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An adduct of Cl-substituted benzotriazole and hydroxy benzophenone as a novel UVA/UVB absorber: Theory-guided design, synthesis, and calculations

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HIGHLIGHTS

- ► A high efficiency UVA/UVB absorber UV-D was synthesized guided on quantum chemistry calculations.
- ▶ The excellent absorption of UV-D comes from three electronic transition bands (S0 \rightarrow S1, S0 \rightarrow S2, S0 \rightarrow S6).
- ▶ Structural parameters, AIM and NBO analysis show IMHB in HBP group is stronger than that in CIBTZ.

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ABSTRACT

A novel UVA/UVB absorber UV-D, a combination of Cl-substituted benzotriazole (CIBTZ) and hydroxybenzophenone (HBP) anti-UV functional groups in one molecule, which absorbs UVA and UVB radiation with high efficiency, was synthesized based on the first principle theory-guided design. The synthesized UV absorber was characterized by ¹H NMR, FT-IR and UV spectroscopy in detail. Systematic quantum chemistry calculations were performed to investigate the stable structure and UV electronic absorption bands of UV-D. Structure parameters, atoms in molecule (AIM) and natural bond orbital (NBO) analysis show that the intramolecular hydrogen bond (IMHB) in HBP part is stronger than that in CIBTZ part. This work shows that the combination of the first principle theory-guided design and organic synthesis can be used to develop highly efficiency UV absorbers effectively.

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1. Introduction

Due to ozone depletion, more and more ultraviolet (UV) radiation has been progressively increased on the earth [1]. UV light (wavelengths between 280 nm and 400 nm) from the sun is known to degrade exposed organic matter. Materials used in exterior applications as well as interior applications are susceptible to photochemical degradation. In order to protect against the damaging effects of UV light, UV absorbers are used to absorb UV light and thereby prevent the damage. An ideal UV absorber must have the key property: highly efficient absorption between 280 and 400 nm coupled with high optical transparency in the visible range.

UV absorbers with an intramolecular hydrogen bridge are widely employed as additives against UV radiation [2,3]. The two

dominant classes of commercially available UV absorbers are benzotriazoles (BZTs) and hydroxybenzophenones (HBPs) [4,5]. Both utilize an excited state intramolecular proton transfer from a hydroxyl group to dissipate light energy. They are transparent to visible light and supposed to dissipate the absorbed light energy in a harmless manner, i.e. to convert the absorbed photon energy into heat without chemical damage [6]. BZTs UV absorbers have relatively strong absorption in 300–385 nm (UV-A) range, while HBPs have middle strong absorption in 280–340 nm (UV-B) range. If the benzotriazole and benzophenone anti-UV functional groups are combined into one molecule which may result in a new type of UV absorber with anti-UVA and UVB function, as Fig. 1 shows. Additionally, light resistance should be enhanced since an adduct of the two anti-UV group can increase the molecular weight of UV absorbers.

In this work, a high efficient UVA/UVB absorber (UV-D) with Clsubstituted benzotriazole ((2-(5-chloro-2H-benzo[d] [1–3]triazol-2-yl)phenol, ClBTZ) and hydroxybenzophenone (HBP) anti-UV functional groups was synthesized based on the first principle theory-guided design. Characterization is performed by ¹H NMR, IR



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Fig. 1. The chemical structures of UV-D and the two monomers CIBTZ and HBP.

and UV spectroscopy. Quantum chemistry calculations were calculated to investigate the stable structure and UV electronic absorption bands. Intramolecular hydrogen bonds (IMHBs) in title UV absorber have been explored by atoms in molecule (AIM) and natural bond orbital (NBO) analysis. This work demonstrates that the first principle theory-design and organic synthesis can cowork with each other effectively to develop highly efficiency UV absorbers.

2. Experimental and computational methods

2.1. Materials

The reagents, UV-366(99%), AlCl₃(Chemical pure, 99%), chlorobenzene (Analytical reagent, 99%), acetone (Analytical reagent, 99.5%), concentrated hydrochloric acid (Chemical pure, 37%) and ethanol (Chemical pure, 99.5%) were bought from Haochem Chemical Co. Ltd. (Shanghai, PR China).

2.2. Equipments

The UV absorption spectrum of UV-D was measured by a UV-2501 PC ultraviolet/visible spectrometer. Fourier transform infrared (FT-IR) spectrum of UV-D was obtained using a Perkin–Elmer 1 FT-IR spectrometer (Spectral range: 400–4000 cm⁻¹, Resolution: 4 cm⁻¹). ¹H NMR spectrum was recorded on a Varian INOVA 400 NMR Spectrometer with tetramethylsilane (TMS) as internal standard in CDCl₃.

2.3. Calculations

Density functional theory (DFT) and time dependent (TD) were done to determine the optimized geometry and UV absorption spectra. DFT method is efficiency in geometry optimizations, but weak in weak interaction energy calculations. Therefore, in this work, by allowing the relaxation of all the parameters, calculation has been found to converge to a optimized geometry at B3LYP/6-31G(d) level, as revealed by the absence of imaginary values in the calculated wavenumbers of all the vibrational modes, while the electronic transition energies and electronic transition orbital were calculated by B3LYP-TD/6-31G(d) method. For the weak interaction energy analysis, second order Moller–Plesset theory (MP2) is more reliable than density functional theory. Herein, in this work, MP2/6-31G(d) was used to perform AIM and NBO analysis to investigate IMHB interaction of UV-D based on the B3LYP/6-31G(d) optimized structure. 6-31G(d,p) and higher basis sets were not performed for limited computer resources. All the DFT and MP2 calculations in this paper were carried out in the Gaussian09 program [7].

3. Results and discussion

3.1. Theory-guided design

Quantum chemistry method TD DFT has been used to simulate the UV absorption spectra successfully [8–10]. Fig. 2 shows the two views and the optimized structure parameters of the novel UV-D absorber with CIBTZ and HBP anti-UV functional groups. Fig. 3 shows that the adduct compound UV-D and the two monomers CIBTZ and HBP absorption spectra at B3LYP-TD/6-31G(d) level. The optimized structural parameters show that there are two intermolecular hydrogen bonds, O-H...N on the ClBTZ group (bond length: 2.628 Å, bond angle: 144.6°) and O–H \cdots O on the HBP group (bond length: 2.565 Å, bond angle: 148.1°) of UV-D, and the benzene ring of the HBP part deviates from the whole molecule skeleton plane, as Table 2 and Fig. 3 shows. ClBTZ shows a relative strong absorption band in UV-A region with a calculated maximum molar absorption coefficient 17,000 L/(mol cm). HBP has a middle strong absorption band in UV-B region with a calculated maximum molar absorption coefficient 12,000 L/(mol cm). The adduct UV absorber has two strong absorption bands with the calculated maximum molar absorption coefficients 27,000 L/ (mol cm) in UV-A region and 18,000 L/(mol cm) in UV-B region respectively. It is clear that the absorption range in UV-D is wider and the absorption strength is much stronger than the other two monomers', as Fig. 2 shows. Therefore, the adduct UV-D should be a high efficiency UV absorber from quantum chemistry calculation results.

3.2. Synthesis

Fig. 4 shows the synthesis principle of UV-D. To a solution of $AlCl_3$ (1.47 g, 11 mmol) in 100 mL of chlorobenzene, 3.65 g of UV-366 (10 mmol) were added at room temperature. The resulting mixture was heated slowly to 120 °C and stirred at this temperature for 12 h. After cooling the resulting solution was poured in 150 g of ice and the mixture was acidified to pH 2 with 10% hydrochloric acid. Then chlorobenzene was removed from the solution by reduced pressure distillation. The precipitate was filtered off



Fig. 2. Two views of the S₀ optimized structure of UV-D at B3LYP/6-31G(d) level. (Bond length in Angstrom, red: O atom, blue: N atom, green: Cl atom, white: H atom, gray: C atom.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Absorption spectra of UV-D and the two monomers CIBTZ and HBP at B3LYP-TD/6-31G(d) level.

and washed with water. The crude product was dissolved in a hot mixture solvent of water (50 mL) and ethanol (50 mL), and the undissolved residue was filtered off. The filtrate then was recrystallisation from acetone and afforded 1.63 g (44.7%) of UV-D as a light yellow solid. FTIR (KBr)/cm⁻¹: 3096 (OH), 1638 (C=O), 703 (C–Cl); ¹H NMR (CDCl₃)/ppm: δ 11.58 (s, 1H, O<u>H</u>...N), 11.45 (s, 1H, O<u>H</u>...O), 8.17 (s, 1H, Ar–<u>H</u>), 8.06 (d, 1H, Ar–<u>H</u>), 7.77 (s, 1H, Ar–<u>H</u>), 7.72 (d, 2H, Ar–<u>H</u>), 7.63 (t, 1H, Ar–<u>H</u>), 7.49–7.55 (m, 3H, Ar–<u>H</u>), 6.72 (s, 1H, Ar–<u>H</u>); MS (m/z, %): 364.1 (M–H, 100), 366.1

(M—H + 2, 34); Element analysis: Found (%): C, 62.42, H, 3.30, N, 11.46; Calcd (%): C, 62.39, H, 3.31, N, 11.49.

3.3. UV-Vis absorption spectrum

Table 1 lists the B3LYP-TD/6-31G(d) computed electronic absorption bands, the corresponding electric transition orbital, and the oscillator strength (f) of UV-D. Fig. 5 presents the absorption spectrum of UV-D in N,N-dimethyllformamide (DMF) solution $(2 \times 10^{-5} \text{ mol/L})$ with the maximum absorption wavelengths indicated above the spectrum, while the theoretical results at B3LYP-TD/6-31G(d) level are also shown with the bar type. Table 1 shows that among the calculated electronic transitions above 280 nm optical region there are three transition-allowed absorption bands $(S_0 \rightarrow S_1, S_0 \rightarrow S_2, S_0 \rightarrow S_6)$ with the oscillator strength (f) 0.4872, 0.2502, 0.2794 respectively. Table 1 and Fig. 5 show that there are two strong absorption bands in experimental UV spectrum which induced by three transition-allowed absorption bands $(S_0 \rightarrow S_1, S_0 \rightarrow S_2, S_0 \rightarrow S_6)$. The maximum experimental molar absorption coefficients are about 25,000 L/(mol cm) at 355 nm and 16,000 L/(mol cm) at 285 nm individually, which agree with the computation results 27,000 L/(mol cm) at 360 nm and 18,000 L/(mol cm) at 287 nm well. Fig. 6 displays the four orbital (93, 94, 95 and 96) associated with the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_6$ electronic transitions. It shows that orbital 93(HOMO-1), 94(HOMO), 95(LUMO) and 96(LUMO + 1) are π orbital. It is clear from Table 1 and Fig. 6 that the electron density of orbital 93 is mainly localized on the share part of CIBTZ group and HBP group, electronic clouds of orbital 94(HOMO, π) and 95 (LUMO, π^*) are mainly delocalized on the CIBTZ group, while orbital 96(LUMO + 1,



Fig. 4. Synthesis principle of UV-D.

Table 1

B3LYP-TD/6-31G(d) calculated transition states, character, transition orbitals, electronic transition energies, and oscillator strengths (f) for UV-D.

T s	`ransition tates	Character	Transition orbitals	Transition energy (eV)		Oscillator strength (f)
				Calc.	Expt. (nm)	
S	$b_0 \rightarrow S_1$	$^{1}(\pi, \pi^{*})$	$94 \rightarrow 95 (0.62)$	3.44 (360 nm)	357	0.4872
S	$o_0 \rightarrow S_2$	$^{1}(\pi, \pi^{*})$	$94 \rightarrow 96 (0.61)$	3.77 (328 nm)		0.2502
S	$S_0 \rightarrow S_3$	$^{1}(\pi, \pi^{*})$	$93 \rightarrow 95 (0.38)$	3.87 (320 nm)		0.0071
S	$S_0 \rightarrow S_4$	$^{1}(\pi, \pi^{*})$	$93 \rightarrow 95(0.57)$	3.90 (318 nm)		0.0091
S	$0 \rightarrow S_5$	$^{1}(\pi, \pi^{*})$	$92 \rightarrow 95(0.62)$	4.17 (297 nm)		0.0087
S	$s_0 \rightarrow S_6$	$^{1}(\pi, \pi^{*})$	$93 \rightarrow 96(0.52)$	4.32 (287 nm)	285	0.2794
S	$0 \rightarrow S_7$	$^{1}(\pi, \pi^{*})$	$91 \rightarrow 95(0.53)$	4.39 (282 nm)		0.0486
S	$s_0 \rightarrow S_8$	$^{1}(\pi, \pi^{*})$	90 → 95(0.57)	4.43 (280 nm)		0.0115

Table 2

Structural parameters, NBO and AIM analysis for IMHB in UV-D at MP2//B3LYP/6-31G(d) level.^a

IMHB	r(O—H) ^b	$r(O {-\!\!\!\!-} H {\cdot} {\cdot} {\cdot} X)^b$	$\angle (0 - H \cdots X)^c$	NBO ^d		AIM ^e		
				ϕ_i	ϕ_j	$\Delta E_{ij}^{(2)}$	ρ	$\nabla^2 ho$
0—H…N 0—H…0	0.990 0.997	2.628	144.6 148 1	n _N	σ^*_{0-H}	31.11	0.0153	1.025 1.248
0—H···0	0.997	2.565	148.1	n_0	$\sigma^*_{\rm O-H}$	36.52	0.0180	1.248

 a NBO and AIM analysis are performed by MP2/6-31G(d) method based on the B3LYP/6-31G(d) optimized structure.

^b Interatomic distances is in Angstrom unit. r(O-H) is the length of the H-bond. $r(O-H\cdots X)$ is the distance from X(O or N) to O-H in the O-H \cdots O and O-H \cdots N hydrogen bonds.

^c $\angle 0 \cdots H = 0$ or $\angle 0 \cdots H = C$ angle is in degree.

^d NBO donor orbitals ϕ_i ; acceptor orbitals ϕ_j and their corresponding secondorder interaction energies $\Delta E_{ij}^{(2)}$ in kcal/mol. ^e ρ (Charge density at the "3, -1" critical point) and $\nabla^2 \rho$ (Laplacian of charge

^e ρ (Charge density at the "3, -1" critical point) and $\nabla^2 \rho$ (Laplacian of charge density at the critical point) in atomic units.

 π^*)'s electronic clouds are mainly delocalized on the HBP group. According to the classic view, we assign the intense experimental 357 nm and 285 nm absorption band to the $\pi \to \pi^*$ transition. Obviously, $S_0 \to S_1 (94 \to 95)$ transition comes from the CIBTZ part, $S_0 \to S_2 (94 \to 96)$ transition is induced by electron transfer from CIBTZ group to HBP group, and $S_0 \to S_6 (93 \to 96)$ transition comes from the HBP part. UV-D has two important UV absorbing chromophores (BZT unit and HBP unit) in one molecule and it maybe combine the UV absorbance of both chromophores. In fact, as shown in Fig. 5 and Figs. S1 and S2 (Supporting information), UV-D has two absorption maxima (λ_{max}) at 285 and 357 nm with molar extinction coefficients (ε_{max}) of 1.63×10^4 and 2.52×10^4 L/(mol cm) and shows much stronger and broader absorbance than some commercial UV absorbers such as UV-320 and UV-531.

3.4. Intramolecular hydrogen bonding (IMHB) interaction

To the synthesized UV-D absorber, there are two intramolecular hydrogen bonded structures. AIM and NBO analysis are performed

0.6 357nm Calc Expt 285nm 0.4 Absorption 0.2 0.0 250 300 350 400 450 500 Wavelength / nm

Fig. 5. UV-D absorption spectrum in DMF (2×10^{-5} mol/L) (line) and comparison with the B3LYP-TD/6-31G(d) calculation results (bar).

to give further insight about IMHB in UV-D, as Table 2 shows. Hydrogen bond structural parameters are also list in Table 2.

The AIM analysis was performed in this work, because it is well known that the electronic density $\rho(r)$ and its Laplacian $\bigtriangledown^2 \rho(r)$ at the bond critical point (BCP) or ring critical point (RCP) or cage critical point (CCP), are very useful parameters for estimation of the relative strength of hydrogen bonding interaction [11–13]. Larger $\rho(r)$ value represents stronger bond interaction. AIM indicates that to UV-D there are two ring critical points O—H…N in CIBTZ group and O…O—H in HBP group. In this case, $\rho(r)$ of the two IMHB are 0.0153 (O—H…N) and 0.0180 (O…O—H) respectively, which are in $\rho(r)$ at critical points range [0.002,0.035]. According to the theory, it is clearly shows there are two hydrogen bonds in UV-D molecule, and IMHB in HBP part is stronger than that in CIBTZ part [14–16].

Hydrogen bonds are, in general, interpreted to be formed due to charge transfer from the proton acceptor to the proton donor, and hence the amount of charge transfer plays a significant role in determining the elongation and contraction of the H···Y bond (X-H···Y). Analysis of the NBO second-order interaction energies $\Delta E_{ij}^{(2)}$ of these hydrogen-bonding interactions points to a different interpretation. $\Delta E_{ii}^{(2)}$ is calculated as

$$\Delta E_{ij}^{(2)} = \frac{\left|\left\langle \phi_i \right| F \left| \phi_j \right\rangle\right|^2}{\left(\varepsilon_i - \varepsilon_j\right)}$$

where F is the Fock operator, and ε_j correspond to the energy eigenvalues of the donor molecular orbital ϕ_i and the acceptor molecular orbital ϕ_j ; $\Delta E_{ij}^{(2)}$ ensures the strength of the donor–acceptor interaction between orbitals ϕ_i and ϕ_j and appears to be well suited to examine hydrogen-bonding interactions [17,18]. NBO analysis indicates the sum $\Delta E_{ij}^{(2)}$ of $O \cdots O$ —H in HBP part is about 36.52 kcal/mol, while in CIBTZ part the $\Delta E_{ij}^{(2)}$ of O—H···N is about 31.11 kcal/mol. These results clearly show that IMHB in HBP part is stronger than



Fig. 6. Molecular orbitals (93, 94, 95 and 96) for the strong absorption bands of UV-D above 280 nm region at B3LYP-TD/6-31G(d) level.

that in CIBTZ part which agrees with the AIM results well. Structure parameters, AIM and NBO analysis show that the IMHB in HBP part is stronger than that in CIBTZ part. Obviously, to UV-D, absorption in UV-A region comes from for CIBTZ part, while absorption in UV-B region comes from HBP part, and electron transfer from CIBTZ group to HBP group enhanced UV-A and UV-B absorption ability.

4. Conclusions

A high efficiency UVA/UVB absorber UV-D with wide and strong absorption ability, was synthesized successfully guided on quantum chemistry calculations, and FT-IR, ¹H NMR, UV spectroscopy were used to characterize the product. The excellent absorption of UV-D comes from three electronic transition bands: $S_0 \rightarrow S_1$ transition absorption associated with CIBZT part mainly, $S_0 \rightarrow S_2$ absorption associated with electron transfer from CIBTZ part to HBP part, and $S_0 \rightarrow S_6$ transition associated with HBP part. Structural parameters, AIM and NBO analysis show that IMHB in HBP group is stronger than that in CIBTZ, and this result can explain why UV-D can absorb UV-A/B light effectively. This work appears that cowork of quantum-chemistry-calculation-guided design and organic synthesis is very powerful to develop high efficiency UV absorbers.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.

07.050. These data include MOL files and InChiKeys of the most important compounds described in this article.

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