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FUNCTIONAL POLYMERS. 61. ULTRAVIOLET SPECTRAL BEHAVIOR OF SELECTED 2(2-HYDROXYPHENYL)2*H*-BENZOTRIAZOLES

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ABSTRACT

Ultraviolet spectra of a number of 2(2-hydroxyphenyl)2*H*-benzotriazoles were studied in nonpolar, polar, and hydrogen bonding solvents. The effect of substituents located in the 4-position of the benzotriazole ring was investigated, and the effect on the UV absorption characteristics of 2(2-hydroxyphenyl)2*H*-benzotriazoles was determined. Substituted resorcinol or phloroglucinol-based 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives were investigated with special emphasis on UV absorption characteristics that were expected to be useful as polymer-bound UV stabilizers in optical lens applications.

†This paper is part of the Ph.D. thesis of Andres Sustic.
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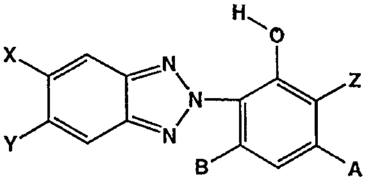
INTRODUCTION

Ever since K. Elbs described the first 2(2-hydroxyphenyl)2*H*-benzotriazoles [1, 2], this class of compounds has had a special kind of attraction. 2(2-Hydroxyphenyl)2*H*-benzotriazoles were found to be not only UV absorbers but were, even more importantly, found to be outstanding UV stabilizers [3]. They have made an increasing impact on polymer materials as the most effective UV stabilizers known today. Photophysical studies recognized that the photoactivation of hydrogen-bonded states [4–7] is the key to their effectiveness, and a mechanism to accommodate the photophysical transition states has been presented [8].

2(2-Hydroxpyhenyl)2*H*-benzotriazole derivatives form hydrogen-bonded structures; the long UV wavelength band of these derivatives (ca. 340 nm) is attributed to a planar form of the molecular, and the short UV wavelength band, which is often found at ca. 300 nm, is typical for 2-(2-hydroxyphenyl)2*H*-benzotriazole derivatives which have no hydrogen-bonded structures or hydrogen-bonding capabilities.

The effect of electron donor or withdrawing groups was found to affect the position of the λ_{max} and the shape of the 340 nm band as it influences the electron density around the hydrogen-bonded part of the 2-(2-hydroxyphenyl)2*H*-benzotriazole molecule (Scheme 1) [10–14].



A = H	B = H	X = H	Y = H	Z = H
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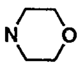
				Bztr

SCHEME 1.

Investigation on the effects of solvents on the UV spectra of 2-(2-hydroxyphenyl)2*H*-benzotriazoles showed that hydrogen bonding was more pronounced in nonpolar solvents, such as hexane, giving broader UV absorption peaks in polar solvents, such as chloroform, which is represented in a decrease of the extinction of the λ_{max} at 340 nm [15]. When 2-(2-hydroxyphenyl)2*H*-benzotriazoles were incorporated into a polymer structure, the general characteristics of the UV spectrum were found to be determined by the "next neighbor" of the macromolecule *and not* by the solvent [15].

As mentioned before, the photophysical behavior of 2(2-hydroxyphenyl)2*H*-benzotriazoles in the excited state depends on the intramolecular proton transfer which is affected by the polarity, but especially by the hydrogen bonding capability of the solvent [6, 16]. The absorption spectrum in a nonhydrogen bonding solvent, such as THF, shows the expected presence of two bands, the long wavelength band (340 nm) and the shorter wavelength band (300 nm).

When the proton-accepting capacity of the solvent was increased, the longer wavelength band decreased in intensity and *ethanol*, the long wavelength band, was almost completely eliminated [see also Refs. 12 and 13].

For some time we have been interested in the incorporation of UV stabilizers into polymeric structures by synthesizing polymerizable UV stabilizers and incorporating them by copolymerization grafting for addition polymers or, for condensation polymers, by using monomers suitable for incorporation by normal condensation techniques.

We had also turned our attention to the incorporation of polymerizable UV stabilizers into co- and ter-polymers [17] that would lead us into the preparation of UV-stabilized polymers that could be used for contact lenses and implant applications. In this case it would be important to synthesize polymers with permanently incorporated (polymer-bond) UV stabilizers unlike UV stabilizers in UV stabilized polymers composition where the composition must be colorless, i.e., must have a sharp cut-off at about 380 nm. Polymers for some ophthalmological applications are hydrophilic with an equilibrium water up-take of about 33–35%, and they must have a high absorbance at 400 nm, be hydrolysis resistant, and not influence the equilibrium water absorption of the polymer [18, 19].

We have reported on the synthesis of 2(2-hydroxyphenyl)2*H*-benzotriazoles with the required characteristics [18]. The objective of this work was to synthesize some of these compounds and to study their structure/UV behavior in nonpolar medium and to compare their spectral behavior in protic media to simulate the situation in the eye.

EXPERIMENTAL PART

Measurements

Ultraviolet spectra, unless otherwise specified, were determined in chloroform on a Varian-Cary 2300 spectrophotometer in a double-beam servo mode. Additional spectra of chloroform or of phosphate buffer (25% methanol, pH 7.8) solutions were determined on a Varian DMS-100 spectrophotometer. The solutions were measured in quartz cells which had either a 0.1-cm or a 1.0-cm optical path length.

All UV spectra are described in detail and presented in their entirety in the Ph.D. thesis of Andres Sustic (see first page footnote).

RESULTS AND DISCUSSION

The synthesis of 2(2-hydroxyphenyl)2*H*-benzotriazoles involved the coupling reactions of *o*-nitrodiazonium salts with substituted phenols followed by reductive cyclization of the azo compounds with sodium dithionate or Zn powder.

In the discussion that follows, the UV spectral data of the substituted 2(2-hydroxyphenyl)2*H*-benzotriazoles are compared vs the spectral data of the unsubstituted 2(2,4-dihydroxyphenyl)2*H*-benzotriazole, BDH, for which ϵ = 23,600 L/mol × cm at 340 nm.

2(2,4-Dihydroxyphenyl)5-fluoro-2*H*-benzotriazole (FBDH) was prepared from the diazonium salt of 4-fluoro-2-nitroaniline and resorcinol. The UV absorption spectrum of FBDH in chloroform showed an absorption band at 341 nm with a molar extinction coefficient of 21,830 L/mol × cm and a shoulder at 295 nm with ϵ = 7600 L/mol × cm. The ratio of the intensities of the peak and shoulder, Abs(341)/Abs(295), was 2.87. In this nonpolar aprotic solvent, this absorbance ratio demonstrates to what extent the hydrogen-bonded [H] form predominates over the nonhydrogen-bonded, nonplanar [N] form (Fig. 1a).

The UV spectrum of FBDH was also measured in a methanol:phosphate buffer solution because this solution, at a pH of 7.8, simulates the pH and salinity of the human eye. It showed absorption bands at 325 and 291 nm with molar extinction coefficients of ϵ = 12,270 and 10,510 L/mol × cm, respectively. The polar solvent has a hypochromic effect on the longer wavelength absorption band, causing that band to hypsochromically shift ca. 16 nm to a lower wavelength. On the other hand, the polar solvent has a hyperchromic effect on the band with λ_{max} at 290 nm. The same type of solvent effect has been observed [6] for 2(2-hydroxy-5-methyl-phenyl)2*H*-benzotriazole in *hydrogen bonding protic solvents.*

The polar solvent shifts the equilibrium favoring the [N] form and *inhibiting* the formation of the hydrogen-bonded form. The Abs(325)/Abs(291) = 1.17 ratio measures to what extent the *intra*molecular hydrogen bond has changed into an *inter*molecular hydrogen bond to the solvent molecules. At 400 nm, the ϵ was 640 L/mol × cm (Fig. 1b).

2(2,4-Dihydroxyphenyl)5-chloro-2*H*-benzotriazole (ClBDH) showed an absorption band at 346 nm (a hypsochromic shift of 14 nm) with ϵ = 23,470 L/mol × cm (Fig. 2a) and a small shoulder at a λ_{max} of ca. 300 nm with about one-fifth the intensity of the band at 346 nm (Fig. 3a) and a very small absorption of ϵ = 130 L/mol × cm at 400 nm. In the methanol:phosphate buffer solvent the λ_{max} was at 332 nm with ϵ = 13,000 L/mol × cm. The polar solvent showed a hypochromic shift. There was a shoulder at ca. 295 nm with an estimated ϵ = 9900 L/mol × cm. There was also a small but significant absorption at 400 nm with ϵ = 1100 L/mol × cm. For ClBDH, the polar solvent had a small effect on the hydrogen-bonded configuration as evidenced by the ratio Abs(332)/Abs(295) = 1.3 (Fig. 2b).

2(2,4,6-Trihydroxyphenyl)5-chloro-2*H*-benzotriazole (ClBTH) with three hydroxyl groups showed a single absorption band at 355 nm with an ϵ of 25,560 L/mol × cm and a significant molar extinction coefficient of 850 L/mol × cm at 400 nm (Fig. 3a). In the methanol:phosphate buffer solution it showed two absorption bands. The 355-nm band was hypsochromically shifted to 329 nm, a difference of 26 nm, with a significant hypochromic effect as evidenced by ϵ = 5520 L/mol × cm. The second band appears at 278 nm with ϵ = 11,500 L/mol × cm. In this case Abs(329)/Abs(278) = 0.48. At 400 nm, the ϵ was 200 L/mol × cm (Fig. 3b).

2(2,4-Dihydroxyphenyl)5-morpholino-2*H*-benzotriazole (MoBDH) showed a major band of λ_{max} at 364 nm with ϵ = 20,900 L/mol × cm and also a minor band at around 300 nm. The tail of the absorption band extended well into the visible region, and at 400 nm the molar extinction coefficient ϵ was 4460 L/mol × cm.

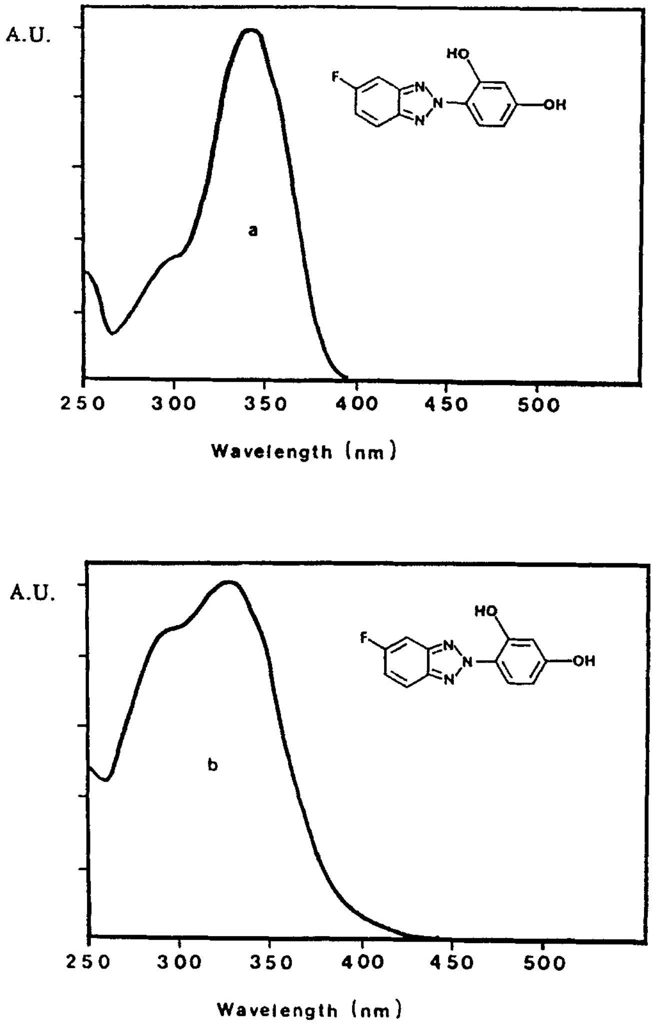
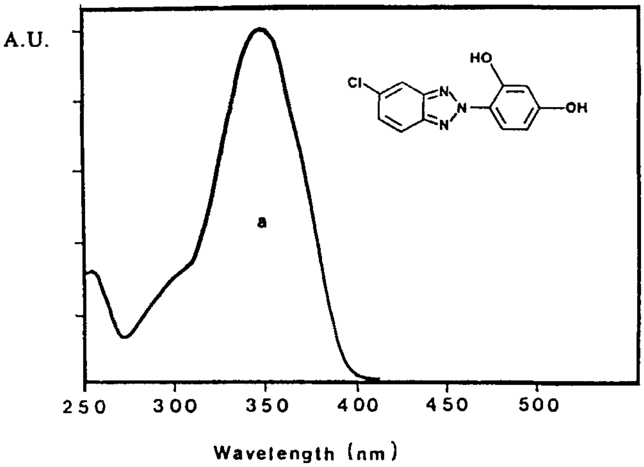


FIG. 1. Ultraviolet spectra of 2(2,4-dihydroxyphenyl)5-fluoro-2*H*-benzotriazole: (a) in chloroform, (b) in methanol; phosphate buffer.

The spectrum of MoBDH in methylene chloride again showed a major absorption band at 364 nm with $\epsilon = 21{,}150$ L/mol × cm with a minor band at around 295 nm; there was again a tailing of the absorption into the visible region with $\epsilon =$ 4890 L/mol × cm at 400 nm (Fig. 4a). The spectrum of MoBDH in methanol: phosphate buffer solution showed a single major absorption band at 345 nm, a hypsochromic shift of 19 nm, and the polar solvent had a hypochromic effect on the absorption intensity, $\epsilon = 13{,}840$ L/mol × cm. There was a complete absence of the absorption band at around 290 nm, some of which could have been shadowed by the strong absorption at 345 nm. The absorption band tailed into the visible region with $\epsilon = 2165$ L/mol × cm at 400 nm (Fig. 4b).



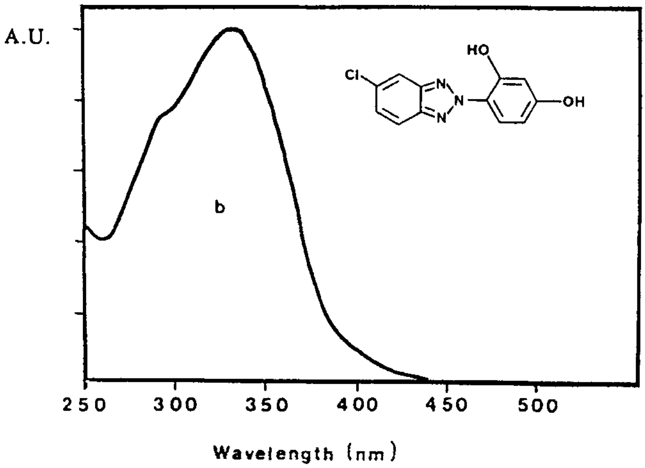


FIG. 2. Ultraviolet spectra of 2(2,4-dihydroxyphenyl)5-chloro-2*H*-benzotriazole: (a) in chloroform, (b) in methanol; phosphate buffer.

2(2,4-Dihydroxyphenyl)2*H*-5,6-dichloro-2*H*-benzotriazole (DCIDBH) in chloroform showed a major band at 338 nm with ϵ = 29,320 L/mol × cm and a shoulder at around 295 nm. In the methanol:phosphate buffer solution the 338 nm band was hypsochromically shifted to a $\lambda_{max}$of 324 nm and the intensity was lowered to ϵ = 16,510 L/mol × cm, while the weak shoulder at 295 nm in the chloroform solution was more intense in the buffer with an ϵ of 14,120 L/mol × cm and a ratio Abs(324)/Abs(295) = 1.17. Also interesting is the fact that while the UV spectrum in chloroform did not have any absorption extending into the visible region, the spectrum in the buffer showed a significant absorption into the visible region with ϵ = 712 L/mol × cm at 400 nm.

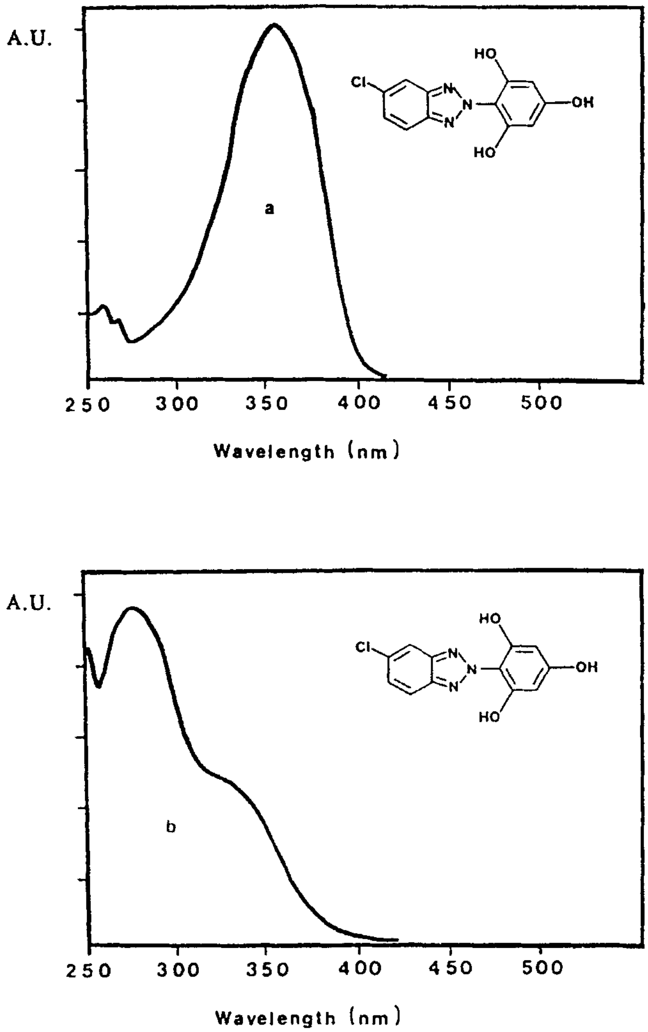


FIG. 3. Ultraviolet spectra of 2(2,4,6-trihydroxyphenyl)5-chloro-2*H*-benzotriazole: (a) in chloroform, (b) in methanol; phosphate buffer.

2(2,4-Dihydroxyphenyl)2*H*-1,3-bis(4-chloro)benzotriazole (CIDBDH) showed an intense absorption band at a λ_{max} of 341 nm with ϵ = 36,780 L/mol × cm.

2(2-Hydroxy-5-[2-hydroxyethylphenyl])2*H*-benzotriazole (HHEPB) showed a major absorption band at a λ_{max} of 335 nm with ϵ = 16,660 L/mol × cm. There was also an absorption with a λ_{max} at 296 nm with an ϵ = 13,700 L/mol × cm and a ratio Abs(335)/Abs(296) of 1.22. In methanol:phosphate buffer, the more intense band was at λ_{max} = 289 nm with ϵ = 13,300 L/mol × cm while a shoulder is centered around λ_{max} = 322 nm with ϵ = 10,620 L/mol × cm, a hypsochromic shift of 13 nm. For the polar solvent, the Abs(322)/Abs(289) ratio is 0.80. At 400 nm there is an absorption with ϵ = 166 L/mol × cm.

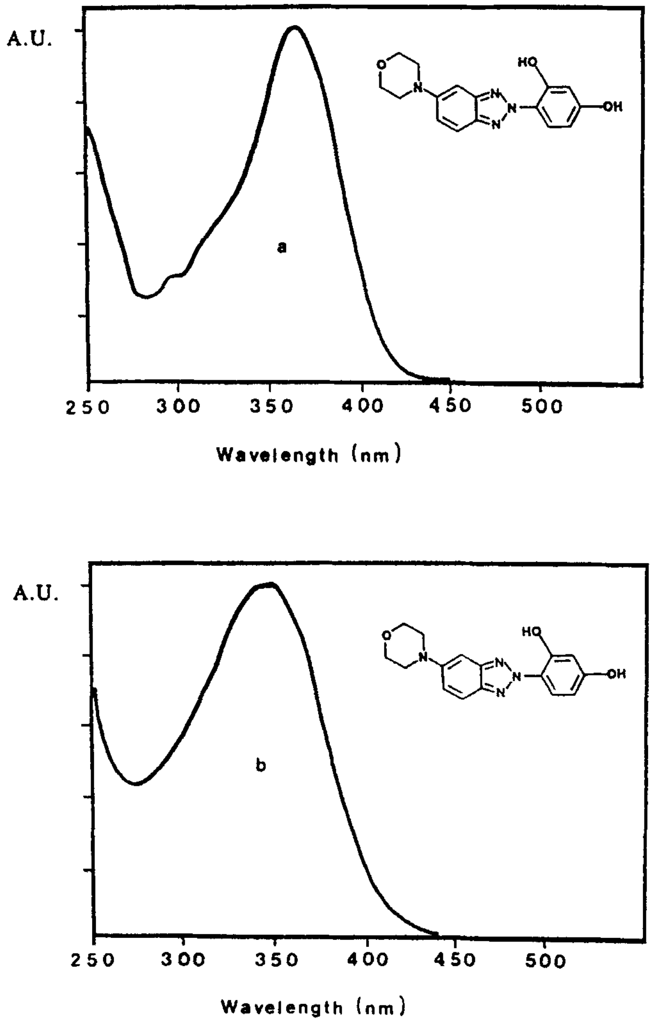


FIG. 4. Ultraviolet spectra of 2(2,4-dihydroxyphenyl)5-morpholino-2*H*-benzotriazole: (a) in chloroform, (b) in methanol; phosphate buffer.

2(2-Hydroxy-5-[3′-carboxypropyl])2*H*-benzotriazole (BHPA) showed two absorption bands, with λ_{max} = 340 nm and ϵ = 17,480 L/mol × cm and a second less intense band with λ_{max} at 303 nm with ϵ = 14,290 Lmol × cm. The Abs(340)/Abs(303) ratio is 1.22.

2(2-Hydroxynaphthalene)2*H*-benzotriazole (1B2HN) and 2(4-hydroxynaphthalene)2*H*-benzotriazole (4B1HN) are isomers. 1B2HN has the hydroxyl group in the ortho-position to the benzotriazole ring system, and its UV spectrum should show an absorption maximum at 330–360 nm. 4B1HN has the hydroxyl group para to the benzotriazole group and should show no λ_{max} between 330–360 nm [see also Ref. 13].

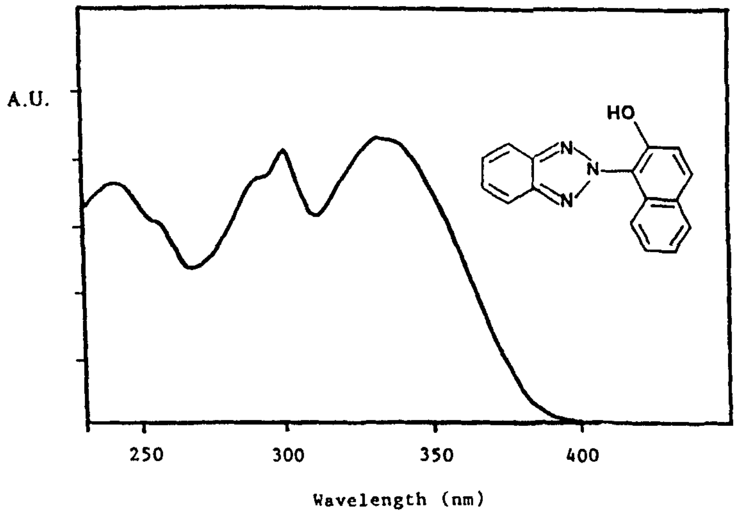


FIG. 5. Ultraviolet spectra of 2(2-hydroxynaphthalene)2*H*-benzotriazole in chloroform.

The UV spectrum of 1B2HN in chloroform showed several absorption bands. The major absorption band has a λ_{max} at 354 nm with ϵ = 11,750 L/mol × cm. A second band has a λ_{max} at 320 nm with ϵ = 11,290 L/mol × cm and a shoulder at 310 nm with ϵ = 10,070 L/mol × cm. Another band is present at λ_{max} = 265 nm with ϵ = 9920 L/mol × cm and a shoulder at 277 nm with ϵ = 8320 L/mol × cm (Fig. 5).

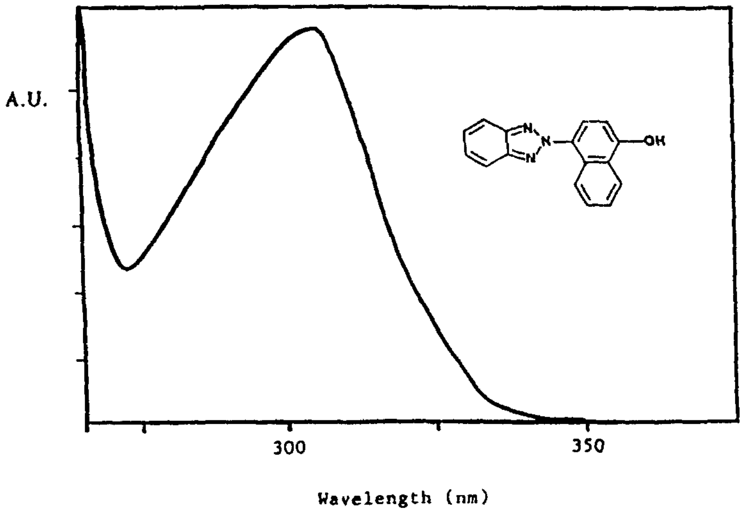


FIG. 6. Ultraviolet spectra of 2(4-hydroxynaphthalene)2*H*-benzotriazole in chloroform.

The λ_{max} in the UV spectrum of 4B1HN in chloroform showed one single major absorption band above 250 nm, specifically at $\lambda_{max} = 316$ nm with $\epsilon = 15{,}860$ L/mol × cm. Not unexpectedly, this absorption band is very similar in shape and in intensity to the absorption band of 2(4-hydroxy-2-methylphenyl)2*H*-benzotriazole, as shown in Ref. 7. Because of its inability to form a hydrogen-bonded tautomer, 4H1HN can be considered a UV absorber but not a UV stabilizer (Fig. 6).

Table 1 shows a compilation of the λ_{max} and the molar absorptivity coefficients, ϵ, of the compounds described in this paper; it also includes data from a few compounds that were previously synthesized. The values can be related to the λ_{max} of the "base" compound. Its hypsochromic shift is 14 nm as compared to BDH as the standard. The intensity of the absorption at 330–350 nm could be enhanced by increasing the number of hydroxyl groups in the 2(2-hydroxyphenyl)2*H*-benzotriazole molecule as well as in the presence of a second benzotriazole ring system. As demonstrated by us [13], an increase in the number of benzotriazole moieties and ortho-hydroxyl groups in one molecule is one way to enhance the photostabilizing capability of the basic chromophor.

TABLE 1. UV Spectra for Various 2(2-Hydroxyphenyl)2*H*-benzotriazole Derivatives in Chloroform

Compound	λ_{max}, nm	ϵ, L/mol × cm	Abs(340)/Abs(300)[a]
BDH[b]	340	23,600	
FBDH	341	21,830	2.87
ClBDH	346	23,470	ca. 5
MBDH[c]	345	26,650	2.41
MoBDH	364	20,900	
DClBDH	338	29,320	
1B2HN	354	11,750	1.17
4B1HN	316	15,860	–
MBTH[d]	349	24,860	3.41
ClBTH	355	25,560	
DBDH	325	32,835	
MDBDH[e]	344	41,400	2.12
ClDBDH	341	36,780	
HHEPB	335	16,660	1.22
BHPA	340	17,480	1.22
2H5M[f]	337	16,390	

[a] Ratio for spectra measured in chloroform.

[b] 2(2,4-Dihydroxyphenyl)2*H*-benzotriazole.

[c] 2(2,4-Dihydroxyphenyl)5-methoxy-2*H*-benzotriazole [13].

[d] 2(2,4,6-Trihydroxyphenyl)5-methoxy-2*H*-benzotriazole.

[e] 2(2,4-Dihydroxyphenyl)2*H*-1,3-bis(4-chloro)benzotriazole [13].

[f] 2(2-Hydroxy-5-methylphenyl)2*H*-benzotriazole is Tinuvin P, a Ciba-Geigy Co. UV stabilizer.

We also explored the effect of the addition of electron-donating groups to the benzotriazole ring [14]. The absorption data for the individual compounds with respect to BDH changed when an electron-donating substituent such as a fluoro, chloro, methoxy, or morpholino group was introduced into the 4-position of the benzotriazole ring. The absorption maxima, λ_{max}, were shifted to longer wavelengths by 5 up to 25 nm, which indicates the effectiveness of a more efficient intramolecular hydrogen bond.

The molar extinction coefficient was even more significantly enhanced by the addition of a second benzotriazole moiety as is evident in 2(2,4-dihydroxyphenyl)2*H*-1,3-bisbenzotriazole. The value of the molar extinction coefficient was more than doubled to over 40,000 L/mol × cm.

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REFERENCES

[1] K. Elbs and W. Keiper, *J. Prakt. Chem.*, *67*(2), 580 (1905).

[2] K. Elbs, O. Hirschel, K. Himmler, W. Turk, A. Henrich, and E. Lehmann, *Ibid.*, *108*, 209 (1924).

[3] G. N. Gantz and W. Summer, *Text. Res. J.*, *27*, 244 (1957).

[4] J. E. A. Otterstedt, *J. Chem. Phys.*, *58*(12), 5716 (1973).

[5] A. L. Huston, G. Scott, and A. Gupta, *Ibid.*, *76*(10), 4978 (1982).

[6] K. P. Ghiggino, A. D. Scully, and I. H. Leaver, *J. Phys. Chem.*, *90*, 5089 (1986).

[7] H. E. A. Kramer, *Farbe Lacke*, *92*(10), 919 (1986).

[8] A. Gupta, G. W. Scott, D. Kliger and O. Vogl, in *Polymers in Solar Energy Utilization* (ACS Symp. Ser. 220, C. G. Gebelein, D. J. Williams, and R. Deanin, Eds.), 1984, p. 293.

[9] S. R. Flom and P. F. Barbara, *Chem. Phys. Lett.*, *94*(5), 488 (1983).

[10] G. S. Dai, S. K. Wu, A. Sustic, F. Xi, and O. Vogl, *Polym. Bull.*, *20*, 67 (1988).

[11] Y. C. Jiang, S. K. Wu, A. Sustic, F. Xi, and O. Vogl, *Ibid.*, *20*, 161 (1988).

[12] Y. C. Jiang, S. K. Wu, A. Sustic, F. Xi, and O. Vogl, *Ibid.*, *20*, 169 (1988).

[13] S. K. Fu, S. L. Li, and O. Vogl, *Monatsh. Chem.*, *117*, 805 (1986).

[14] A. Sustic and O. Vogl, *Polymer*, In Press.

[15] S. J. Li, A. C. Albertsson, A. Gupta, W. Bassett, and O. Vogl, *Monatsh. Chem.*, *115*, 853 (1984).

[16] A. D. Scully, S. W. Bigger, K. P. Ghiggino, and O. Vogl, *J. Photochem. Photobiol.* A.: Chem., *55*, 387 (1991).

[17] W. Dickstein and O. Vogl, *J. Macromol. Sci.—Chem.*, *A22*, 387 (1985).

[18] A. Sustic and C. L. Zhang, *J. Macromol. Sci.—Pure Appl. Chem.*, *A30*, 741 (1993).

[19] J. J. Falcetta, J. Park, and C. G. Smith, US Patent 5,133,745 (1992), Eur. Patent Appl. EP 343,996 (1991).