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Functional Polymers. LVII. Electronic Absorption Spectra of Benzotriazole Derivative/Electron Acceptor Systems

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FUNCTIONAL POLYMERS. LVII.† ELECTRONIC ABSORPTION SPECTRA OF BENZOTRIAZOLE DERIVATIVE/ELECTRON ACCEPTOR SYSTEMS

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ABSTRACT

The electronic absorption spectra of charge-transfer complexes (CTC) of benzotriazole derivatives including 2(2*H*-hydroxyphenyl)2*H*-benzotriazole-containing copolymers with various electron acceptors were investigated. While no charge-transfer interaction was observed with weak acceptors, strong acceptors such as trinitrofluorenone and pyromellitic anhydride exhibited an absorption of the contact charge-transfer type with these donors. When the very strong acceptor tetracyanoethylene was used as acceptor, new peaks of a CTC type appeared at longer wavelengths. From the wavelengths of the absorption maxima and the equilibrium constants of the CTC, the electron-donating ability of several related (2(2-hydroxyphenyl)2*H*-benzotriazole derivatives was estimated as

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follows: 2(2-Hydroxy-5-methylphenyl)2*H*-benzotriazole > 2*H*-benzotriazole > 2(4-hydroxyphenyl)2*H*-benzotriazole > 2(2-acetoxy-5-methylphenyl)2*H*-benzotriazole > copolymers containing 2(2-hydroxyphenyl)2*H*-benzotriazole groups.

INTRODUCTION

2(2-Hydroxy-5-methylphenyl)2*H*-benzotriazole (HMB) and its derivatives have been studied extensively as very efficient UV light absorbers [1, 2]. Some reports [3] indicate that they have very low triplet energy and consequently could be employed as energy acceptors in triplet energy transfer processes. However, no mention was made of their electron-donating ability although a considerable number of nitrogen-containing compounds, including heterocyclic compounds, are known to be good electron donors [4, 5].

It was the objective of this work to investigate the electronic absorption spectra produced by the interaction between 2(2-hydroxyphenyl)-2*H*-benzotriazole derivatives and various electron acceptors, from which the electron-donating ability of 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives and 2(2-hydroxyphenyl)2*H*-benzotriazole groups containing copolymers would be evaluated.

EXPERIMENTAL PART

A. Materials

2(2-Hydroxy-5-methylphenyl)2*H*-benzotriazole (HMB) was commercial grade Tinuvin P obtained from the Ciba-Geigy Company. 2(4-Hydroxyphenyl)2*H*-benzotriazole (HPB) was prepared according to Ref. 6; 2(2-acetoxy-5-methylphenyl)2*H*-benzotriazole (AMB) was synthesized by acetylation of HMB.

All other chemicals were chemical-grade reagents and were purified according to established methods.

The preparation of 2(2-hydroxyphenyl)2*H*-benzotriazole groups containing copolymers with MMA were described previously [7, 8]. The composition of the copolymers was established from UV absorption measurements by using a Beckman Du-7 SUV Spectrophotometer.

B. Measurements

The absorption spectra were recorded with a Shimadzu UV-240 Spectrophotometer. Dichloromethane, chloroform, acetone, and tetrahydrofuran (THF) were used as the solvent; they were all spectral-grade quality.

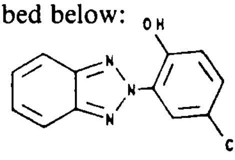
The molecular weight and molecular weight distribution (MWD) of the copolymers were determined by a GPC Shimadzu LC-4 instrument.

RESULTS AND DISCUSSION

Absorption Spectra of 2(2-Hydroxyphenyl)2*H*-benzotriazole Derivatives

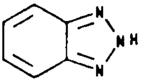
The chemical structure and the λ_{max} values of the absorption spectra of the 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives and related copolymers used in our work are described below:

2(2-Hydroxy-5-methylphenyl)-
2*H*-benzotriazole (HMB)



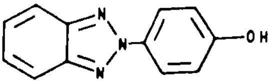
300 nm
340 nm

2*H*-Benzotriazole (B)



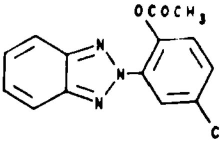
250 nm
280 nm

2(4-Hydroxyphenyl)2*H*-benzotriazole (HPB)



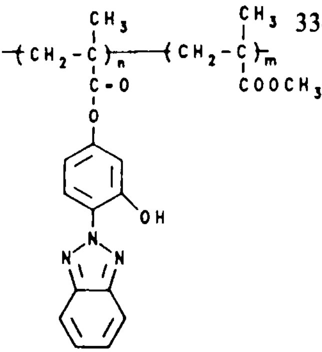
318 nm

2(2-Acetoxy-5-methylphenyl)2*H*-benzotriazole (AMB)



300 nm

Copolymer of 2(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole with methyl methacrylate (Copolymer I)



295 nm/
334 nm

Interaction with Weak Electron Acceptors

No spectral change was observed when solutions of any of the above benzotriazole derivatives were added to weak electron acceptors such as acrylonitrile (AN), or even to a somewhat stronger acceptor, such as fumaronitrile (FN). From these observations it might be inferred that charge-transfer interaction had not taken place in these systems. It is known that aromatic amines such as *N,N*-dimethylaniline (DMA) form charge-transfer complexes (CTC) with these acceptors, resulting in broadening of the absorption bands to longer wavelengths or the appearance of a new CTC absorption peak [4]. Therefore, benzotriazole and its derivatives are weaker electron donors than aromatic amines or substituted anilines.

Interaction with Strong Electron Acceptors

When stronger electron acceptors such as trinitrofluorenone (TNF), pyromellitic anhydride (PMAD), or 2,4,5,7-tetranitrofluorenone (TENF) were added to solutions of our four selected benzotriazole derivatives, the absorption bands of the latter broadened in the direction of longer wavelengths, indicating the occurrence of charge-transfer interactions. Figure 1 shows the spectra of the HMB/PMDA system.

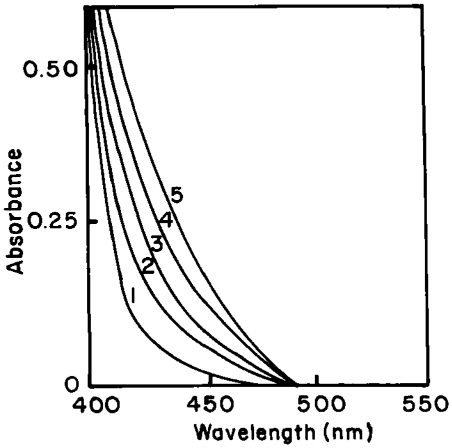


FIG. 1. Absorption spectra of HMB/PMDA system. [HMB] = 7.5 × $10^{-2}M$. [PMDA]: (1) 0, (2) 2 × $10^{-2}M$, (3) 3 × $10^{-2}M$, (4) 4.9 × $10^{-2}M$, (5) 6.1 × $10^{-2}M$.

From the Benesi-Hildebrand equation [6, 7, 9, 10]:

$$\frac{1}{\text{O.D.}} = \left(\frac{1}{k}\cdot\epsilon_c b\right)\frac{1}{a} + \frac{1}{\epsilon_c b}$$

the equilibrium constant *k* of the CTC can be calculated. In the equation, O.D. and ϵ_c represent the absorbance of the CTC and its extinction coefficient at the wavelength measured, *b* represents the constant concentration of the electron donor, and *a* represents the varying concentrations of the electron acceptor. Figure 2 shows the Benesi-Hildebrand plot of the HMB systems with various acceptors. For HMB/TNF and HMB/PMDA, the plots intersect the vertical ordinate at minus values, implying that the equilibrium constants are zero and the complexes of the two examples belong to the contact charge-transfer (CCT) type [11]. On the other hand, for the strong acceptor TENF, the Benesi-Hildebrand plot intersects at a positive value; the equilibrium constant *k* was calculated to be 0.07.

Interaction with Tetracyanoethylene (TCNE)

TCNE is one of the strongest electron acceptors. When it was added to a dichloromethane solution of HMB, the solution became yellow and a new absorption peak indicative of the CTC appeared at 530 nm (Fig.

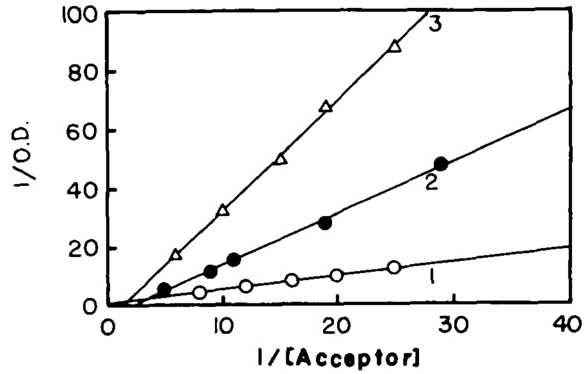


FIG. 2. Benisi-Hildebrand plots: (1) HMB/TENF, (2) HMB/TNF, (3) HMB/PMDA.

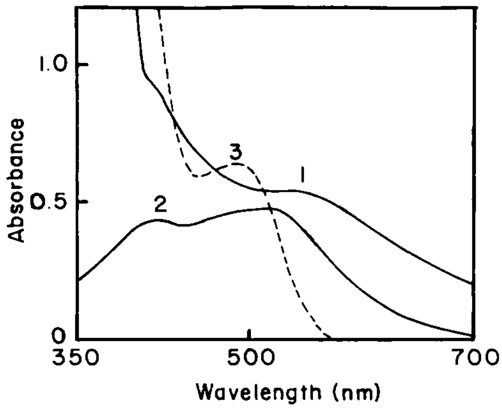


FIG. 3. Absorption spectra in CH_2Cl_2. (1) HMB ($3.0 \times 10^{-3}M$)/TCNE ($5.0 \times 10^{-2}M$); (2) B (3.3×10^{-2} M)/TCNE ($2.0 \times 10^{-2}M$); (3) *m*-cresol (1.0×10^{-2} M)/TCNE (4.0×10^{-2} M).

3). At a total concentration of 4×10^{-2} M, the absorbance of the systems showed a maximum at concentrations of 2×10^{-2} M of each, i.e., at a 1:1 mole ratio, indicating that a 1:1 complex had been formed (Fig. 4).

HMB may be considered to consist of the structural elements of benzotriazole and *p*-cresol, both of which are electron-donating molecular structures. Figure 3 shows the absorption maximum of the CTC of 2*H*-benzotriazole/TCNE at 508 nm—a shorter wavelength than the

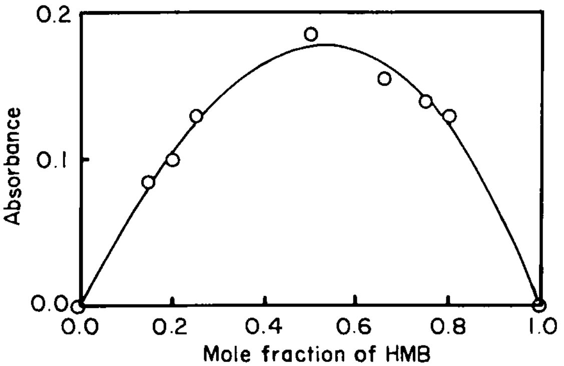
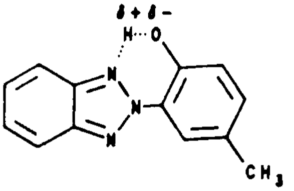


FIG. 4. Relationship between the absorbance of HMB/TCNE mixture solution and the mol % of HMB. (Total concentration: 4.0×10^{-2} M, in CH_2Cl_2.)

HMB/TCNE system. The CTC spectrum of *m*-cresol/TCNE showed an even shorter wavelength (λ_{max} = 500 nm). For a given acceptor, the stronger donor usually exhibits a CT absorption at a longer wavelength [12, 13]. The stronger electron-donating ability of HMB seems to come from the cooperative contribution of the 2*H*-benzotriazole unit and the cresol unit.

HPB also forms CTC with TCNE; the spectra are shown in Fig. 5. An absorption peak at 470 nm indicates that HPB is an even weaker electron donor than *m*-cresol/TCNE. The mere deficiency of a methyl group in the molecule does not seem to be a sufficient explanation for the difference. However, the intramolecular hydrogen bond in HMB could possibly make the hydroxy group a stronger electron-donating group. A driving force might be the coplanarity of the molecule.



Alteratively, the structure of HPB (according to NMR analysis) shows

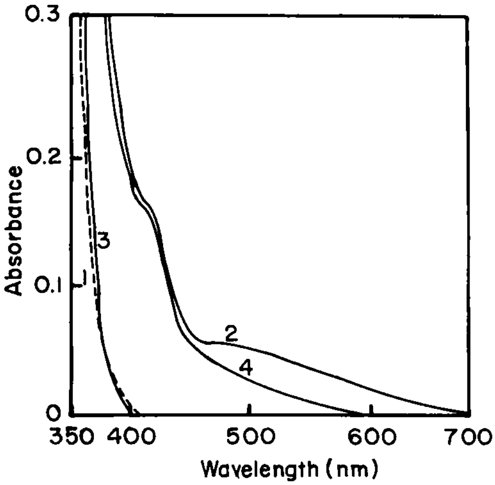


FIG. 5. Absorption spectra in CH_2Cl_2. (1) [HPB] = 3.0×10^{-3} *M*; (2) [HPB] = 3.0×10^{-3} *M*, [TCNE] = 3.6×10^{-2} *M*; (3) [AMB] = 3.0×10^{-3} *M*; (4) [AMB] = 3.0×10^{-3} *M*, [TCNE] = 3.6×10^{-2} *M*.

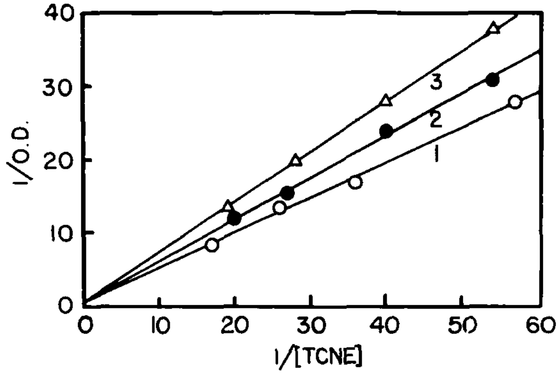


FIG. 6. Benisi-Hildebrand plots. (1) HMB/TCNE (530 nm), (2) HPB/TCNE (470 nm), (3) APB/TCNE (460 nm).

a twist between the benzene ring and the benzotriazole ring in its ground state; this structural conformation may prevent HPB from interacting with the electron-acceptor molecules to form CTC.

AMB is the acetylation product of MHB; its electron-donating ability is much weaker than that of HMB because the acetyl substituent is now slightly electron withdrawing rather than donating as in the case of the hydroxy substituent, and intramolecular hydrogen bonding cannot occur. Only a CTC shoulder was observed in the spectrum of the AMB/TCNE system (FIg. 5).

The Benesi-Hildebrand plots of some of the CTC systems are displayed in Fig. 6. The equilibrium constants *k* were calculated and are presented in Table 1. The *k* values decreased in the following sequence:

TABLE 1. CTC of TCNE with Benzotriazole Derivatives

Electron donor	λ_{max} (nm)	*k*
HMB	530	0.48
B	508	0.40
HPB	470	0.24
AMB	Shoulder	0.15

HMB > B > HPB > AMB

which is in agreement with the sequence of electron-donating ability estimated from the λ_{max} of the CTC absorption.

Interaction with Lewis Acid

Benzotriazole derivatives can interact not only with acceptors of the π-type, as discussed above, but also with acceptors of the Lewis acid type such as zinc chloride. The complexes show a yellow color and a broadening of the absorption spectra. In Fig. 7 the terms of degree of broadening are as follows:

HMB > HPB > AMB

It was known that 4-vinylpyridine (4-Vp), a weak electron donor, becomes a very strong acceptor when it forms a complex with zinc chloride [14, 15]. As the complex $(4\text{-Vp})_2ZnCl_2$ was added to a HMB solu-

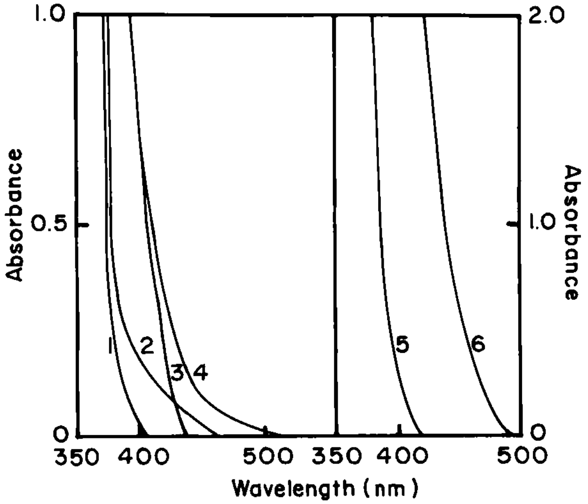


FIG. 7. Absorption spectra in THF. (1) [APB] = 5 × 10^{-2} *M*; (2) [APB] = 5 × 10^{-2} *M*, $[ZnCl_2]$ = 0.2 *M*; (3) [HMB] = 5 × 10^{-2} *M*; (4) [HPB] = 5 × 10^{-2} *M*, $[ZnCl_2]$ = 0.2 *M*; (5) [HMB] = 2.5 × 10^{-2} *M*; (6) [HMB] = 2.5 × 10^{-2} *M*, $[ZnCl_2]$ = 0.1 *M*.

tion, a significant charge-transfer absorption band was observed (Fig. 8).

Interaction between Copolymers Containing B Groups and TCNE

Like small molecule compounds, copolymers containing an electron donor group of the benzotriazole (B) type can also form CTC with TCNE. This is indicated by the development of a yellow color and the appearance of a new absorption, which increases in intensity as the concentration of TCNE increases (Fig. 9). The intensity is, however, weaker than in the same cases when small molecules were used as the donors. The Benesi–Hildebrand plots (Fig. 10), however, all intersect the vertical ordinate at zero; the equilibrium constant *k* values are consequently zero (Table 2).

CT complexes of polymer donors with low molecular acceptors have been the subject of several investigations [12, 16–21]. The difference in the values was observed for the electron donors which are part of a

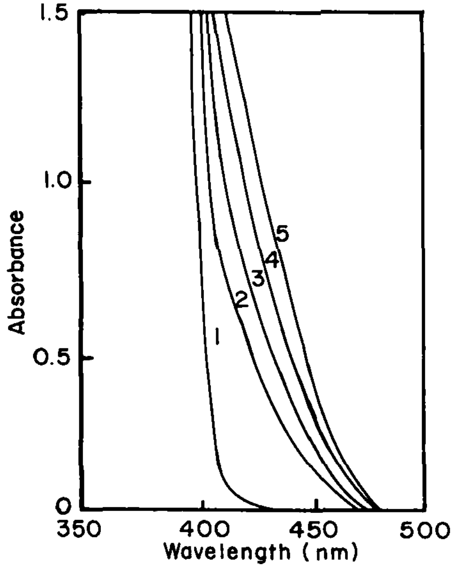


FIG. 8. Absorption spectra of HMB/(4-Vp)$_2$ZnCl$_2$ system in CH$_2$Cl$_2$. [HMB] = 2 × 10^{-2} *M*, [(4-Vp)$_2$ZnCl$_2$]: (1) 0, (2) 0.042 *M*, (3) 0.095 *M*, (4) 0.20 *M*, (5) 0.33 *M*.

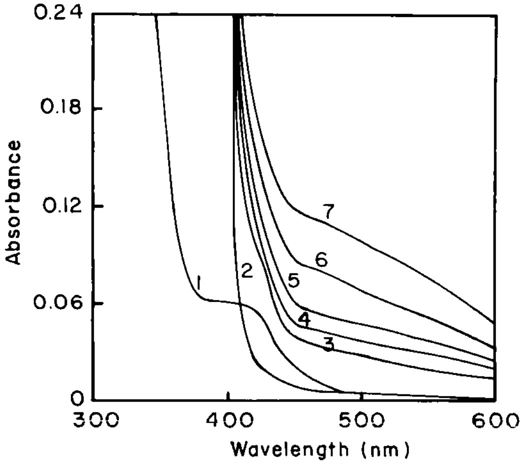


FIG. 9. Absorption spectra of Copolymer 2/TCNE system in $CHCl_3$. (1) [TCNE] = 1.33×10^{-2} *M*; (2)-(7) [Copolymer 2] = 7.99 mg/mL. [TCNE]: (2) 0, (3) 5.0×10^{-3} *M*, (4) 7.5×10^{-3} *M*, (5) 1.1×10^{-2} *M*, (6) 1.7×10^{-2} *M*, (7) 2.5×10^{-2} *M*.

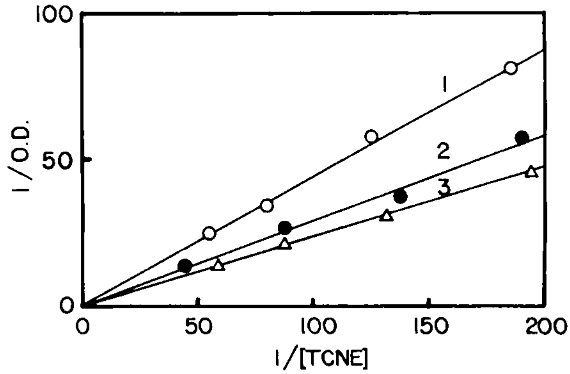


FIG. 10. Benisi-Hildebrand plots of 2*H*-benzotriazole containing copolymer/TCNE systems (in $CHCl_3$, 530 nm). (1) Copolymer 1, content of BZ: 3.5%. (2) Copolymer 1, content of BZ: 10.7%. (3) Copolymer 2, content of BZ: 16.4%.

TABLE 2. CTC of TCNE with 2(2-Hydroxyphenyl)2*H*-benzotriazole Containing Copolymers[a]

Electron donor	Copolymer 1	Copolymer 1	Copolymer 2
Bx content (mol %)	3.5	10.7	16.4
M_n	8.4×10^5	6.8×10^5	3.2×10^5
MWD	1.9	3.2	2.0
k	0	0	0

[a] Solvent: chloroform. Wavelength of measurement: 530 nm.

polymer chain as compared to the corresponding monomeric donors (small molecules). The difference depends on the kinds of donor and acceptor compounds. Although in most papers [12, 16–21] an increase of the *k* values was reported when the monomeric donor was replaced by the corresponding polymeric donor; however, in a few cases [16–21] a decrease was also found. Our systems belong to the latter category; a greater entropy of complex formation with polymeric donors may be responsible for the low *k* values [21] of our polymeric CTC complexes.

CONCLUSIONS

a) 2(2-Hydroxy-5-methylphenyl)2*H*-benzotriazoles (HMB is an example), a well-known and efficient UV light absorbing compound, and other benzotriazole derivatives have been shown to form CT complexes with strong electron acceptors, including Lewis acids. The electron-donating ability of the molecule originates in both the benzotriazole and *p*-cresol portions of the molecule. b) The intramolecular hydrogen bond in HMB provides the possibility of a copolanar structure for the molecule, making it more electron-donating than similar structures which cannot form hydrogen-bonded structures. c) Copolymers containing 2(2-hydroxyphenyl)2*H*-benzotriazole groups showed a lower electron-donating capability than did the corresponding small molecules.

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