

Available online at www.sciencedirect.com



Chinese Chemical Letters 23 (2012) 1019-1022



www.elsevier.com/locate/cclet

Synthesis, spectroscopic properties and applications of novel *N*-heterocycle-containing benzotriazoles as UV absorbers

Zhi Hua Cui^{a,b,*}, Xi Dong Wang^a, Jiang Chao Guo^a, Wei Guo Chen^{a,b}

^a Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education of China, Zhejiang Sci-Tech University, Hangzhou 310018, China

^b Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China

> Received 4 May 2012 Available online 19 July 2012

Abstract

Two novel *N*-heterocycle-containing benzotriazole compounds, 5-(5-chloro-2-benzotriazolyl)-6-hydroxy-1,4-dimethyl-3-carbonitrile-2-pyridone (**2**) and 4-(5-chloro-2-benzotriazolyl)-5-methyl-2-phenyl-3-pyrazolone (**4**), were synthesized from reactant 4chloro-2-nitroaniline*via*diazotization, azo coupling, reductive cyclization and acidification. Their structures were confirmed byFT-IR, ¹H NMR, mass spectroscopy and elemental analysis. Their spectral properties were investigated and compared with that of acommon commercial benzotriazole UV absorber Tinuvin 326. It is found that the novel*N*-heterocycle-containing benzotriazolecompounds exhibit sharp single peak in the range of 280–400 nm and have much higher molar extinction coefficients than that ofTinuvin 326. Their anti-UV protection properties on polyester fabric were also evaluated and compound**4**was much superior tocompound**2**due to its higher exhaustion.

© 2012 Zhi Hua Cui. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Benzotriazole; UV absorber; Pyrazolone; Pyridone; Anti-UV protection

It is widely recognized that ultraviolet rays (UVR) in sunlight is an important factor causing skin aging, eye disease [1] and photodegradation to some organic substances such as polymers and colorants [2,3]. In practice, addition of UV absorber is an effective and convenient method for protecting polymers and colorants against photodegradation [4,5]. 2-(2-Hydroxyphenyl)-benzotriazole derivatives are one sort of efficient UV absorber absorbing in the wavelength region of 300–360 nm and hardly absorbing visible light. The stabilizing mechanism of these type of compounds is based on the formation of intramolecular hydrogen bonds (IMHB) between the *o*-hydroxyl group of the phenyl ring and the nitrogen atom of the benzotriazole moiety and the excited state intramolecular proton transfer (ESIPT) mechanism by $O \cdots H \cdots N$ tunneling [6]. Since the discovery of 2-(2-hydroxyphenyl)-benzotriazole as a UV absorber chromophore, most efforts have been focused on the effect of substituent variation in benzotriazole chromophore [7] than chromophore variation itself. In view of the influence of heterocycle on the spectral property, two novel *N*-heterocycle-containing benzotriazole derivatives **2** and **4** have been synthesized in this research (see Scheme 1).

^{*} Corresponding author at: Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education of China, Zhejiang Sci-Tech University, Hangzhou 310018, China.

E-mail address: zhhcui@zstu.edu.cn (Z.H. Cui).

^{1001-8417/\$-}see front matter © 2012 Zhi Hua Cui. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved. http://dx.doi.org/10.1016/j.cclet.2012.06.024



Scheme 1. Synthetic routes of *N*-heterocycle-containing benzotriazole compounds. Reagents and conditions: (a) NaNO₂/HCl; (b) *N*-methyl-3-cyano-6-hydroxy-4-methyl-2-pyridone, 0–5 °C; (c) thiourea dioxide, NaOH, 83 °C, 3 h; (d) HCl; (e) 1-phenyl-3-methyl-5-pyrazolone, 0–5 °C.

We hope the introduction of heterocycles (pyrazolone and pyridone) into benzotriazole chromophore might improve their UV absorbance.

The synthesis processes of benzotriazole **2** and **4** are shown in Scheme 1. Firstly, compound **1** and **3** were synthesized from 4-chloro-2-nitroaniline diazonium salts with *N*-methyl-3-cyano-6-hydroxy-4-methyl-2-pyridone and 1-phenyl-3-methyl-5-pyrazolone using classical reaction for the synthesis of the azocompounds [8]. Subsequently, compound **1** was dissolved in aqueous solution containing NaOH (0.55 mol) and water (300 mL). The solution was heated and kept the temperature at about 83 °C, and thiourea dioxide(0.25 mol) was added in four times within 2 h. After a total reaction time of 3 h, the solution was poured in ice water and acidified to pH 2.0 with concentrated hydrochloric acid, and then the product benzotriazole **2** was filtered and dried in vacuum. Benzotriazole **4** was also synthesized using the same process described above where compound **1** was replaced by compound **3**. The crude products were purified by recrystallization from ethanol.

5-(5-Chloro-2-benzotriazolyl)-6-hydroxy-1,4-dimethyl-3-carbonitrile-2-pyridone (2): yield: 86%. IR (ATR/ cm⁻¹): 3346 (OH), 2206 (CN), 1643 (C=O), 1106 (C-Cl). ¹H NMR (400 MHz, DMSO- d_6): δ 8.11 (s, 1H, Ar-H), 8.02 (d, 1H, Ar-H), 7.46 (d, 1H, Ar-H), 3.12 (s, 3H, N-CH₃), 1.68 (s, 3H, CH₃). MS (ESI, negative): *m*/*z* 314.0 (M-H)⁻. Element analysis: found (%): C, 53.21; H, 3.24; N, 22.23; Calcd. (%): C, 53.26; H, 3.19; N, 22.18.

4-(5-Chloro-2-benzotriazolyl)-5-methyl-2-phenyl-3-pyrazolone (**4**): yield: 88%. IR (ATR/cm⁻¹): 2818 (CH₃), 1631 (C=O), 1049 (C-Cl). ¹H NMR (400 MHz, DMSO- d_6): δ 8.08 (s, 1H, Ar–H), 7.99 (d, 1H, Ar–H), 7.94 (d, 2H, Ar–H), 7.43 (d, 1H, Ar–H), 7.40 (d, 2H, Ar–H), 7.18–7.16 (m, 1H, Ar–H), 2.25 (s, 3H, CH₃). MS (ESI, positive): m/z 326.1 (M+H)⁺, 348.1 (M+Na)⁺. Element analysis: found (%): C, 59.06; H, 3.67; N, 21.44; Calcd. (%): C, 58.99; H, 3.71; N, 21.50.

Both benzotriazole 2 and 4 may exist in two tautomeric forms (enol form and keto form) under unexcited states (Fig. 1). The infrared spectrum of benzotriazole 2 shows one broad hydroxy band at about 3346 cm^{-1} , which is



Fig. 1. The tautomerism between keto and enol forms of benzotriazole 2 and 4 and their UV absorbing mechanism.



Fig. 2. UV–vis absorption spectra of benzotriazole 2, 4 and Tinuvin 326. (a) In ethanol $(2 \times 10^{-5} \text{ mol/L})$; (b) in chloroform $(2 \times 10^{-5} \text{ mol/L})$.

assigned to the enol form. The infrared spectrum of benzotriazole **4** shows one intense carbonyl band at about 1631 cm^{-1} , which is assigned to the keto form. Both of them can mainly exist as or convert to enol form firstly and absorb UV light by ESIPT mechanism (Fig. 1) similar to 2-(2-hydroxyphenyl)-benzotriazole derivatives. In the ¹H NMR spectra of benzotriazole **2** and **4**, the signals corresponding to OH proton resonance of the enol form and CH proton resonance of the keto form do not appear. It indicates benzotriazole **2** and **4** mainly exist as enol form in DMSO- d_6 solution and their active hydrogen signal in OH often disappear due to hydrogen exchange with DMSO- d_6 .

The UV–vis spectra of the benzotriazole derivatives **2**, **4** and Tinuvin 326 measured in ethanol and chloroform according to their solubility are shown in (a) and (b) in Fig. 2, respectively. The absorption maximum (λ_{max}) of benzotriazole **2** and **4** is at 327 nm in ethanol and 339 nm in chloroform, respectively. And only one sharp peak appears in the range of 280–400 nm, which has great difference with Tinuvin 326 exhibiting two peaks at about 310 nm and 350 nm. The molar extinction coefficients (ε_{max}) of benzotriazole **2** (29,600 L/mol cm at 327 nm in ethanol) and benzotriazole **4** (19,500 L/mol cm at 339 nm in chloroform) are much larger than that of Tinuvin 326 (18,900 L/mol cm at 351 nm in ethanol, 16,300 L/mol cm at 353 nm in chloroform).

Benzotriazole 2 and 4 had been milled in the presence of a dispersing agent NNO (1:1, w/w) with glass beads (1 mm in diameter) for 4 h to form their aqueous suspension, respectively. Then the aqueous suspensions were applied to polyester fabrics by an exhaustion dyeing at conditions of liquor-to-fabric of 40:1, concentration of 0.5-2.0% on weight of fiber (owf) and dyebath pH 5.0. Dyeing was started at room temperature and increased to $130 \,^{\circ}$ C, and held for 1 h. Then the fabrics were carried out and rinsed with water. The exhaustion and UV protection data were listed in Table 1. It was clear that the treated fabric provided effective protection against UVR. The application of benzotriazole 2 at 0.5% owf increased the ultraviolet protection factor (UPF) to 62 (the UPF of blank polyester fabric is only 37). However, with the amount increase of benzotriazole 2 to 1.0% owf and even 2.0% owf, no obvious UPF increase for polyester fabric was found which maybe be induced by their poor exhaustion (less than 11%). On the contrary, benzotriazole 4 has better exhaustion on polyester fabric (more than 50%). The application of benzotriazole 4 at 0.5% owf sharply increased the UPF over 180. With application of benzotriazole 4 at 2.0% owf, the UPF of polyester fabric even reached 380. The higher UPF of the dyed polyester fabric means benzotriazole 4 is much superior to benzotriazole 2 and acts as an effective UV absorber due to its higher exhaustion, although it shows much lower molar extinction coefficient compared with benzotriazole 2.

Table 1 Exhaustion, T(UVA), T(UVB) and UPF data recorded on dyed polyester fabrics.

Owf (%)	Benzotriazole 2				Benzotriazole 4			
	Exhaustion (%)	T(UVA) (%)	T(UVB) (%)	UPF	Exhaustion (%)	T(UVA) (%)	T(UVB) (%)	UPF
0.5	10.9	8.73	0.80	62	63.2	2.51	0.30	183
1.0	5.4	7.93	0.72	67	56.9	1.72	0.27	226
2.0	3.9	7.09	0.62	75	51.0	1.17	0.27	380

The UPF of blank polyester fabric is 37.

In conclusion, the present work describes an efficient and simple method for the syntheses of two novel *N*-heterocycle-containing benzotriazole UV absorbers. Their structures were characterized by FT-IR, ¹H NMR, mass spectroscopy and elemental analysis. The novel UV absorbers exhibited higher molar extinction coefficient at the absorption maximum than commercial benzotriazole UV absorber Tinuvin 326. It is also found that benzotriazole **4** is more valuable for anti-UV protection on polyester fabric than benzotriazole **2** due to its higher exhaustion.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21106135 and 51173168), Zhejiang Provincial Natural Science Foundation of China (Nos. Y4090227 and Y5080021) and Zhejiang Provincial Key Innovation Team (No. 2010R50038).

References

- [1] R.R. Cordero, P. Roth, A. Georgiev, Energy Convers. Manage. 46 (2005) 2907.
- [2] D. Rosu, L. Rosu, C.N. Cascaval, J. Photochem. Photobiol. A: Chem. 194 (2008) 275.
- [3] N. Gandra, A.T. Frank, O.L. Gendre, Tetrahedron 62 (2006) 10771.
- [4] M. Zayat, P. Garaia-Parejo, D. Levy, Chem. Soc. Rev. 36 (2007) 1270.
- [5] F. Waiblinger, J. Keck, M. Stein, J. Phys. Chem. A 104 (2000) 1100.
- [6] J. Pospisil, S. Nespurek, Prog. Polym. Sci. 25 (2000) 1261.
- [7] N.A. Evans, J. Rosevear, P.J. Waters, Polym. Degrad. Stab. 14 (1986) 263.
- [8] A.I. Vogel, B.S. Furniss, Vogel's Textbook of Practical Organic Chemistry, 4th ed., Longman, London, 1978, p. 715.