{-1}$ at 400 nm.

The i.r. spectrum of CIBDH showed an absorption peak at 3220 cm^{-1} due to the phenolic –OH stretch. The ^1H n.m.r. spectrum showed multiple peaks between 6.5 and 8.3 ppm, corresponding to the six phenoxy and benzotriazole protons, and a broadened singlet peak at 10.4 ppm due to the two hydroxyl protons.

MoBDH was synthesized from 5-morpholino-2-nitroaniline. The substitution reaction with morpholine was attempted directly on FBDH without success.

It is apparently necessary that the *ortho* or *para* positions be occupied by a strong electron-withdrawing substituent, such as the nitro group, to promote the reaction. Another requirement is that the substrate should have a good leaving group, such as fluoro or chloro. The solvent medium also plays a very important role in stabilizing the ionic transition state. Bernasconi *et al.*²² determined that this type of reaction proceeded best in DMSO, a highly polar, non-hydrogen-bonding solvent.

5-Chloro-2-nitroaniline was dissolved in DMSO and the substitution product was obtained in 80% yield, with m.p. $184\text{--}186^\circ\text{C}$. 5-Morpholino-2-nitroaniline was diazotized with sodium nitrite and the diazonium chloride salt was coupled with 1,3-dihydroxybenzene to the azocompound. Reductive cyclization gave MoBDH in 20% yield of pure product with m.p. $237.5\text{--}239.5^\circ\text{C}$. MoBDH is quite sensitive to air and the reductive cyclization should be carried out in a nitrogen atmosphere.

The most relevant features in the ^1H n.m.r. spectrum of MoBDH are the two triplets at 3.0–3.5 and at 3.5–4.0 ppm, due to the four protons of the methylene groups adjacent to the nitrogen atom, and to the four methylene protons adjacent to the oxygen atom, respectively. The spectrum also showed multiplets between 6.5 and 8.0 ppm due to the six phenoxy and benzotriazole protons; the two hydroxyl protons show as two separate singlets at 10.0 and 10.6 ppm. The ratio of integrated peak areas was consistent with the proposed structure.

The u.v. spectrum of MoBDH in chloroform proved to be interesting. It showed a major band at 364 nm with $\epsilon = 20896\text{ l mol}^{-1}\text{ cm}^{-1}$ and also a minor band at around 300 nm. The tail of the absorption band extends well into the visible region, and at 400 nm the molar extinction coefficient is $4460\text{ l mol}^{-1}\text{ cm}^{-1}$. The spectrum of

MoBDH in methylene chloride again showed a major absorption band at 364 nm, with $\epsilon = 21152\text{ l mol}^{-1}\text{ cm}^{-1}$. There was a minor band at around 295 nm, again with an absorption tailing into the visible region with $\epsilon = 4890\text{ l mol}^{-1}\text{ cm}^{-1}$ at 400 nm.

For the synthesis of DCIBDH, 4,5-dichloro-2-nitroaniline was carefully diazotized in concentrated sulfuric acid with sodium nitrite. The diazonium solution was added to 1,3-dihydroxybenzene. A red azocompound was obtained which was isolated and reduced in an alkaline solution with zinc powder and gave 35% of DCIBDH with m.p. $264\text{--}265^\circ\text{C}$.

The u.v. spectrum of DCIBDH in chloroform showed a major band at 338 nm with $\epsilon = 29318\text{ l mol}^{-1}\text{ cm}^{-1}$ and a shoulder at around 295 nm.

The i.r. spectrum of DCIBDH showed an absorption peak at 3410 cm^{-1} corresponding to the phenolic hydroxyl group. The ^1H n.m.r. spectrum showed multiple peaks between 6.5 and 6.8 and a doublet between 7.6 and 7.8 ppm, corresponding to the three phenoxy protons, and a sharp singlet at 8.6 ppm due to the two benzotriazole protons. It also showed the two hydroxyl protons as two separate singlets at 10.2 and 10.5 ppm. The peak at 10.5 ppm could be assigned to the *ortho*-hydroxyl proton hydrogen bonded to the benzotriazole ring.

CIDBDH was prepared from 4-chloro-2-nitroaniline and 1,3-dihydroxybenzene (resorcinol). The intermediate azocompound was reduced in sodium hydroxide solution with zinc powder. Pure CIDBDH was obtained in 20% yield as a yellow powder with m.p. $210\text{--}212^\circ\text{C}$.

The i.r. spectrum of CIDBDH showed an absorption peak at 3220 cm^{-1} due to the phenolic stretch. The u.v. spectrum of CIDBDH in chloroform showed an intense absorption band at 341 nm, with $\epsilon = 36780\text{ l mol}^{-1}\text{ cm}^{-1}$.

HHEPB was prepared from 2-nitroaniline and 4-hydroxyphenethyl alcohol. The azo intermediate was reductively cyclized in a sodium hydroxide solution with zinc powder and gave HHEPB in 35% yield, m.p. $127\text{--}128^\circ\text{C}$. The elemental analysis, i.r. and ^1H n.m.r. spectra of HHEPB were consistent with the expected structure.

The u.v. spectrum of HHEPB in chloroform showed a major absorption band at 335 nm, with $\epsilon = 16661\text{ l mol}^{-1}\text{ cm}^{-1}$. There is also a band at 296 nm with $\epsilon = 13706\text{ l mol}^{-1}\text{ cm}^{-1}$ and a ratio $\text{Abs}(335)/\text{Abs}(296)$ of 1.22.

The i.r. spectrum of HHEPB showed an absorption peak at 3430 cm^{-1} due to the phenolic stretch. The ^1H n.m.r. spectrum showed two triplets at 2.7–2.9 and 3.7–3.9 ppm which are due to the protons of the methylene groups immediately adjacent to the phenoxy and the hydroxyl groups, respectively. It also showed multiplets between 7.0 and 8.1 ppm, corresponding to the seven protons of the phenoxy and benzotriazole groups. A very broad band at c. 10.6 ppm is based on the phenolic proton.

BHPA was prepared from 2-nitroaniline and 3(4-hydroxyphenyl)propionic acid. The intermediate azocompound was reduced as usual and gave BHPA as a yellow powder in 33% yield.

The u.v. spectrum of BHPA in chloroform showed two absorption bands, a major band at 340 nm with $\epsilon = 17480\text{ l mol}^{-1}\text{ cm}^{-1}$, and a second less intense band

at 303 nm with $\epsilon = 14\,290\text{ l mol}^{-1}\text{ cm}^{-1}$. The ratio $\text{Abs}(340)/\text{Abs}(303)$ is 1.22.

The i.r. spectrum of BHPA showed a broadened absorption peak at 3150 cm^{-1} due to the carboxylic acid O–H stretch, and a peak at 1720 cm^{-1} due to the carboxylic acid C=O stretch. The ^1H n.m.r. spectrum of BHPA showed triplets at 2.5–2.7 and at 2.8–3.0 ppm, due to the two protons of the methylene groups adjacent to the carboxylic acid group and to the two protons of the methylene adjacent to the phenoxy group, respectively. The spectrum also showed multiplets between 7.1 and 8.2 due to the seven phenoxy and benzotriazole protons.

1B2HN and 4B1HN were synthesized in order to determine the effect of coupling the 2H-benzotriazole moiety on the electronic absorption spectrum of a polyaromatic molecule such as naphthalene. 1B2HN and 4B1HN were prepared from 2-nitroaniline and 2-hydroxynaphthalene or 1-hydroxynaphthalene, respectively. In either case, the intermediate azocompound precipitated from the solution and was reduced in a sodium hydroxide solution with zinc powder. 1B2HN with m.p. $145.5\text{--}147^\circ\text{C}$ and 4B1HN with m.p. $200\text{--}202^\circ\text{C}$ (light yellow powder) were obtained.

The u.v. spectrum of 1B2HN in chloroform showed several absorption bands. The major absorption band is found at 354 nm, with $\epsilon = 11\,750\text{ l mol}^{-1}\text{ cm}^{-1}$. A second band is found at 320 nm with $\epsilon = 11\,290\text{ l mol}^{-1}\text{ cm}^{-1}$, with a shoulder at 310 nm with $\epsilon = 10\,070\text{ l mol}^{-1}\text{ cm}^{-1}$. Another band is found at 265 nm with $\epsilon = 9920\text{ l mol}^{-1}\text{ cm}^{-1}$ and a shoulder at 277 nm with $\epsilon = 8320\text{ l mol}^{-1}\text{ cm}^{-1}$.

The u.v. spectrum of 4B1HN in chloroform showed one single major absorption band above 220 nm, specifically at 316 nm, with $\epsilon = 15\,860\text{ l mol}^{-1}\text{ cm}^{-1}$. Not unexpectedly, this absorption band is very similar in shape and intensity to the absorption band of 2(4-hydroxy-2-methylphenyl)2H-benzotriazole, as shown in ref. 13.

Conclusions

The syntheses of several mono- and disubstituted 2(2-hydroxyphenyl)2H-benzotriazole derivatives were reported. Their characterization was carried out by elemental analysis and by spectroscopic means. The synthesis of the compounds proceeds through the formation of the diazonium chloride salt and by its reaction with a di- or trihydroxybenzene; an isolatable compound, the azocompound, is formed. Subsequent

reduction in a strongly basic medium with elemental zinc allows the formation of the benzotriazole derivative, usually in yields of the pure product in the range of 7–55 wt%, typically around 35–50 wt%.

Potassium ionization of desorbed species has proved to be a useful spectroscopic technique for the determination of the elemental composition of the benzotriazoles and also, as will be shown in a future article, for the determination of the molecular weights of isomers and low-molecular-weight 2(2-hydroxyphenyl)2H-benzotriazole containing oligomers.

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REFERENCES

- 1 Allen, N.S. *Chem. Soc. Rev.* 1986, **15**, 373
- 2 Elbs, K. and Keiper, W. *J. Prakt. Chem.* 1905, **67**(2), 580
- 3 Elbs, K., Hirschel, O., Himmler, K., Turk, W., Henrich, A. and Lehmann, E. *J. Prakt. Chem.* 1924, **108**, 209
- 4 Gantz, G.N. and Summer, W. *Text. Res. J.* 1957, **27**, 244
- 5 Milionis, J. and Hardy, W. US patent 3 159 646, 1964
- 6 Karvas, M. and Holcik, J. *Chem. Rev.* 1967, **17**(10), 543
- 7 Balaban, L., Borkovec, J. and Rysavy, D. Czech. patent 108 792, 1963
- 8 J.R. Geigy A.G. Swiss patents 408 942, 410 968, 434 280; French patents 1 324 898, 1 325 404, 1 325 406; US patents 3 218 332, 3 629 191, 3 629 192, 1961
- 9 Li, S.J., Gupta, A. and Vogl, O. *Monatsh. Chem.* 1983, **114**, 937
- 10 Xi, F., Bassett, W. Jr and Vogl, O. *Makromol. Chem.* 1984, **185**(12), 2497
- 11 Li, S.J., Bassett, W. Jr, Gupta, A. and Vogl, O. *J. Macromol. Sci., Chem.* 1983, **A20**(3), 309
- 12 Fu, S.K., Li, S.J. and Vogl, O. *Monatsh. Chem.* 1986, **117**, 805
- 13 Li, S.J., Bassett, W. Jr, Xi, F. and Vogl, O. *Acta Polym.* 1985, **36**(2), 81
- 14 Heller, H.J. *Eur. Polym. J. Suppl.* 1969, **89**, 105
- 15 Vogl, O. and Li, S.J. US patent 4 745 194, 1988
- 16 Sustic, A. PhD thesis, Polytechnic University, Brooklyn, NY, 1992
- 17 Suhr, H. *Chem. Berichte* 1964, **97**, 3268
- 18 Fierz-David, H.E. and Blangley, L. in 'Fundamental Processes of Dye Chemistry', Interscience Publishers, New York, 1949, p. 241
- 19 Arnold, C. Jr and Renschler, C.L. *Polym. Commun.* 1988, **29**, 95
- 20 Zollinger, H. in 'Azo and Diazo Chemistry', Interscience Publishers, New York, 1965, pp. 137–175
- 21 Simonsick, W.J. *J. Appl. Polym. Sci.* 1989, **43**, 257
- 22 Bernasconi, C.F., Kaufmann, M. and Zollinger, H. *Helv. Chem. Acta* 1966, **49**(8), 2563