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Functional Polymers. XXII. Ultraviolet Absorbers with 2(2-Hydroxyphenyl)2H-benzotriazole and 2-Hydroxybenzophenone (or Acetophenone) Chromophors in the Same Molecule

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Functional Polymers. XXII.* Ultraviolet Absorbers with 2(2-Hydroxyphenyl)2H-benzotriazole and 2-Hydroxybenzophenone (or Acetophenone) Chromophors in the Same Molecule

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ABSTRACT

Benzotriazolization of 2,4-dihydroxyacetophenone and 2,4-dihydroxybenzophenone has given dibenzotriazolized products: 3,5-[di(2H-benzotriazole-2-yl)]2,4-dihydroxyacetophenone, and 3,5-[di(2H-benzotriazole-2-yl)]2,4-dihydroxybenzophenone. These compounds are expected to be effective and useful UV absorbers as they both

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have the 2(2-hydroxyphenyl)2H-benzotriazole unit and the 2-hydroxybenzophenone (or acetophenone) unit in the molecule. The compounds were characterized by their spectral behavior and particularly by careful study of their UV spectrum.

INTRODUCTION

Since the discovery of 2(2-hydroxyphenyl)2H-benzotriazoles as effective UV absorbers and UV stabilizers, especially for plastics materials, much attention has been paid to the synthesis of novel and unusual 2(2-hydroxyphenyl)2H-benzotriazole derivatives [1-6]. More recently attention has shifted to less volatile, more compatible, and ultimately polymerizable, polymeric, and polymer bound UV stabilizers of the 2(2-hydroxyphenyl)2H-benzotriazole (2HB) category [7-14]. Initial photophysical studies showed them to be effective UV stabilizers; there are some thoughts that some of these compounds might also act as quenchers of the excited states. Before the use of the 2HB's, UV stabilizers of the category of 2-hydroxybenzophenones were and are still being used extensively. Few polymerizable 2-hydroxybenzophenone ultraviolet stabilizers [15, 16] are now commercially available.

Although considerable synthetic work was done on the synthesis of 2HB's many years ago [17, 18], no attempts were made to combine the 2HB and the 2-hydroxybenzophenone chromophors in one molecule. It was further found, very recently [19], that it was relatively easy to introduce more than one benzotriazole unit in one molecule when highly activated, multihydroxylated phenyl compounds, such as resorcinol or phloroglucinol, were used to produce a new series of compounds with interesting UV absorbing properties.

The objective of this work was to synthesize UV absorbing compounds that have both the 2HB (one or two units) and the 2-hydroxybenzophenone or the 2-hydroxyacetophenone chromophor in a single molecule. The acetophenone structure is also useful as an intermediate for the preparation of the corresponding vinyl or isopropenyl UV absorbing compounds of the 2HB category.

EXPERIMENTAL

Materials

o-Nitroaniline (Aldrich Chemical Co.) and 2,4-dihydroxyacetophenone (Aldrich Chemical Co.) were recrystallized and dried for 1 d at 60°C and 1 mm. 2,4-Dihydroxybenzophenone (Aldrich Chemical Co.) and most solvents such as benzene, chloroform, methanol, and ethanol were used as received.

Chloroform-d (99.8% D), (Norell, Inc.) and dimethylsulfoxide-d₆ (99.9% D) (Aldrich Chemical Co.) were used as received.

Measurements

Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer, Model 283. Solid samples were measured in the form of potassium bromide pellets.

¹H-NMR spectra were recorded on a Varian A-60 spectrometer and ¹³C-NMR spectra on a Varian CTF-20 spectrometer with complete proton decoupling with TMS as the internal standard. The compounds were dissolved in deuterated DMSO or CHCl₃ (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 s; pulse delay, 1.0 s; and 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.

Preparations

3,5-[Di(2H-benzotriazole-2-yl)]2,4-dihydroxyacetophenone (DBDA). A solution of o-nitroaniline (55 g, 0.4 mol) in concentrated hydrochloric acid (150 mL) was diazotized with a solution of sodium nitrite (28 g, 0.4 mol) in water (100 mL) at 0°C, following known procedures [10]. The cold solution of o-nitrobenzenediazonium chloride was added over a period of 1 h with stirring to a solution of 2,4-dihydroxyacetophenone (30 g, 0.2 mol), sodium hydroxide (16 g, 0.4 mol), and sodium carbonate (90 g, 0.72 mol) in water 900 mL at 5-10°C. The red azo compound was washed 3 times with water of about 60°C, dissolved in 600 mL of aqueous 2 N sodium hydroxide (1.2 mol), and reductively ring-closed at 50°C in 1 h with zinc dust (120 g, 1.84 mol) and an additional 40% sodium hydroxide (150 mL) solution.

After 1 d at room temperature the suspension was filtered and the residue was extracted twice with 10% aqueous sodium hydroxide; 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. Precipitated crude DBDA was isolated by filtration, air-dried, and extracted 3 d with benzene in a Soxhlet extracted. DBDA (25 g, 32% yield) was isolated from the benzene extract. Recrystallization from chloroform and benzene (1:1) gave pure DBDA as pale yellow needles, mp 265-267°C. The UV

TABLE I. Ultraviolet Absorption of Various Benzotriazole Derivatives^a

Compound	λ_{\max}	ϵ (L/mol·cm) $\times 10^{-3}$	λ_{\max}	ϵ (L/mol·cm) $\times 10^{-3}$	λ_{\max}	ϵ (L/mol·cm) $\times 10^{-3}$	λ_{\max}	ϵ (L/mol·cm) $\times 10^{-3}$
DBDA	252	23.5	273	30.8	322	29.7	343	23.2 (shoulder)
DBDB	246	21.5	285	35.1	327	29.3		

^aAbsorptions determined in solutions of chloroform. Concentration: 2×10^{-5} mol/L.

absorption data are shown in Table 1. IR (KBr): 3420 cm^{-1} (O-H stretching).

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

Analysis: Calculated for $\text{C}_{20}\text{H}_{14}\text{N}_6\text{O}_3$: C, 62.17%; H, 3.65%; N, 21.75%. Found: C, 61.98%; H, 3.48%, N, 21.76%.

3,5-[Di(2H-benzotriazole-2-yl)]2,4-dihydroxybenzophenone (DBDB).

The synthesis of DBDB followed essentially the same procedure as described for the synthesis of DBDA except that a molar ratio of o-nitrobenzenediazonium chloride/2,4-dihydroxybenzophenone was 2:1 and sodium bicarbonate (118 g, 1.4 mol) and sodium carbonate (110 g, 0.88 mol) were used in the coupling reaction rather than sodium hydroxide and sodium carbonate. Crude DBDB was extracted for 2 d with ethanol in a Soxhlet apparatus. The ethanol extract yielded 8 g (9%) of DBDB. Recrystallization from chloroform/ethanol (3:1) gave yellow needles, mp $254\text{-}255^\circ\text{C}$. The UV absorption data are presented in Table 1. IR (KBr): 3420 cm^{-1} (O-H stretching).

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

Analysis: Calculated for $\text{C}_{25}\text{H}_{16}\text{N}_6\text{O}_3$: C, 66.96%; H, 3.60%; N, 18.74%. Found: C, 66.73%; H, 3.25%; N, 18.53%.

RESULTS AND DISCUSSION

Two benzotriazolyl substituted dihydroxybenzenes have been synthesized: 3,5-[di(2H-benzotriazole-2-yl)]2,4-dihydroxyacetophenone (DBDA) and 3,5-[di(2H-benzotriazole-2-yl)]2,4-dihydroxybenzophenone (DBDB) (Scheme 1).

DBDA was prepared by condensation of o-nitrobenzenediazonium chloride with 2,4-dihydroxyacetophenone and reductive ring closure with zinc dust and sodium hydroxide. The compound was isolated in 32% yield as yellowish needles, mp $265\text{-}267^\circ\text{C}$. Elemental analysis showed that this compound was the dibenzotriazolized resorcinol; no monosubstituted derivative could be isolated in spite of considerable modifications of the reaction conditions.

DBDB was synthesized by condensation of o-nitrobenzenediazonium chloride with 2,4-dihydroxybenzophenone. The yield of this compound was approximately 10%; DBDB was also obtained as yellow needles, mp $254\text{-}255^\circ\text{C}$. It should be pointed out that the yields given here are not necessarily maximum yields as the reaction conditions have not been optimized in terms of the pH for the condensation of the diazonium salt with the dihydroxyaceto- or benzophenone to give the azo dye.

TABLE 2. ^{13}C -NMR Chemical Shift Data for 2H-Benzotriazole Substituted 2,4-Dihydroxyacetophenone and 2,4-Dihydroxybenzophenone

Assignment	Chemical Shift	Obs		Obs		
		Int ^a	CS ^b	Int ^a	CS ^b	
Phenoxy group	a	21	153.1	155.9	153.1	157.0
	b	12	118.7	119.5	119.5	120.3
	c	13	159.9	159.2	159.7	162.8
	d	22	113.1	113.4	113.8	112.8

DBDA

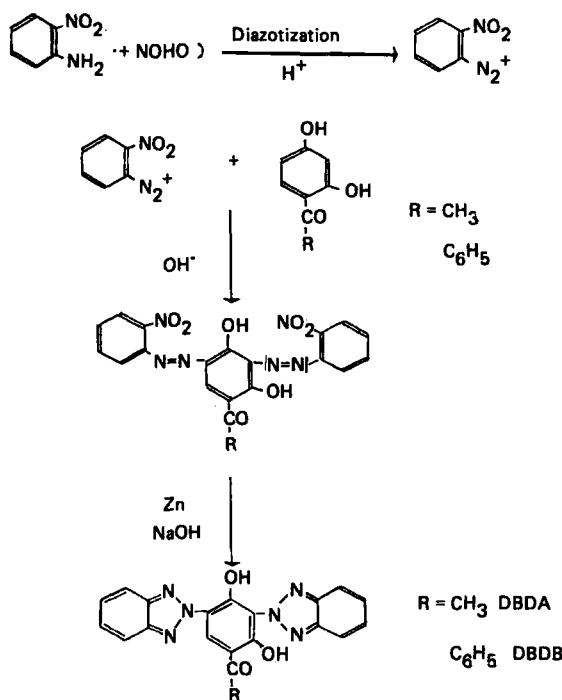
DBDB

e	31	126.4	128.9	58	128.6	131.4
f	21	119.1	120.9	28	119.7	121.1
Benzotriazole group						
1 ^c	35	143.0	143.2	25	143.3	143.2
2 ^c	94	117.5	117.6	102	117.8	117.6
3 ^c	120	128.0	127.0	105	128.1	127.0
4 ^c	21	144.8	144.4	33	144.9	144.4
5 ^c	112	118.3	118.3	90	118.5	118.3
6 ^c	125	126.8	126.5	100	127.1	126.5
Substituent						
g	8	189.2	202.3	12	194.0	199.4
h	35	26.3	26.1	25	137.2	138.3
i	-	-	-	125	128.8	128.2
j	-	-	-	105	129.2	128.6
k	-	-	-	45	132.8	131.2

^aRelative intensity.

^bChemical shift values (ppm from internal TMS) samples in CDCl₃.

^cTentative assignments.



SCHEME 1.

This is the first time that compounds have been prepared that have two important UV absorbing chromophors in one molecule, 2-(2-hydroxyphenyl)2H-benzotriazole and 2-hydroxyaceto- (or benzo-) phenone. The synthesis of these two compounds makes UV absorbers available for the study of the photophysical behavior of compounds with two different chromophors. In spite of substantial efforts, the monobenzotriazolized compounds have not been prepared.

Acetophenone derivatives are not only desirable *per se* but they also provide intermediates for the projected subsequent synthesis of polymerizable UV stabilizers. The acetyl group (after acetylation of the phenolic hydroxyl groups in the molecule) can in principle be transformed via reduction to the secondary alcohol and dehydration to the vinyl (styrene) compound or by reaction with methyl Grignard and dehydration to the isopropenyl (α -methylstyrene) derivative.

Compounds DBDA and DBDB show infrared characteristics typical for their structures; the infrared spectrum of DBDA is shown in Fig. 1.

The ¹³C-NMR chemical shift data of DBDA and DBDB showed characteristic chemical shift values expected for such compounds; good agreement of the experimental data were found with most of the calculated

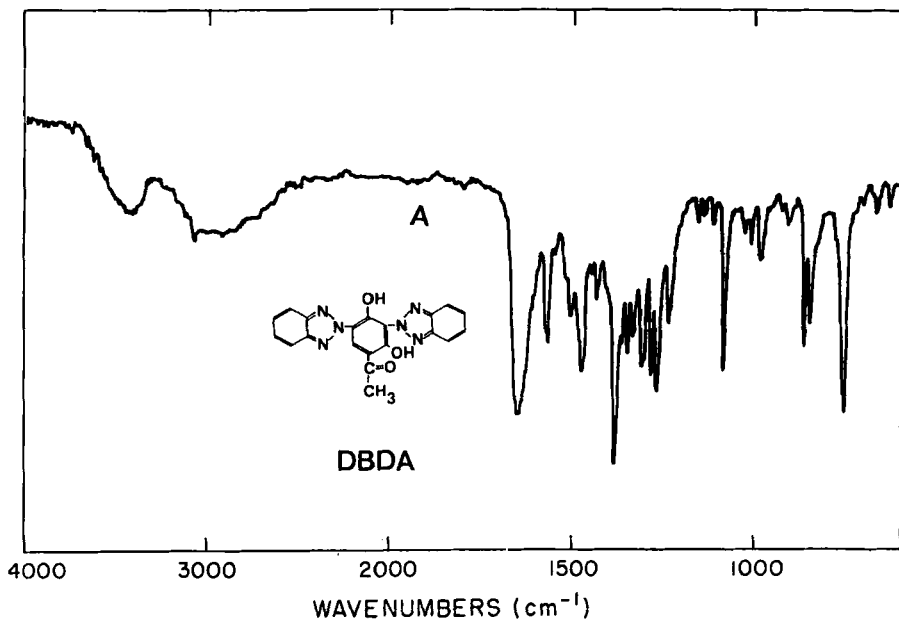


FIG. 1. Infrared spectra of 3,5-[di(2H-benzotriazole-2-yl)]2,4-dihydroxyacetophenone (DBDA).

values with the exception of the substituted carbon atom a, the carbon atom to which the hydroxyl group is attached but flanked with two benzotriazolyl groups; these chemical shift data of the carbon atom e substituted with a hydrogen and, interestingly enough, the carbonyl carbon atom g also show deviations from the calculated values (Table 2 and Fig. 2).

The ultraviolet spectra of the two benzotriazole derivatives, DBDA and DBDB, are shown in Fig. 3 with the numerical value of the spectra described in Table 1. DBDA has four maxima with λ_{\max} at 252, 273, 322, and 343 nm with extinction coefficients from 23×10^3 to 31×10^3 L/mol·cm, while DBDB has λ_{\max} at 246, 285, and 327 nm and extinction coefficients of 21.5×10^3 , 35.1×10^3 , and 29.3×10^3 L/mol·cm. It is interesting to compare the spectral characteristics of DBDA and DBDB with the spectra of the monosubstituted resorcinol BDH and the dibenzotriazolized resorcinol DBDH. BDH has a single absorption maximum at about 340 nm with an extinction coefficient of about 23×10^3 L/mol·cm. DBDH also has a single but broad absorption with a λ_{\max} peaking around 330 nm and an extinction coefficient of nearly 40×10^3 L/mol·cm. DBDA and DBDB have four maxima; the two maxima with a λ_{\max} above 300 nm do not have as high extinction co-

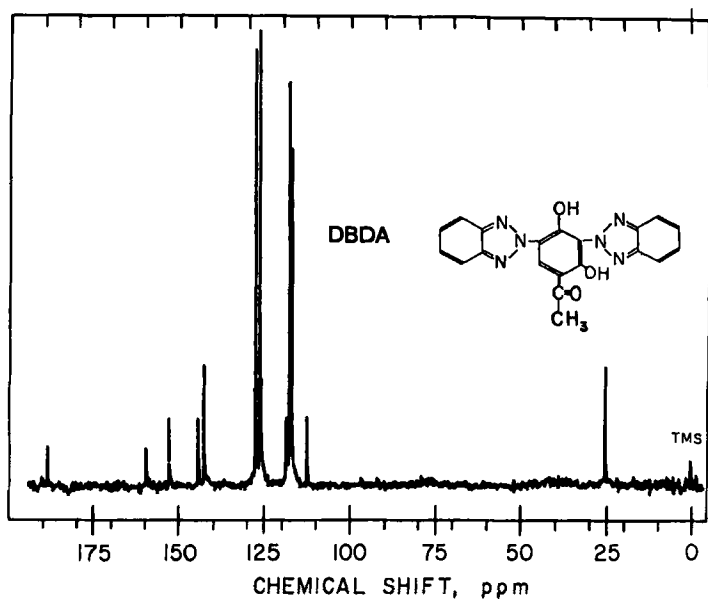


FIG. 2. ^{13}C -NMR spectra of 3,5-[di(2H-benzotriazole-2-yl)]2,4-hydroxyacetophenone (DBDA).

efficient as DBDH but higher than BDH. The important maxima with a λ_{max} at 273 and 285 nm in DBDA and DBDB constitute additional strong absorption maxima that are not present in either DBDH or BDH; these two maxima even exceed the extinction coefficient of 30×10^3 L/mol \cdot cm.

The absorption behaviors of the two new compounds DBDA and DBDB may provide new and additionally useful energy dissipation possibilities from the exceptionally broad absorption bands which range from about 250 to 360 nm. Although the absorption is not as high as the 40×10^3 L/mol \cdot cm that has been observed with benzotriazolized resorcinol and di- and tribenzotriazolized photoglucinol derivatives, the spectral bands are more structured and have substantially higher absorption in the range of 260 to 300 nm.

Photophysical studies of these compounds are presently underway.

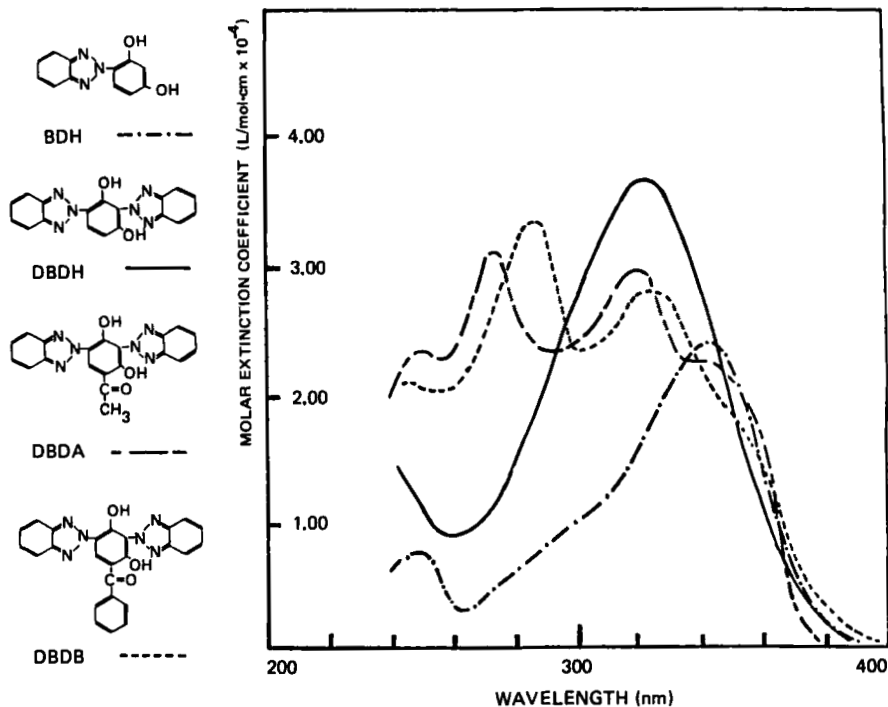


FIG. 3. Ultraviolet spectra of 2-(2H-benzotriazole-2-yl)1,5-dihydroxybenzene (BDH); 2,4-[di(2H-benzotriazole-2-yl)]1,3-dihydroxybenzene (DBDH); 3,5-[di(2H-benzotriazole-2-yl)]2,4-dihydroxyacetophenone (DBDA); and 3,5-[di(2H-benzotriazole-2-yl)]2,4-dihydroxybenzophenone (DBDB).

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