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Functional polymers. LVI. Photochemical behavior of 2(2-hydroxyphenyl)2H-benzotriazole derivatives

4. Spectroscopic study of ultraviolet absorbers with more than one 2(2-hydroxyphenyl)2H-benzotriazole group and more than one ortho-hydroxy group in the molecule*

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SUMMARY

Introduction of a second benzotriazole unit into 2(2-hydroxyphenyl)2H-benzotriazole structures causes a significant hyperchromic effect on the absorption spectra, the addition of a second hydrogen bonding hydroxyl group causes a small bathochromic shift, but a significant effect on the fluorescence spectrum.

INTRODUCTION

2(2-Hydroxyphenyl)2H-benzotriazole derivatives have been known for some time for their excellent performance as ultraviolet stabilizers, especially when they were used for the stabilization of plastic materials. As a consequence, the study of the spectroscopic characteristics of 2(2-hydroxyphenyl) 2H-benzotriazole derived ultraviolet absorbers has become of increasing interest [1-8].

It is now well established [9,10] that 2(2-hydroxyphenyl) 2H-benzotriazole derivatives form hydrogen bonded structures; these structures when excited give ultraviolet spectra with a λ maximum of 335-350 nm, depending on the nature of the substituents in the aromatic rings. 2(2-Hydroxyphenyl)2H-benzotriazoles which do not have or form intramolecular hydrogen bonded structures absorb at 290-310 nm. When irradiated with light of the proper wavelength, intramolecular hydrogen bonded structures are photoexcited and are capable of proton transfer which results in energy consumption by way of a mechanism which dissipates the excitation energy into harmless vibrational energy.

It has been found from the fluorescence spectra of 2(2-hydroxyphenyl)2H-benzotriazole derivatives that the fluorescence emission of these compounds, when excited with light of a wavelength of about 300 nm is more intense than the fluorescence emission of the same compound when it is excited at about 340 nm. On the basis of these results the following hypothesis for photo excitation and energy dissipation of 2(2-hydroxyphenyl)2H-benzotriazole derivatives had been proposed [4-8]:

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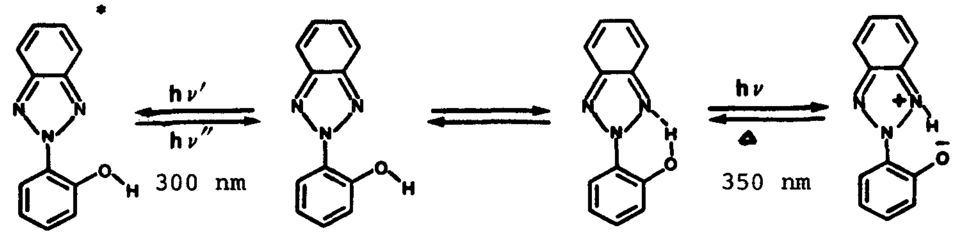
* Functional Polymers. LV., Y.C. Jiang, S.K. Wu, A. Sustic, F. Xi, and O. Vogl, Polymer Bulletin 20, 161 (1988)



[N] [H]

In the ground state of the 2(2-hydroxyphenyl)2H-benzotriazole molecule, there are two possible conformational isomers: a) the [N] state which has the ortho-hydroxyl group of the 2(2-hydroxyphenyl)2H-benzotriazole group in a transoid conformation, b) the [H] state which has the ortho-hydroxyl group in cisoid and truly hydrogen bonding conformation. Torsion along the N-C bond connecting the benzotriazole ring and the benzene ring may also play a role, because it has been known that in the ground state the 2(2-hydroxyphenyl)2H-benzotriazoles are not coplanar; they may be twisted out of plane by about 20° to 40°. Excitation at 300 nm causes the formation of the cisoid structure and excitation at 340 nm causes the formation of the coplanar photoexcited state.

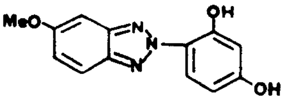
Equilibria between these individual states seem to exist, and undoubtedly depend on the substituents on the benzotriazole and phenyl rings. It has been found [9], that when the substituent on the phenyl ring is an electron-withdrawing group or the substituent on the benzotriazole is electron-donating, intramolecular hydrogen bonding occurs most readily.

In order to obtain a more detailed picture of the behavior of 2(2-hydroxyphenyl)2H-benzotriazole derivatives, and because 2(2-hydroxyphenyl)2H-benzotriazoles with more than one benzotriazole group and more than one ortho-hydroxyl group in the same molecule have become readily available [11-15], spectroscopic investigations of these newly synthesized "multi"benzotriazoles were undertaken.

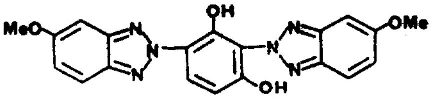
EXPERIMENTAL PART

The following compounds were prepared and purified according to previously described procedures [11-15].

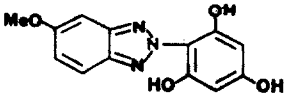
(1) 2(2,4-dihydroxyphenyl)2H-4-methoxy-benzotriazole.



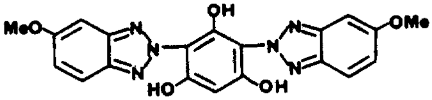
(2) 2(2,4-dihydroxyphenyl)2H-1,3-bis(4-methoxy)-benzotriazole.



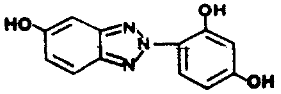
(3) 2(2,4,6-trihydroxyphenyl)2H-benzotriazole.



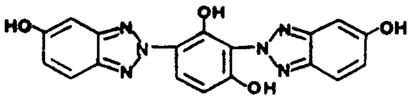
(4) 2(2,4,6-trihydroxyphenyl) 2H-1,3-bis(4-methoxy)-benzotriazole.



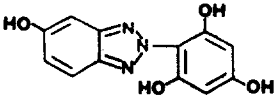
(5) 2(2,4-hydroxyphenyl)2H-4-hydroxy-benzotriazole.



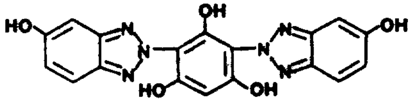
(6) 2(2,4-dihydroxyphenyl)2H-1,3-bis(4-hydroxy)-benzotriazole.



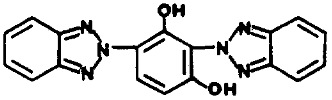
(7) 2(2,4,6-trihydroxyphenyl) 2H-4-hydroxy-benzotriazole



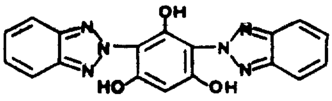
(8) 2(2,4,6-trihydroxyphenyl) 2H-1,3-bis(4-hydroxy)-benzotriazole.



(9) 2(2,4-dihydroxyphenyl)2H-1,3-bis-benzotriazole.



(10) 2(2,4,6-trihydroxyphenyl) 2H-1,3-bis-benzotriazole.



The absorption spectra of all these compounds were measured in dichloroethane solutions at concentrations of about 10^{-5} moles/L at room temperature on a Hitachi 340 Ultraviolet-Visible spectrometer; the fluorescence spectra were determined with a Hitachi MPF-4 spectrometer.

RESULTS AND DISCUSSION

The absorption and fluorescence spectra of some 2(2-hydroxyphenyl)2H-benzotriazole derivatives with more than one 2(2-hydroxyphenyl)2H-benzotriazoles group and more than one ortho-hydroxyl group in the molecule have been measured and some interpretation of the spectra is being offered.

From Figures 1 and 2 it can be seen that the absorption spectrum of the individual compounds changed when a substituent, such as a methoxy- or a hydroxy- group, was introduced into the 4 position of the benzotriazole ring. The absorption maxima of these compounds, which are normally observed at 330-340 nm, and are attributed to the excited state of the hydrogen bonded molecule, are shifted to longer wavelengths, 340-360 nm. This change seems to indicate a more extensive stabilization of the excited state of these compounds. It has also been observed that methoxy- or hydroxy-substituted 2(2-hydroxyphenyl)-2H-benzotriazole compounds with substituents in the 4-position of the benzotriazole ring have absorption maxima at 340-350 nm with a higher extinction coefficient than that observed at about 300 nm. As a consequence, the absorption maxima at 300 nm, noticed in our earlier investigations [9,10], were not observed in the absorption spectra of the 2(2-hydroxyphenyl)2H-benzotriazoles of this series.

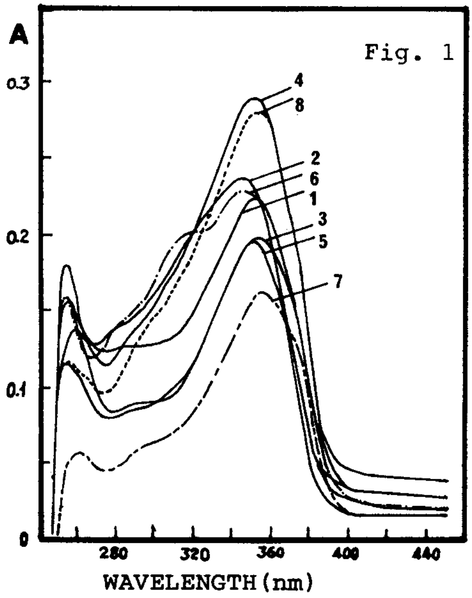


Fig. 1

Absorption Spectra of Compounds 1 to 8 in Dichloroethane Solutions. Conc.: 1×10^{-5} Molar.

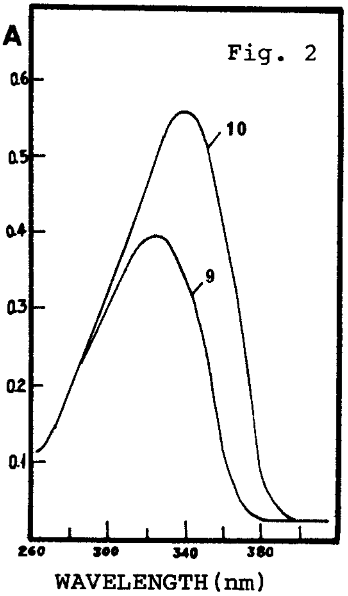


Fig. 2

Absorption Spectra of Compounds 9 and 10 in Dichloroethane Solutions. Conc.: 1.2×10^{-5} Molar.

In order to compare the extinction coefficients of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives, the absorption peaks at 330-350 nm were taken as standards; by plotting symmetrically the absorption at 300 nm, the results, shown in Table 1, were obtained.

Table 1.

Molar Extinction Coefficients of 2(2-Hydroxyphenyl)2H-benzotriazole Derivatives

Compound Number	Number of Bzt Units	Number of -OH Groups	Molar Extinction Coefficient, (Wavelength in nm)		ε 350 nm/ ε 300 nm
1	1	2	33,700 14,000	(350) (300)	2.41
2	2	2	36,000 17,000	(344) (300)	2.12
3	1	3	30,000 8,000	(352) (300)	3.41
4	2	3	48,800 20,000	(350) (300)	2.44
5	1	2	29,000 9,600	(350) (300)	3.02
6	2	2	34,500 22,000	(346) (300)	1.57
7	1	3	25,000 7,000	(355) (300)	3.57
8	2	3	48,000 21,700	(352) (300)	2.21
9	2	2	34,000	(330)	
10	2	3	46,000	(330)	

It can be seen from Table 1, that the 2(2-hydroxyphenyl)-2H-benzotriazole derivatives with two benzotriazole groups in the same molecule, with the corresponding ortho-hydroxyl groups associated with the structure, i.e., compounds 2, 4, 6, 8, 9, 10 have strong absorptions at 350 nm, especially when the number of ortho-hydroxyl groups is more than one. When comparing the ratios of ε350 nm/ ε300 nm (indicating the possible numbers of intramolecular hydrogen bonding structures of the ortho-hydroxyl groups to the benzotriazole rings, compared to structures that do not form intramolecular hydrogen bonds), it was found that the compounds with more than one ortho-hydroxyl group in the molecule have a higher ratio, which seems to indicate a greater efficiency of hydrogen bond formation to the benzotriazole rings when more than one ortho-hydroxyl group is in the molecule.

This correlation is very important, because the absolute value of the molar absorption at 350 nm seems to be determined by the number of 2(2-hydroxyphenyl)2H-benzotriazole units in the molecules, but the value of the ratio of ϵ 350 nm/ ϵ 300 nm seems to be determined by the efficiency of the hydrogen bond formation in the molecule and presumably the efficiency of the compound to function as an ultraviolet stabilizer.

The influence of electron-donating and electron withdrawing groups in the $4'$ position on the extinction coefficient and the ratio can be found in Table I. Compounds 2, 6, 9 have as their substituents methoxy, hydroxy- and hydrogen-groups; their molar extinction coefficients at λmaximum are 36,000, 34,500 and 34,000, respectively. These results indicate that the introduction of hydroxyl or methoxyl groups in the $4'$ position of the benzotriazole ring resulted in a slight increase in the absorption coefficient of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives, indicating a more efficient intramolecular hydrogen-bonding. In another group of compounds of comparable structure, 4, 8, 10 where the substituents were also methoxy, hydroxy- and hydrogen- groups respectively, their molar extinction coefficients at λ maximum similarly increased from 46,000 to 48,800, which also indicates that the introduction of electron donating groups in the 4 position of the benzotriazole rings enhanced the formation of intramolecular hydrogen bonds.

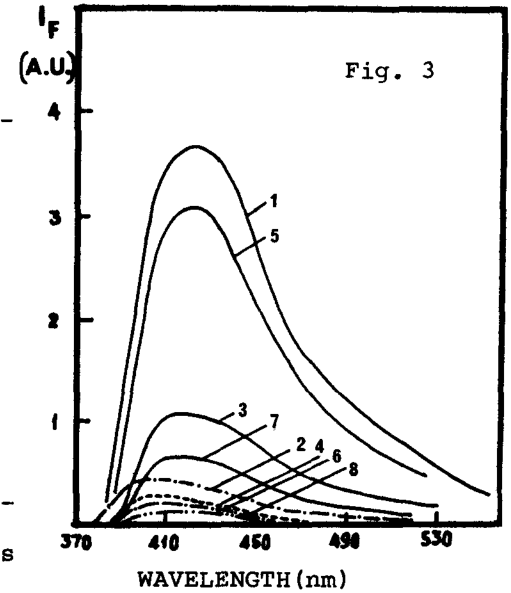


Fig. 3

Fluorescence Spectra of Compounds 1 to 8 in Dichloroethane Solution. Conc.: $5x10^{-5}$ Molar. λ exc.= 300nm.

Fluorescence spectra of a series of compounds from the class of 2(2-hydroxyphenyl)2H-benzotriazoles excited with light of a wavelength of 300 nm are shown in Figure 3. Compounds 1 and 5, 2(2-hydroxyphenyl)2H-benzotriazole derivatives obtained from resorcinol, which are substituted by methoxy- and hydroxy-groups in the $4'$-position of the benzotriazole ring, have stronger fluorescence and their ability of consuming photoexcitation energy is relatively poor. If, however, an additional ortho-hydroxy group was introduced into the molecule, such as in the case of compounds 3 and 7, both 2(2-hydroxyphenyl)2H-benzotriazole derivatives similar to 1 and 5, but derived from phloroglucinol, instead of resorcinol, their fluorescence at 410-420 nm was dramatically weakened.

Figure 3 also shows the fluorescence spectra of 2, 4, 6 and 8. These compounds show only a very weak fluorescence. All four compounds have two benzotriazole rings in the molecule and a substantially higher extinction coefficient at 340-350 nm as compared to 2(2-hydroxyphenyl)2H-benzotriazole derivatives with only one benzotriazole ring in the molecule. This observation indicates that the absolute value of the extinction coefficient also seems to represent a factor that plays an important role in consuming energy.

The fluorescence spectra described in this work were generated by irradiating the compounds in solution at a wavelength of 300 nm assuming that isomerization caused by irradiation of light of this wavelength takes place.

CONCLUSION

We conclude that the energy-consuming process proceeds as follows: The non hydrogen-bonding [N] state of the 2(2-hydroxyphenyl)2H-benzotriazole containing molecule absorbs photoenergy; subsequently, isomerization takes place which changes the transoid [N]* state into the cisoid, hydrogen-bonding [H] state or there can be energy transfer to the [H] ground state which then dissipates the photoexcitation energy by proton tranfer from the excited [H] state to the ground state:

The process can be expressed as follows:

$$[N] \xrightarrow{h\nu} [N]^*$$

$$[N]^* \xrightarrow{\text{isomerization}} [H]$$

$$[N]^* + [H] \xrightarrow{\text{energy transfer}} [H]^* + [N]$$

$$[H]^* \xrightarrow{\text{proton transfer}} [H] + \Delta$$

This proposed sequence of events seems to be in agreement with the results of the investigation of the fluorescence spectroscopy of ultraviolet absorbing compounds with more than one 2(2-hydroxyphenyl)2H-benzotriazole and with more than one ortho-hydroxy group in the molecule.

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