

Functional polymers. LIV. Photochemical behavior of 2(2-hydroxyphenyl)2H-benzotriazole derivatives
2. Influence of substituents on the ultraviolet spectra of 2(2-hydroxyphenyl)2H-benzotriazoles*

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SUMMARY

The absorption spectra of 2(2-hydroxyphenyl)2H-benzotriazoles derivatives substituted with electron-donating and withdrawing groups in various positions on the phenyl ring allowed to estimate the relative stability of the hydrogen-bonded structures as evidenced by the $\epsilon_{340 \text{ nm}}/\epsilon_{300 \text{ nm}}$ ratio.

Photodegradation studies of poly-cis-1,4-butadiene-1,3 with and without 2(2-hydroxyphenyl)benzotriazole absorbers with various substituents show that compounds with R=H are better photostabilizers than those with R≠H.

INTRODUCTION

The photodegradation of synthetic polymers can be retarded or inhibited by adding ultraviolet stabilizers. They absorb preferentially the energy of photoexcitation, become excited and are capable of dissipating the energy of the photoexcited state of the molecule into vibrational energy. Deterioration of the substrate by photochemical or photochemically initiated reactions is therefore prevented. It has been suggested that the efficiency of an ultraviolet stabilizer usually depends on the possibility of forming a hydrogen-bond and on the ease of hydrogen-bond formation.

2(2-Hydroxyphenyl)2H-benzotriazole [2-(2H-benzotriazole-2-yl)-phenol] derivatives are good examples of efficient ultraviolet stabilizers [1]. They absorb in the wavelength region of 300-360 nm, have high molar absorption coefficients and their photoexcited state has a mechanism by which it can dissipate the excitation into vibrational energy [2]. It is now possible to design and to modify the appropriate basic structures by placing the selected substituents in various positions of the molecule to obtain stabilizers with superior properties.

Substituents in the 2(2-hydroxyphenyl)2H-benzotriazole molecule affect the distribution of electron density which changes the formation and stability of the intramolecular hydrogen-

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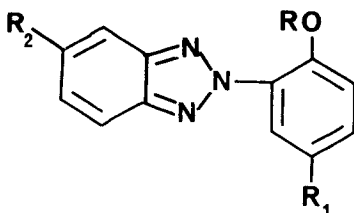
bond in the excited state. The ultraviolet spectrum is modified and the compounds act slightly differently as photostabilizers.

It was the objective of this work to investigate the hydrogen bond formation of various 2(2-hydroxyphenyl)2H-benzotriazoles with different substituent groups by comparing the details of their ultraviolet spectra. The photostabilizing efficiency of these 2(2-hydroxyphenyl)2H-benzotriazole derivatives was also studied using poly-cis-1,4-butadiene-1,3 (PB) as the substrate.

EXPERIMENTAL PART

The structures of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives with different substituents, studied in this work, are shown in Table 1.

The general structure of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives studied in this work is as follows:



The compounds listed in Table 1 were synthesized according to previously published methods [3,4].

The absorption spectra of the sample solutions were measured on a Hitachi 340 UV-Vis spectrophotometer, the fluorescence emission spectra on a Hitachi MPF-4 fluorescence spectrophotometer. The measurements were carried out in solution (1×10^{-4} molar in dichloroethane) and at room temperature.

Poly-cis-1,4-butadiene-1,3 (PB) samples (Ameripol CB 200) were obtained from the Goodrich Corp. and were purified by several reprecipitations before use.

For evaluating the photostabilizing capability of the 2(2-hydroxyphenyl)2H-benzotriazoles, PB, as the model polymer, was photodegraded in solution. The solution viscosities of the polymer solutions (in the presence and absence of the ultraviolet stabilizing compounds (Table 1) were measured after irradiation at various time intervals. Viscosity measurements were carried out in a quartz viscometer [5], suitable for measurements during photochemical experiments at 30°C ($\pm 0.5^{\circ}\text{C}$).

As the light source for the irradiation studies, a 500 W Xenon lamp (USHIU U1-501) was used.

Table 1

Sample No.	Name of Compounds	R	R ₁	R ₂
1	2(2-hydroxy-5-vinylphenyl)-2H-benzotriazole	-H	-CH=CH ₂	-H
2	2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole	-H	-C=CH ₂ CH ₃	-H
3	2(2-hydroxy-5-ethylphenyl)-2H-benzotriazole	-H	-C ₂ H ₅	-H
4	2(2-hydroxy-5-acetylphenyl)-2H-benzotriazole	-H	-C-CH ₃ O	-H
5	2(2-acetoxy-5-ethylphenyl)-2H-benzotriazole	-C-CH ₃ O	-C ₂ H ₅	-H
6	2(2-acetoxy-5-acetylphenyl)-2H-benzotriazole	-C-CH ₃ O	-C-CH ₃ O	-H
7	2(2-hydroxy-5-methylphenyl)-2H-5-ethylbenzotriazole	-H	-CH ₃	-C ₂ H ₅
8	2(2-acetoxy-5-methylphenyl)-2H-5-ethylbenzotriazole	-C-CH ₃ O	-CH ₃	-C ₂ H ₅
9	2(2-hydroxy-5-methylphenyl)-2H-5-vinyl-benzotriazole	-H	-CH ₃	-CH=CH ₂
10	2(2-acetoxy-5-methylphenyl)-2H-benzotriazole	-C-CH ₃ O	-CH ₃	-H
11	polymer of 1	-H	-CH-CH ₂ - 	-H
12	polymer of 9	-H	-CH ₃	-CH-CH ₂ -

RESULTS AND DISCUSSION

The study of the spectral characteristics of a number of 2(2-hydroxyphenyl)2H-benzotriazoles has been carried out and the results have allowed us to draw some general conclusions.

On photoexcitation, the proton of the hydroxyl-group in the ortho-position of the phenyl group becomes attached to the 2-nitrogen atom of a 2(2-hydroxyphenyl)2H-benzotriazole derivative causing the molecule to have a strong absorption between 330 and 350 nm. In contrast, the absorption of 2-phenyl-2H-benzotriazole derivatives which have no hydrogen bonding is around 300 nm. This observation was confirmed when spectra of

typical unsubstituted 2-phenyl-2H-benzotriazoles or 2-acylated derivatives of 2(2-hydroxyphenyl)2H-benzotriazoles were compared with 2(2-hydroxyphenyl)2H-benzotriazole derivatives which have free ortho-hydroxyl groups.

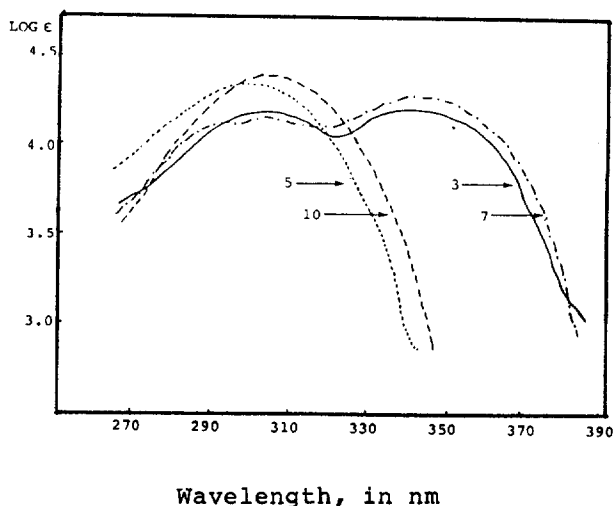
The absorption spectra of a series of 2(2-hydroxyphenyl)-2H-benzotriazoles in which R=H (compounds 1, 2, 3, 4, 7, 9, 11, 12) (Table 2) were measured and compared to the absorption spectra of another series of compounds in which R≠H (compounds 5, 6, 8, 10) (Table 2). It was found (Figure 1) that for compounds in which R=H, the absorption maxima were in the region of 300 nm and 330-350 nm. In the spectra of those compounds where R≠H, only the absorption maxima at 300 nm were observed. It has consequently been concluded that the compounds where the substituents R≠H, do not or cannot form intramolecular hydrogen-bonds. The absorption maximum near 340 nm which is characteristic for intramolecular hydrogen-bonding in the 2(2-hydroxyphenyl)2H-benzotriazole is not observed in these compounds. We have concluded that the earlier assignment of the absorption maximum (at 340 nm) [8] of the spectra of 2(2-hydroxyphenyl)2H-benzotriazole to the hydrogen bonded excited state was correct.

Table 2

Sample No.	Molar Absorption Coefficient (λ (nm))	Sample No.	Molar Absorption Coefficient (λ (nm))
1	14,800 (300) 12,000 (344)	7	14,100 (302) 19,200 (342)
2	14,060 (300) 11,500 (340)	8	20,100 (308)
3	26,600 (288) 16,000 (340)	9	4,600 (298) 5,800 (336)
4	14,400 (300) 18,000 (330)	10	24,600 (304)
5	21,960 (300)	11	12,300 (300) 11,800 (336)
6	21,000 (308)	12	14,850 (308) 19,500 (346)

Table 2 shows the absorption maxima and absorption coefficients of compounds 1-12. Those compounds, where R≠H (5, 6, 8, 10) have only one absorption maximum at about 300 nm while the other compounds where R=H, have two absorption maxima, one at about 300 nm and the other at about 340 nm. Table 2 shows also that the extinction coefficients at the absorption maxima of the compounds which have only one absorption maximum are higher than 20,000, while the compounds for which R=H, which have two absorption maxima, have lower extinction coefficients and the absorption maxima are also lower.

Fig. 1.
Absorption Spectra
of 5, 10, 3, 7 in
1,2-Dichloroethane
Solution



We have established that the intramolecular hydrogen-bond causes a decrease of the absorption of the portion of the molecule which causes the absorption at about 300 nm, presumably the non-hydrogen-bonded absorption at the expense of the now developing hydrogen-bonding absorption at 340 nm.

Table 3 shows a comparison of the ratio of the two extinction coefficients $\epsilon_{340 \text{ nm}} / \epsilon_{300 \text{ nm}}$ measured at the wavelengths of the two absorption maxima for compounds 1, 2, 3, 4. The following order of the ratios of the extinction coefficients was found: $4 > 2, 1 > 3$.

Table 3

Sample No.	Substituent Group R_1	Ratio of Coefficients	Characteristics
1	$-\text{CH}=\text{CH}_2$	0.81	extended conjugated system
2	$-\text{C}(\text{CH}_3)=\text{CH}_2$	0.82	extended conjugated system
3	$-\text{C}_2\text{H}_5$	0.60	electron donating group
4	$-\text{C}-\text{CH}_3$ O	1.20	electron withdrawing group

These results seem to demonstrate that when an electron withdrawing group (such as an acetyl group) is substituted in position R_1 the capability of the 2(2-hydroxyphenyl)2H-

benzotriazole group to form the intramolecular hydrogen-bond is increased. In contrast, if an electron donating group is placed in the R_1 position (such as an ethyl group) the capability of the hydrogen atom of the ortho-hydroxy-group to form an intramolecular hydrogen bond is decreased. When R_1 is an olefinic vinyl group, the molecule has an extended conjugated system and the electron density in the phenyl ring is decreased, which leads to a decrease in the capability of the compound to form the intramolecular hydrogen bond.

If the substituent in the R_2 position of the 2(2-hydroxyphenyl)2H-benzotriazole is changed, the situation is different. When an electron donating group is in the R_2 position, the electron density of the nitrogen atom in 3-position of the benzotriazole ring is increased providing a favorable situation for the proton of the ortho-hydroxyl group to form the hydrogen-bonded structure in the excited state. Thus, for the compounds 7 and 12, the ratios of $\epsilon_{340 \text{ nm}} / \epsilon_{300 \text{ nm}}$ were found to be 1.36 and 1.31 respectively; for compound 9 the ratio is slightly smaller, only 1.26.

According to the above results, the following conclusion can be drawn. When $R \neq H$, there is only one peak (at 300 nm) in the absorption spectrum of a 2-phenyl-2H-benzotriazole molecule and the extinction coefficient is always higher than 20,000.

When $R=H$, two peaks are observed in the absorption spectrum of a 2(2-hydroxyphenyl)2H-benzotriazole molecule, one of which is the hydrogen-bonded absorption at 330-340 nm. When $R=H$ and R_1 is an electron withdrawing group, such as an acetyl group, an intramolecular hydrogen-bond formation is favored. When $R=H$ and R_2 is an electron donating group, such as an ethyl-, methoxy- or a hydroxyl-group, hydrogen-bond formation is favored. When the R_2 group is electron withdrawing, hydrogen-bond formation is not favored.

Typical fluorescence emission spectra of compounds of the types described above are shown in Figure 2. Compounds where $R \neq H$ (compounds 5 or 6) when excited with light of $\lambda = 300 \text{ nm}$ emit their fluorescence at 370 nm. On the other hand, a compound where $R=H$ (such as in compound 7), when excited with light of a wavelength of $\lambda = 300$ or 340 nm, emits its fluorescence at a slightly longer wavelength.

For an ultraviolet absorber to be a good ultraviolet stabilizer, several photochemical conditions should be met. Not only does the absorption coefficient in the region of the wavelength of harmful radiation have to be high but also the ultraviolet radiation that has been absorbed and has formed the excited molecule has to have a mechanism through which the energy of the photoexcited state can be dissipated into harmless vibrational energy [7].

The kinetics of the photodegradation of poly-cis-1,4-butadiene-1,3 measured by the decrease of the viscosity of the polymer solution with various photostabilizers are shown in Figures 3 and 4. These measurements demonstrated the effectiveness of some of the ultraviolet stabilizing compounds. The efficiency of the photostabilization of the compounds in which $R=H$ is higher than the efficiency of the compounds where $R\neq H$. The capability for the photostabilization of PB by the monomeric and polymeric ultraviolet stabilizing compounds such as 1 through 11, and 9 through 12, has followed the now established rule. When the olefinic vinyl group of the monomer is located in the R_1 position, the corresponding polymer had a poorer photostabilization capability than that of the monomer.

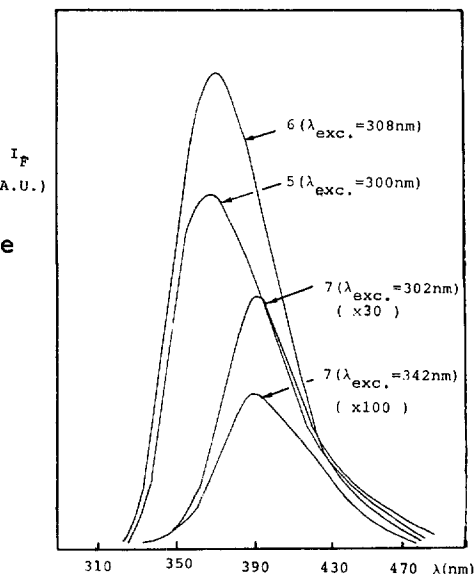


Fig. 2. Fluorescence Spectra of Compounds 5, 6, 7 Excited Light of Different Wavelengths

This result indicates that when the R_1 group was an electron-withdrawing group, it favored hydrogen-bond formation. When the polymerizable monomer is polymerized and the olefinic vinyl group in R_1 position is transformed into a saturated electron donating hydrocarbon group (the polymer backbone chain), the capability of hydrogen-bond formation of the monomer unit in the polymer molecule is decreased.

On the other hand, when an electron donating group occupies the position R_2 , the hydrogen-bond formation is favored. Consequently, polymerization of the ultraviolet stabilizing vinyl monomers will produce a macromolecule with a better photostabilizing capability.

Several questions related to these generalizations still need to be answered. Compound 4 has substituents which should favor hydrogen-bond formation, but this compound shows a poor performance as a photostabilizer. This might be caused by preferential photodegradation of the carbonyl function of the acetyl group of 2(2-hydroxy-5-acetylphenyl)2H-benzotriazole.

A group, such as an acetyl group is capable of undergoing photochemical reactions and of sensitizing the photodegradation of the polymer.

Our results show that the correct evaluation and ultimately the design of ultraviolet absorbers which can act as effective photostabilizers will undoubtedly require the intimate knowledge of a number of facts: among them are the details

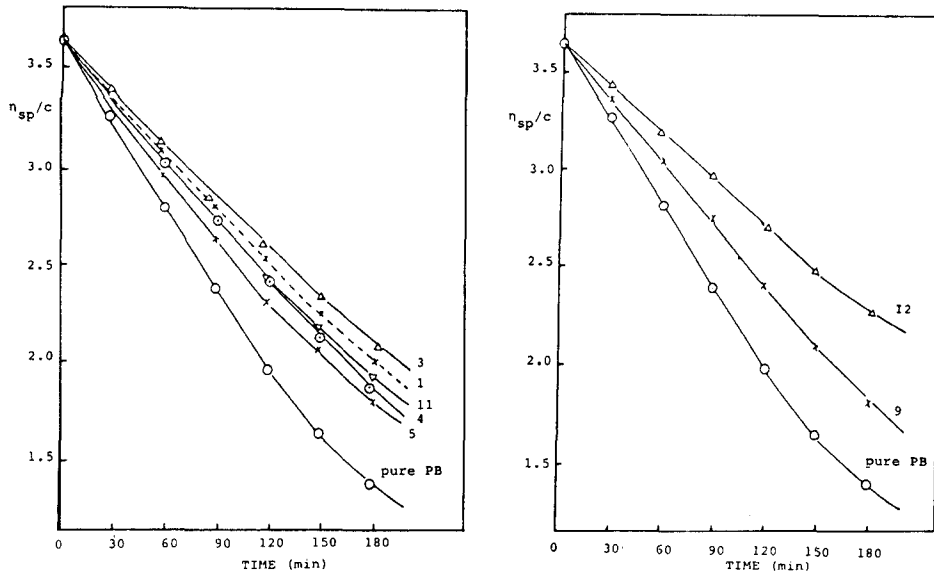


Fig. 3. Change of the Viscosity Number for PB (1.36 g/100 mL) and 4. in 1,2-Dichloroethane Solution (10:1) during Irradiation in the Presence of Air and Photostabilizers at the Concentration: 9.1×10^{-4} Molar.

of the chemical structures of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives and the substituent effects on 2(2-hydroxyphenyl)2H-benzotriazoles.

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