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Functional Polymers, XL**
Syntheses of Mono- and Di(4-methoxy)benzotriazole-Substituted 2,4-Dihydroxyaceto(or benzo)phenones***

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Eight benzotriazoles and (4-methoxy)benzotriazoles, mono- or di-substituted derivatives of 2,4-dihydroxyaceto(or benzo)phenone were synthesized by azo coupling of (4-methoxy)2-nitrobenzenediazonium chloride with 2,4-dihydroxyaceto(or benzo)phenone followed by reductive cyclization. Pure mono-substituted compounds were very difficult to prepare. Careful selection of the *pH* for the azo coupling and selection of the proper reagents for the reductive cyclization were essential. All compounds were characterized by their ultraviolet, infrared ^{1}H and ^{13}C NMR spectra and their elemental analysis. These compounds have both the 2(2-hydroxyphenyl)2*H*-benzotriazole unit and a 2-hydroxyaceto(or benzo)phenone unit in the same molecule and are effective and useful ultraviolet absorbers.

(Keywords: Functional polymers; 2(2-Hydroxyphenyl)2 H-benzotriazoles; 2-Hydroxyphenylaceto(benzo)phenones; Azo coupling; Reductive cyclization; Ultraviolet stabilizers)

Funktionelle Polymere, 40. Mitt.: Synthese von mono- und di(4-methoxy)benzotriazol-substituierten 2,4-Dihydroxyaceto(oder benzo)phenonen

Es wurden acht Benzotriazole und 4-Methoxybenzotriazole — mono- oder disubstituierte Derivate von 2,4-Dihydroxyaceto(oder benzo)phenonen — über Azokopplung von 4-Methoxy-2-nitrobenzoldiazoniumchlorid mit 2,4-Dihydroxyaceto(oder benzo)phenonen und nachfolgender reduktiver Cyclisierung synthetisiert. Reine monosubstituierte Verbindungen waren sehr schwer herzustellen. Sorgfältige Wahl des *pH*-Wertes für die Azo-Kupplung und geeignete Reagentien für die reduktive Cyclisierung waren dabei wesentlich. Alle Verbindungen wurden mittels UV-, IR-, ^{1}H-NMR- und ^{13}C-NMR-Spektren und

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*** Dedicated to Prof. Dr. *K. Komarek,* Vienna, on the occasion of his 60th birthday with best wishes.

Elementaranalysen charakterisiert. Die synthetisierten Verbindungen besitzen jeweils eine 2-(2-Hydroxyphenyl)-2*H*-benzotriazol-Einheit *und* eine 2-Hydroxyaceto(oder benzo)phenon-Einheit im gleichen Molekül und stellen effektvolle und nützliche Ultraviolett-Absorber dar.

Introduction

2(2-Hydroxyphenyl)2*H*-benzotriazoles with various substituents in the benzotriazole and/or the phenol rings are well known as ultraviolet-absorbing compounds, and effective ultraviolet stabilizers[1—3], especially for plastics materials. Recently, attention has focused on less volatile, more compatible, polymerizable, polymeric and polymer-bound ultraviolet stabilizers of the 2(2-hydroxyphenyl)2*H*-benzotriazole (2BH) family[4—11]. Ultraviolet stabilizers of the 2-hydroxybenzophenone type are also well known and are still being used extensively for ultraviolet stabilization of polymeric materials. Some polymerizable 2-hydroxybenzophenone ultraviolet stabilizers[12, 13] are now commercially available.

We have already reported the synthesis of dibenzotriazole-substituted 2,4-dihydroxyaceto(or benzo)phenone (*DBAP, DBBP*) which combine 2(2-hydroxyphenyl)2*H*-benzotriazole and 2-hydroxybenzo(aceto)phenone chromophores in the same molecule[14]. These two compounds, as excepted, have unusual spectral characteristics with high extinction coefficients between 250 nm and 350 nm and an almost complete cut-off of the absorption below 400 nm. At the time of this research, all attempts to synthese monobenzotriazole-substituted 2,4-hydroxyaceto(or benzo)phenones (*BAP, BBP*) had been unsuccessful.

The objective of this work was to synthesize *BAP* and *BBP*, to complete the synthesis of the series of mono-and di(4-methosy-) benzotriazole-substituted 2,4-dihydroxyaceto(or benzo)phenone and to study their characteristics as ultraviolet absorbers. The acetophenone structures were also considered useful as intermediates for the preparation of the corresponding vinyl and isopropenyl derivatives, polymerizable ultraviolet-absorbing compounds of the 2HB category[10, 15].

Experimental Part

2-Nitroaniline (Eastman Kodak Co.) was used as received. 4-Methoxy-2-nitroaniline (Aldrich Chemical Co.) was recrystallized from aqueous ethanol solution (ethanol/water, 6/1). 2,4-Dihydroxyacetophenone (Aldrich Chemical Co.) was recrystallized from a dilute solution of hydrochloric acid (water/conc. hydrochloric acid, 12/1). 2,4-Dihydroxybenzophenone (Aldrich Chemical Co.) was used as received.

Sodium nitrite (97%, Aldrich Chemical Co.), urea (Aldrich Chemical Co.), zinc powder, sodium hydrosulfite (purified grade), sodium hydroxide, sodium

carbonate, sodium acetate, and acetic acid (Fisher Chemical Co.) were used as received.

Solvents such as benzene, chloroform, acetone, and ethanol were used as received. Deuterochloroform (99.8% D) and dimethylsulfoxide-d_6 (99.9% D) were obtained from the Aldrich Chemical Co.

Infrared spectra were recorded on a Perkin-Elmer spectrometer, Model 727; solid samples were measured in the form of potassium bromide pellets.

^{1}H NMR Spectra were recorded on a Varian A-60 spectrometer or on a Varian EM 390 spectrometer, the ^{13}C NMR spectra on a Varian CTF-20 spectrometer with complete proton decoupling; *TMS* was used as the internal standard. All compounds were measured in $CDCl_3$ or *DMSO*-d_6 in 10% or saturated solutions.

Ultraviolet absorption spectra were measured in chloroform (Spectrograde, Aldrich Chemical Co.) solutions on a Beckman M VI spectrometer or on a Varian Cary 2300 spectrophotometer in a double-beam servo mode (1.0 cm optical path length). The maximum absorbances and corresponding wavelengths were determined by dialing in the wavelength and recording the absorbance values presented on the digital display.

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.

Di(4-methoxy)benzotriazole-Substituted 2,4-Dihydroxyaceto(or benzo)phenone

Four di-substituted 2(2-hydroxyphenyl)2*H*-benzotriazoles were prepared: (a) 3,5[Di(2*H*-benzotriazole-2-yl)]2,4-dihydroxyacetophenone (*DBAP*)*, (b) 3,5-[di(2*H*-benzotriazole-2-yl)]2,4-dihydroxybenzophenone (*DBBP*)**, (c) 3,5[di-(2*H*-4′-methoxybenzotriazole-2-yl)]2,4-dihydroxyacetophenone (*DMBAP*)***, and (d) 3,5[di(2*H*-4′-methoxybenzotriazole-2-yl)]2,4-dihydroxybenzophenone (*DMBBP*)****.

The syntheses of *DBAP* and *DBBP* have already been reported[14, 15]. In our continuing work, we found that during the final step, the reductive cyclization with zinc powder, the major portion of the product became tightly bound to the insoluble residue, primarily zinc powder and other zinc-containing reaction products, and it was difficult to extract all the actual reaction products from the zinc sludge with dilute alkali solution. We have now improved the work-up, which increased the yield of *DBAP* and *DBBP* to 50% compared to the previously reported yields of 32% and 9%, respectively. We are reporting in this paper the improved procedure of the synthesis.

Preparation of DBAP. A solution of 2-nitroaniline (27.6 g, 0.2 mol) in dilute hydrochloric acid solution (120 ml conc. hydrochloric acid/water, 1/1) was diazotized with a solution of sodium nitrite (14.0 g, 0.2 mol) in water (50 ml) at 0 °C. After completing the addition of sodium nitrite, the mixture was allowed to stir for 0.5 h and was tested with starch-potassium iodide test paper until the iodine reaction was negative.

The cold solution of 2-nitrobenzenediazonium chloride was added over a period of 1 h, with stirring, to a solution of 2,4-dihydroxyacetophenone (15.2 g,

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* [2(2,4-Dihydroxy-5-acetylphenyl)1,3-2*H*-bisbenzotriazole].

** [2(2,4-Dihydroxy-5-benzoylphenyl)1,3-2*H*-bisbenzotriazole].

*** [2(2,4-Dihydroxy-5-acetylphenyl)1,3-2*H*-bis(4-methoxy)benzotriazole].

**** [2(2,4-Dihydroxy-5-benzoylphenyl)1,3-2*H*-bis(4-methoxy)benzotriazole].

Table 1. *Ultraviolet absorption of mono- and di-(methoxy)benzotriaz*

Compound	λ_{max} (nm)	ε (l/mol·cm)·10^{-4}	λ_{max} (nm)
BAP	243	1.35	283
DBAP	252	2.45	273
MBAP	248	1.79	285
DMBAP	248	3.03	278
BBP	248	1.55	—
DBBP	246	2.15	285
MBBP	248	1.80	294 (sh)
DMBBP	249	2.80	285

[a] Absorption determined in chloroform solution. Concentration: $2 \cdot 10^{-5}$ mol/l.

0.1 mol), sodium hydroxide (8 g, 0.2 mol), and sodium carbonate (45 g, 0.36 mol) in water (450 ml) at 5–10 °C, during which time a red precipitate of the azo compound appeared. The suspension was filtered and the filter cake was washed three times with water (about 60 °C), the filter cake was dissolved in 300 ml aqueous 2 *N* sodium hydroxide (0.6 mol) and the reductive cyclization of the azo compound was carried out with zinc dust (60 g, 0.92 mol) under nitrogen at 50 °C in 1 h. During this reductive cyclization, additional 40% sodium hydroxide solution (75 ml) was added dropwise; the mixture was then allowed to continue to react at room temperature for one day.

The suspension was separated by filtration and the filtrate was acidified at ~ 10 °C to *pH* 1 with dilute hydrochloric acid (1 : 1); a solid precipitated, which was isolated by filtration and air dried (crude *DBAP*). The filter cake consisting of a mixture of zinc powder and the residue of the main reaction product was treated with hydrochloric acid (1 : 1) to dissolve the zinc salts. The suspension was filtered to isolate crude *DBAP* which was air dried. The combined products of *DBAP* were extracted for 2 days with benzene in a *Soxhlet* extractor; *DBAP* (19.4 g, 50% yield) was isolated from the benzene extract. Recrystallization from chloroform and benzene (1 : 1) gave pure *DBAP* as pale yellow needle crystals, m.p. 272–274 °C. The ultraviolet absorption data are shown in Table 1 and the spectra in Fig. 1. IR (KBr): 3 420 cm^{-1} (O—H stretching).

^1H NMR: δ 2.7 (CH_3, 3 H, singlet), 7.2–7.6 and 7.7–8.1 (protons of the benzotriazole group, 8 H, multiplet), 9.1 (6-proton of phenoxy group, 1 H, singlet), and 11.7 and 13.3 ppm (OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Calculated for $C_{20}H_{14}N_6O_3$: C 62.17, H 3.65, N 21.75. Found: C 61.98, H 3.48, N 21.76.

It should be mentioned that the crude reaction product which was obtained from the filtrate after reductive cyclization and before recrystallization was washed with acetone. From the acetone solution, 2.0 g of 1,3[di(2*H*-benzotriazole-2-yl)]2,4-dihydroxybenzene (*DBDH*) [2(2,4-dihydroxyphenyl)1,3-2*H*-bisbenzotriazole] was isolated and characterized by its melting point; its purity was identified by TLC, elemental analysis, and by its IR and NMR spectrum[16]. Apparently, during the diazonium salt reaction to synthesize *DBAP* about 10% of the acetyl groups had been lost.

stituted 2,4-dihydroxyaceto(or benzo)phenone[a]

ε (l/mol·cm)·10^{-4}	λ_{max} (nm)	ε (l/mol·cm)·10^{-4}	λ_{max} (nm)	ε (l/mol·cm)·10^{-4}
2.80	315	2.65		
3.20	322	3.35	342 (sh)	2.65
2.45	334	2.18		
2.83	335	3.23	350 (sh)	2.76
—	302[b]	2.95[b]		
3.51	327	2.93	350 (sh)	1.80
2.25	332	2.75	340 (sh)	2.60
3.00	340	3.70	350 (sh)	2.00

[b] Broad peak. $\varepsilon \sim 2.5 \cdot 10^4$ l/mol·cm between 285 nm and 329 nm.

Preparation of DBBP. The synthesis of *DBBP* followed essentially the same procedure as was described for the synthesis of *DBAP* except that 2,4-dihydroxybenzophenone was used as the starting material instead of 2,4-dihydroxyacetophenone. Crude *DBBP* was extracted for 2 days with ethanol (or benzene) in a *Soxhlet* extractor. *DBBP* (22.3 g, 50% yield) was isolated from the ethanol (or benzene) extract. Recrystallisation from chloroform/ethanol (3 : 1) gave yellowish *DBBP*, m.p. 254–255 °C. The ultraviolet absorption data are

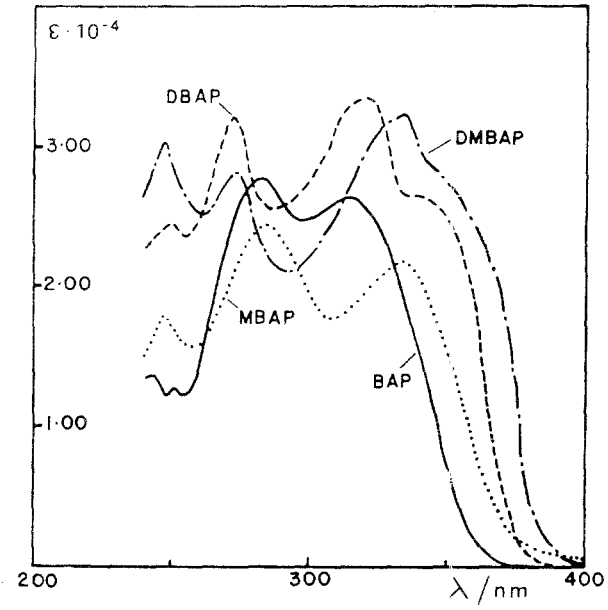


Fig. 1. Ultraviolet spectra of *BAP, DBAP, MBAP,* and *DMBAP*

presented in Table 1 and the spectra in Fig. 2. IR (KBr): 3420 cm^{-1} (O—H stretching).

^1H NMR: δ 7.2–8.1 (protons of the benzotriazole group and phenyl ring, 13 H, broad), 9.1 (6-proton of phenoxy group, 1 H, singlet), and 13.0 and 13.3 ppm (OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Calculated for $C_{25}H_{16}N_6O_3$: C 66.96, H 3.57, N 18.74. Found: C 66.73, H 3.25, N 18.53.

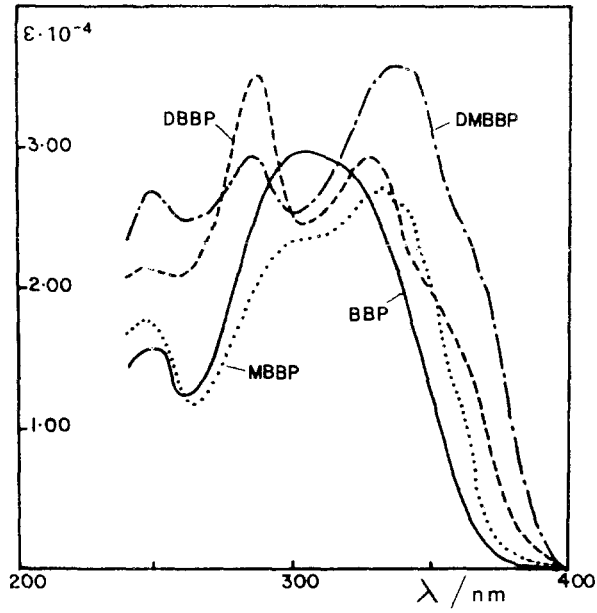


Fig. 2. Ultraviolet spectra of *BBP, DBBP, MBBP,* and *DMBBP*

Preparation of DMBAP. The synthesis procedure for *DMBAP* was the same as that described for the synthesis of *DBAP* except that 4-methoxy-2-nitroaniline was used instead of 2-nitroaniline.

The precipitate, which was obtained from the filtrate after the reductive cyclization, was extracted for 2 days with benzene in a *Soxhlet* extractor. The crude product (12 g) was isolated from the benzene extract; it was washed with cold acetone; 6.2 g of a powder remained, which was recrystallized from benzene/ethanol (2 : 1); 2.2 g of *DMBAP* was obtained (5% yield) as greenish-white crystal, m.p. 221–223 °C. The ultraviolet absorption data are presented in Table 1 and the spectra in Fig. 1. IR (KBr): 2940 cm^{-1}, 2840 cm^{-1} (—CH_3, C—H stretching).

^1H NMR: δ 2.7 (—$\overset{O}{\overset{\|}{C}}$—$CH_3$, 3 H, singlet), 3.87, 3.90 (—OCH_3, 6 H, singlet), 7.0–7.2 and 7.7–7.9 (protons of the benzotriazole group, 6 H, multiplet), 8.8 (6-proton of phenoxy group, 1 H, singlet), and 12.8 and 13.2 ppm (—OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Table 2. ^{13}C *NMR Chemical shift data*[a] *for mono- and di-(methoxy)benzotriazole-substituted 2,4-dihydroxy-aceto(benzo)phenone*

Assignment[b]	Compounds (solvent)							
	BAP (*DMSO-d_6*)	*DBAP* ($CDCl_3$)	*MBAP* ($CDCl_3$)	*DMBAP* (*DMSO-d_6*/ $CDCl_3$)	*BBP* (*DMSO-d_6*)	*DBBP* ($CDCl_3$)	*MBBP* (*DMSO-d_6*)	*DMBBP* ($CDCl_3$)
a	159.9	153.1	157.4	153.3	160.4	153.1	158.4	153.1
b	107.6	118.7	109.1	118.6	107.8	119.5	107.8	118.5
c	160.5	159.9	160.0	159.5	160.6	159.7	160.6	159.3
d	112.6	113.1	114.7	112.5	112.3	113.8	112.2	112.4
e	134.7	126.4	132.4	126.9	136.3	128.6	136.3	126.6
f	118.1	119.1	115.6	112.5	118.2	119.7	119.0	118.5
1(1')[c]	144.2	143.0(144.8)	139.2	139.3(140.8)	144.2	143.3(144.9)	140.4	138.8(141.4)
2(2')[c]	117.0	117.5(118.3)	94.1	94.5 (94.9)	117.6	117.8(118.5)	95.1	94.0 (95.0)
3(3')[c]	126.8	128.0(126.8)	157.0	159.7(158.7)	126.8	128.1(127.1)	160.7	160.2(161.1)
4(4')[c]			118.6	119.0(119.5)			117.6	118.3(119.4)
5(5')[c]			123.4	122.1(122.9)			121.5	122.6(123.6)
6(6')[c]			143.9	144.2(145.6)			145.2	143.8(146.1)
C=O	203.6	189.2	202.2	199.7	199.1	194.0	199.1	199.7
R = —H	—	—						
—OCH_3			55.7	55.5 (55.7)			55.5	55.6 (55.7)
R' = —CH_3	26.3	26.3	27.1	26.7				
R' = Phenyl								
CO—C					137.3	137.2	137.3	137.1
ortho-C					128.5	128.8	128.5	128.8
meta-C					128.8	129.2	128.8	129.3
para-C					132.0	132.8	132.0	132.6

[a] Chemical shift values (ppm) relative to *TMS*. Calculated and assigned according to *Ewing*'s table[18], using mono- and di-(4-methoxy)benzotriazole-substituted resorcinol derivatives as model compounds[16, 17].

[b] For numbering see Scheme 1.

[c] Tentative assignments.

Calculated for $C_{22}H_{18}N_6O_5$: C 59.19, H 4.04, N 18.83. Found: C 58.94, H 3.92, N 18.85.

DMBAP was prepared earlier and described previously; after reductive cyclization, the zinc powder residual cake, which contained the main portion of the product, had been discarded and consequently the yield had been low. After washing the crude product with acetone (1.5 g, 5% yield), additional 3(2*H*-4′-methoxybenzotriazole-2-yl)2,4-dihydroxyacetophenone (*MBAP*) [2(2,4-dihydroxy-5-acetyl)2*H*-(4-methoxy) benzotriazole] was also obtained. The characterization of *MBAP* are listed below under preparation of *MBAP*.

Preparation of DMBBP. The synthesis procedure for *DMBBP* was essentially the same as that described for *DBAP* except that the molar ratio of 4-methoxy-2-nitrobenzenediazonium chloride/2,4-dihydroxybenzophenone was 1 : 1, and the reaction was carried out on a smaller scale (0.05 mol). Crude *DMBBP* was extracted with benzene. *DMBBP* (4 g, 31.5% yield based on 4-methoxy-2-nitroaniline) was isolated from the benzene extract. Recrystallization from benzene, chloroform, and ethanol (2 : 2 : 1) gave yellowish crystals, m.p. 248–249 °C. The ultraviolet absorption data are presented in Table 1 and the spectra in Fig. 2. IR (KBr): 2940 cm^{-1}, 2840 cm^{-1} (—CH_3, C—H stretching).

^{1}H NMR: δ 3.89, 3.93 (—OCH_3, 6 H, singlet), 7.0–7.2 and 7.6–8.0 (protons of benzotriazole group and phenyl ring, 11 H, multiplet), 8.9 (6-proton of phenoxy group, 1 H, singlet), and 12.9 and 13.2 ppm (—OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Calculated for $C_{27}H_{20}N_6O_5$: C 63.78, H 3.94, N 16.54. Found: C 63.51, H 3.81, N 16.38.

Preparation of Mono-(Methoxy)Benzotriazole-substituted 2,4-Dihydroxyaceto(or benzo)phenone

We prepared also four mono-substituted compounds: (a) 3(2*H*-benzotriazole-2-yl)-2,4-dihydroxyacetophenone (*BAP*) [2(2,4-dihydroxy-5-acetylphenyl)2*H*-benzotriazole], (b) 3(2*H*-benzotriazole-2-yl)2,4-dihydroxybenzophenone (*BBP*) [2(2,4-dihydroxy-5-benzoylphenyl)2*H*-benzotriazole], (c) 3(2*H*-4′-methoxybenzotriazole-2-yl)-2,4-dihydroxyacetophenone (*MBAP*) [2(2,4-dihydroxy-5-acetylphenyl)2*H*-(4-methoxy)benzotriazole], and (d) 3(2*H*-4′-methoxybenzotriazole-2-yl)-2,4-dihydroxybenzophenone (*MBBP*) [2(2,4-dihydroxy-5-benzoylphenyl)2*H*-(4-methoxy)benzotriazole].

The syntheses of the mono-(methoxy)benzotriazole-substituted compounds were much more difficult as compared to the syntheses of the dibenzotriazole-substituted compounds. In the past, a mixture of di- and mono-benzotriazole-substituted compounds had always been obtained in our syntheses; usually the dibenzotriazole-substituted compound was the main product. Separation, isolation, and purification of the mono-substituted compounds was always difficult.

Preparation of BAP. A solution of 2-nitroaniline (13.8 g, 0.1 mol) in hydrochloric acid solution (60 ml, conc. hydrochloric acid/water, 1/1) was diazotized with a solution of sodium nitrite (7.0 g, 0.1 mol) in water (25 ml) at 0 °C. After finishing the addition of the sodium nitrite solution, the reaction was continued for 0.5 h and the reaction mixture was diluted to 200 ml. The cold 2-nitrobenzenediazonium chloride solution was added over a period of 1 h, with stirring, to a solution of 2,4-dihydroxyacetophenone (15.2 g, 0.1 mol) and sodium hydroxide (20 g, 0.5 mol) in water (300 ml) at 0 °C. After 2 h at 0 °C, the mixture was allowed to warm to room temperature. A red precipitate of the azo compound had formed; the suspension was neutralized with dilute hydrochloric acid to $pH \sim 5$–7,

filtered, and washed with water/ethanol (1 : 1). The azo compound was suspended in 2 *N* aqueous sodium hydroxide solution (300 ml) and reductively cyclized at 55 °C in 2 h with zinc dust (40 g, 0.6 mol), with further addition of 40% sodium hydroxide (40 ml).

After one day, the suspension was filtered, the filtrate acidified to *pH* 1 with hydrochloric acid (1 : 1) at ~ 10 °C. A precipitate, a mixture of *DBAP* and *BAP*, was isolated by filtration and extracted with benzene. The benzene extract was evaporated to dryness and washed with acetone (2.4 g of *DBAP*). The acetone solution was decolorized and evaporated to dryness. The residue which was obtained was extracted several times with hot 30% aqueous ethanol. Upon cooling of the solution, *BAP* (1.5 g, 6% yield) precipitated as white crystals, which after recrystallization from benzene gave pure *BAP*, m.p. 198–200 °C. The ultraviolet absorption data are shown in Table 1 and the spectra in Fig. 1. IR (KBr): 3 420 cm^{-1} (O—H stretching).

^1H NMR: δ 2.6 (CH_3, 3 H, singlet), 6.7–6.8, 7.5–7.6, and 8.0–8.1 (protons of the benzotriazole group and 2.6 protons of the phenoxy group, 6 H, multiplet), 11.7 and 13.2 ppm (—OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Calculated for $C_{14}H_{11}N_3O_3$: C 62.45, H 4.09, N 15.61. Found: C 62.44, H 4.25, N 15.72.

Additional 9 g of *DBAP* were isolated from the zinc powder residue; the total yield of *DBAP* was 60% (11.4 g) based on 2-nitroaniline.

Preparation of BBP. The procedures for the diazotization and the coupling reaction of the diazonium salts were the same as those described for the synthesis of *BAP* except that 2,4-dihydroxybenzophenone was used instead of 2,4-dihydroxyacetophenone and the reaction was carried out on a smaller scale (0.05 mol). The reductive cyclization was carried out in a different way: After the coupling reaction, the azo compound was washed with 300 ml of aqueous ethanol (1 : 1) and suspended in 800 ml of 5% aqueous sodium hydroxide solution. Sodium hydrosulfite (60 g) was added at room temperature, and the reaction was kept at room temperature for 0.5 h; then the temperature was raised to the boiling point and kept for 1 h (during which period a light-yellow precipitate formed). After the reaction was judged complete, the mixture was cooled to ~ 10 °C and the suspension containing a yellow precipitate (the sodium salt of *DBBP*) was filtered. The filtrate was acidified to *pH* 2 with dilute hydrochloric acid which precipitated additional product. The combined solids were extracted with 85% ethanol; from the solution 11.4 g of crude *BBP* was obtained as a yellowish powder. The 85% ethanol-insoluble product (2.9 g) was mainly *DBBP*. The filtrate was decolorized and diluted with water to a 50% ethanol solution; additional material precipitated. Filtration gave a solution which was evaporated and the residue was extracted with benzene. Crude *BBP* (0.8 g, 5% yield) was recrystallized from benzene and gave pure *BBP*, m.p. 201–203 °C. The ultraviolet absorption data are shown in Table 1 and the spectra in Fig. 2. IR (KBr): 3 420 cm^{-1} (O—H stretching), 3 070 cm^{-1} (benzene ring, C—H stretching).

^1H NMR: δ 6.7–6.8, 7.5–7.6, 8.0–8.1 (protons of the benzotriazole group and 2.6 protons of the phenoxy group, 6 H, multiplet), 7.7–7.8 (protons of the benzene ring, 5 H, multiplet), 11.7 (broad) and 12.8 ppm (OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Calculated for $C_{19}H_{13}N_3O_3$: C 68.88, H 3.93, N 12.69. Found: C 69.04, H 3.89, N 12.60.

In this synthesis of *BBP*, about 4.7 g of *DBBP* was also obtained; the yield was 42% based on 2-nitroaniline.

Preparation of MBAP. The synthesis procedure was the same as that described for *BAP* except that 4-methoxy-2-nitroaniline was used instead of 2-nitroaniline and the reaction was carried out on a smaller scale (0.05 mol).

After reductive cyclization, the suspension was filtered and the filtrate was acidified to *pH* 1 to precipitate the crude product, which was obtained in 25% yield (3.7 g). *DMBAP* (0.9 g, 8% yield based on 4-methoxy-2-nitroaniline) was also isolated from the mother liquor. Recrystallization of *MBAP* from benzene gave greenish crystals, m.p. 167–170 °C. The ultraviolet absorption data are shown in Table 1 and the spectra in Fig. 1. IR (KBr): 2940 cm^{-1} (C—CH_3, C—H stretching).

^{1}H NMR: δ 2.6 (—CO—CH_3, 3 H, singlet), 3.9 (—O—CH_3, 3 H, singlet), 6.7–6.8, 7.1–7.4, and 7.8–8.1 (protons of the benzotriazole group and 2.6 protons of the phenoxy group, 5 H, multiplet), and 11.7 (broad) and 13.2 ppm (—OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Calculated for $C_{15}H_{13}N_3O_4$: C 60.20, H 4.35, N 14.05. Found: C 60.05, H 4.32, N 13.77.

Preparation of MBBP. The procedure was the same as that described for the synthesis of *BBP* expect that 4-methoxy-2-nitroaniline was used instead of 2-nitroaniline and the reaction was carried out on a 0.1 mol scale.

After reductive cyclization, cooling, and filtering, 3.3 g of yellow precipitate were separated, which proved to be *DMBBP.* The filtrate was acidified to *pH* 1 with dilute hydrochloric acid (1 : 1), which produced a suspension from which *DMBBP* (4.9 g) was isolated by filtration. After cooling, another part (about 3 g) of yellow powder was precipitated which proved to be mainly *DMBBP*[17]. The filtrate was decolorized and diluted with water to a 50% ethanol solution; more *DMBBP* precipitated and was removed. The solution was then diluted with water to a 30% ethanol solution, and 4.1 g of *MBBP* (yield 11%) precipitated. On adding more water, 1.8 g of pinkish crystal precipitated which were identified by TLC to be *MBDH.* Recrystallization from benzene (with a small amount of acetone) gave greenish-yellow crystals, m.p. 172–174 °C. The ultraviolet absorption data are shown in Table 1 and the spectra in Fig. 2. IR (KBr): 3420 cm^{-1} (O—H stretching), 2840 cm^{-1}, 2940 cm^{-1} (—CH_3, C—H stretching).

Measurement of the IR spectrum immediately after recrystallization and drying showed a sharp peak at 1700 cm^{-1} (medium intense); but if the crystals were set aside for several weeks and then their IR spectrum was measured, the peak at 1700 cm^{-1} had disappeared (Fig. 2).

^{1}H NMR: δ 3.9 (—OCH_3, 3 H, singlet), 6.7–6.8, 7.1–7.2, 7.3–7.4, and 7.9–8.0 (protons of the benzotriazole group and 2.6 protons of the phenoxy group, 6 H, multiplet), 7.6–7.7 (benzene ring, 5 H, multiplet), 11.7 (broad) and 12.8 ppm (OH, 2 H, singlet). The ^{13}C NMR chemical shift data are presented in Table 2.

Calculated for $C_{20}H_{15}N_3O_4$: C 66.48, H 4.16, N 11.63. Found: C 66.39, H 4.46, N 10.78.

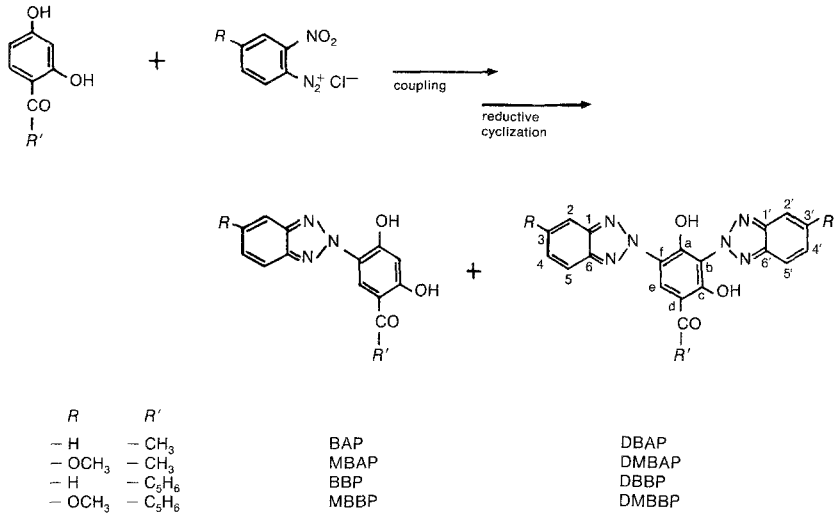
This synthesis of *MBBP* gave also 8.1 g of *DMBBP,* a yield of 32% based on 4-methoxy-2-nitroaniline.

Results and Discussion

A series of eight new ultraviolet stabilizers based on mono- or dibenzotriazole (or methoxybenzotriazole)-substituted 2,4-dihydroxyacetophenone (or 2,4-dihydroxybenzophenone) derivatives have been synthesized (Scheme 1) by azo coupling of 2-nitrobenzenediazonium

chloride or 2-nitro-4-methoxybenzodiazonium chloride with 2,4-dihydroxyaceto(or benzo)phenone followed by reductive cyclization (Table 3).

Scheme 1



R	R'		
– H	– CH_3	BAP	DBAP
– OCH_3	– CH_3	MBAP	DMBAP
– H	– C_5H_6	BBP	DBBP
– OCH_3	– C_5H_6	MBBP	DMBBP

Table 3. *Melting points and yields of mono- and di-(methoxy)benzotriazole-substituted 2,4-dihydroxyaceto(or benzo)phenones*

Compound	m.p. (°C)	Yield (%)	Compound	m.p. (°C)	Yield (%)
DBAP	272–274	60	*BAP*	198–200	6
DMBAP	221–223	10	*MBAP*	166–168	25
DBBP	254–255	50	*BBP*	201–203	5
DMBBP	248–249	30	*MBBP*	172–174	10

Recently we have been able to synthesize readily mono(methoxy)benzotriazole-substituted resorcinols (*BDH* or *MBDH*)[16, 17] in good yields. After attaching an acetyl or benzoyl group into the 4-position of resorcinol (*ortho* and *para* to the phenolic hydroxyl groups), the situation was quite different because of the strong electron withdrawing effect of the acetyl or benzoyl groups. The mono(4-methoxy)benzotriazole-substituted 2,4-dihydroxyaceto(or benzo)-phenone was difficult to isolate and purify.

Many variations of reaction conditions were tried in our attempts to synthesize the mono-substituted compounds by decreasing the reactivity of 2,4-dihydroxyaceto(or benzo)phenone toward the coupling reaction with the diazonium salt of (4-methoxy)2-nitroaniline. Under acid conditions (dilute hydrochloric acid) (using reaction conditions that were used before for the preparation of *BDH* and *MBDH*[16, 17]), no coupling occurred. When the *pH* of the reaction medium was adjusted to 2.8 to 3.2 for the preparation of *BAP* or when the reaction was carried out in a buffer solution of acidic acid/sodium acetate (*pH* 4.8 to 5.2) for the preparation of *BBP* and *MBBP*, only incomplete coupling occurred. After reductive cyclization, the di-substituted compounds were still the main product; only negligible amounts of the mono-substituted derivatives were formed.

We have also attempted to decrease the reactivity of the diazonium salt (for producing *MBBP*) by changing the diazonium chloride to diazonium acetate and carrying out the reaction in a medium of sodium acetate/acetic acid buffer solution or in aqueous sodium hydroxide solution. After reductive cyclization with zinc powder/sodium hydroxide, *MBBP* was now the main product, but the yield was very low and a significant formation of the disubstituted product was observed.

In aqueous sodium hydroxide medium, a mixture of *MBBP* and *DMBBP* was formed. Similarly, when the coupling reaction was followed by reductive cyclization with zinc/sodium hydroxide, to prepare *BAP*, the reaction product was a mixture of *DBAP* (60%) and *BAP* (6%). Nearly pure *BAP* could be separated from *DBAP* by extracting the mixture with 25–30% aqueous ethanol.

For the preparation of *BBP* or *MBBP*, the coupling of 2-nitro-4-methoxybenzenediazonium chloride was carried out in aqueous sodium hydroxide medium. When zinc powder/sodium hydroxide was used as the reducing agent for the reductive cyclization step, a dark, complex mixture was always obtained which was difficult to purify. Therefore, the reducing reagent for the reductive cyclization was changed by using sodium hydrosulfite ($Na_2S_2O_4$) in 2 *N* aqueous sodium hydroxide. The reaction was carried out at boiling temperature for 1–2 h to prepare *BBP* or *MBBP*. After this reductive cyclization, a mixture of di- and mono-substituted compounds was still obtained and the yield of mono-compounds was low; however, the separation and purification was now possible and was done successfully. When the coupling reaction was carried out at lower temperatures and a dilute diazonium salt solution was used for the azo coupling the synthesis of mono-substituted compounds was also facilitated.

During the synthesis procedure, we made the following observations: In the reductive cyclization step, no matter what kind of reducing agent was used, a substantial part of di-substituted compounds always pre-

cipitated. Apparently, the solubility of di-substituted compounds, even in basic aqueous solution, is limited and, in the case of zinc powder/sodium hydroxide as the reducing agent, a complex formed between the di-substituted compounds and the zinc residue.

It should be mentioned that some *DBDH* was also obtained during the preparation of *DBAP*. This means that some deacylation occurred during the coupling reaction. During the preparation of *BBP* and *MBBP*, some *DBDH* and *BDH* (or *DMBDH* and *MBDH*) was also obtained. This means that some debenzoylation also took place. We are planning to study the mechanism of the deacylation of these compounds further.

All the compounds of this work were characterized by their elemental analysis and their IR, UV, and ^{1}H and ^{13}C NMR spectra. The IR spectra showed the absorption peaks characteristic for compounds of this type. One interesting phenomenon should be pointed out which we are investigating further: When the IR spectrum of *MBBP* was measured as soon as the compound was recrystallized and dried, an absorption peak of 1 700 cm^{-1} showed on the spectrum. After the compound was set aside for several weeks and its IR spectrum was measured again, the absorption peak was no longer present. The spectra of *MBBP* before and after

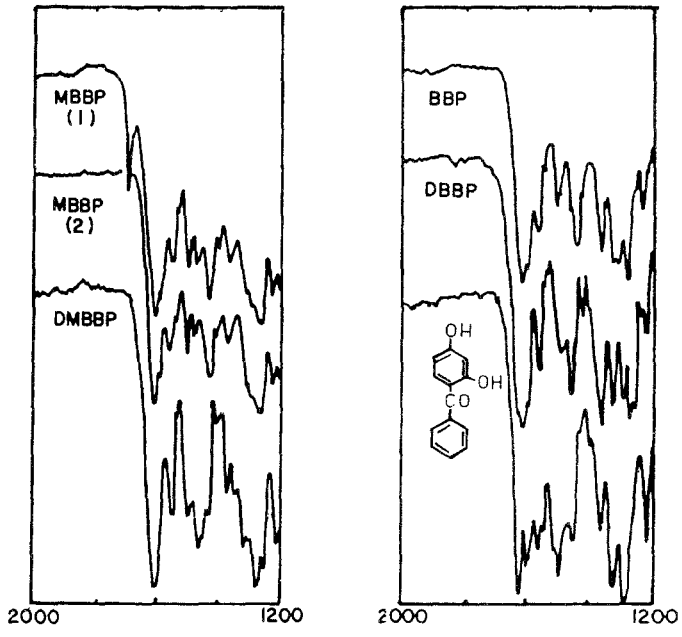


Fig. 3. Infrared spectra of *BBP*, *DBBP*, *MBBP*, *DMBBP*, and 2,4-dihydroxybenzophenone

standing are shown in Fig. 3, together with the IR spectra of *DMBBP, BBP, DBBP,* and 2,4-dihydroxybenzophenone for comparison. The reason for this phenomenon is as yet unknown, but the possibility exists that a keto-enol tautomer isomerism develops upon standing.

The numeric values of the ultraviolet absorption data measured in chloroform of this series of compounds are shown in Table 1 and their actual spectra in Figs. 1 and 2. The ultraviolet absorption of di-substituted compounds has a broad absorption with considerably higher extinction coefficients as compared to the corresponding mono-substituted compounds. The absorption band at about 275–285 nm of the di-substituted compounds always showed a hypsochromic shift as compared to their corresponding mono-substituted compounds. On the other hand, the absorption band at about 320–340 nm of the di-substituted compounds showed a bathochrome effect as compared to their corresponding mono-substituted compounds. These phenomena were most apparent when comparing the ultraviolet spectra of *DBBP* and *BBP*. In the ultraviolet spectrum of *BBP*, these are two absorption bands combined to form a broad absorption band (285–329 nm) with the maximum at about 302 nm.

The ^{13}C NMR chemical shift values are tabulated in Table 2. They are calculated and assigned according to *David F. Ewing*'s table[18] by using mono- and di-(methoxy)benzotriazole-substituted resorcinol as model compounds, respectively[16,17]. Good agreements between the experimental data and most of the calculated values were found.

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