Chemical Physics 500 (2018) 15–18

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Excited state properties of 2′-hydroxychalcone analogues functionalized with a diene moiety studied by steady state and laser flash photolysis

Yukino Shinozaki [a], Minoru Yamaji [b,*], Tatsuo Arai [a,*]

[a] Graduate School of Pure and Applied Science and Tsukuba Research Center for Interdisciplinary Materials Sciences (TIMS), University of Tsukuba, Tennoudai, Tsukuba, Ibaraki 305-8571, Japan
[b] Division of Molecular Science, Graduate School of Science and Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan

ARTICLE INFO

Article history:
Received 9 September 2017
In final form 10 November 2017
Available online 11 November 2017

ABSTRACT

2′-Hydroxychalcone (HC) analogues **1** and **2** having a diene part tethering the phenyl and naphthyl chromophores, respectively, were prepared, and their photochemical and photophysical properties were studied. Fluorescence from these compounds was absent in solution and the solid state. Based on the results obtained upon steady state and laser flash photolyses, compound **2** was found to be substantially stable on photoirradiation without undergoing intersystem crossing to the triplet state whereas compounds **1** showed transient absorption due to the triplet tautomer. The deactivation processes in the excited states were discussed by considering energetic reaction diagrams for the corresponding tautomers and isomers.

1. Introduction

When ultraviolet light in the UV-A (315–380 nm), UV-B (280–315 nm) and UV-C (200–280 nm) regions from the sun is directly absorbed to the human skin, we may suffer from medical disorders, such as suntan, sunburn and DNA lesion, respectively. It is, thus, required to develop UV-sunscreens protecting human body to reduce undesirable light effects to human body. One of the most world-widely used UV-A sunscreens is 4-tert-butyl-4′-methoxydibenzoylmethane (trade name, Avobenzone) which undergoes tautomerization and isomerization upon UV-A and -B light irradiation as the sunscreen mechanism [1]. Methoxycinnamic acid [2–4] and oxybenzone [5–10] are typical UV-sunscreens for commercial use. These sunscreens are, however, unstable against prolonged photoirradiation and ready to undergo photocleavage reaction to give radical species resulting in skin protein damage [11]. Therefore, photostable chemicals are demanded to show desirable absorption profile at UV-A, -B and -C domains and highly efficient light energy conversion to thermal energy without chemical reactions that cause skin damaging [11].

Generally, excited states of aromatic compounds deactivate to the ground state by radiative and non-radiative processes in solution. Non-radiative deactivation from the excited singlet state to the ground state usually may take place via internal conversion or by chemical reactions such as *cis-trans* isomerization or hydrogen atom transfer when the excited aromatic molecules may have the C=C double bond or the carbonyl moiety. Otherwise, deactivation of lowest excited singlet (S_1) states may proceed via intersystem crossing to the lowest triplet (T_1) state. However, formation of triplet states is not desirable for the compound used as UV sunscreen, because the triplet state is ready to sensitize molecular oxygen to give highly reactive excited state singlet oxygen. Thus, molecules undergoing non-radiative deactivation from the singlet excited state other than intersystem crossing may be desirable as UV sunscreen. As to the non-radiative deactivation processes from the excited state, isomerization and proton or hydrogen atom transfer reactions are candidates. We have been, thus, studying the excited state properties of 2′-hydroxychalcone (HC) and its derivatives as well as related compounds having C=C double bond and intramolecular hydrogen bonding. We have already reported that HC undergoes ultrafast deactivation through excited-state intramolecular hydrogen atom transfer (ESIHT) to produce the tautomer, which deactivates to the ground state of the starting material after reverse proton atom transfer in the ground state [12–15]. The fluorescence quantum yield of HC is as small as 10^{-6} because of the facile deactivation to the ground state and undergoing intersystem crossing to the triplet state [16]. As the triplet states would produce reactive singlet oxygen, suppression of intersystem crossing is necessary for applying it to UV sunscreen. We have been, thus, preparing various compounds related to HC to resolve this issue [17–21]. In this context, we wish to report here photophysical and photochemical features of newly prepared chalcone related

---

* Corresponding authors.
E-mail addresses: yamaji@gunma-u.ac.jp (M. Yamaji), arai@chem.tsukuba.ac.jp (T. Arai).

https://doi.org/10.1016/j.chemphys.2017.11.006
0301-0104/

compounds which have a diene part replaced with the C=C double bond in the HC skeleton (Chart 1). Based on the revealed photophysical and photochemical features, we proposed the possibilities of applying these compounds to efficient UV-sunscreen materials.

2. Experimental

The preparation procedure and the NMR data of the compounds **1** and **2** are described in Supplementary Materials. 2′-Hydroxycalcone (HC) commercially purchased was purified by repeated recrystallizations from ethanol. Benzene (spectroscopic grade from Dojin), methanol (spectroscopic grade from Wako) and ethanol (spectroscopic grade from Kishida) were used as the solvent without further purification while 2-methyltetrahydrofuran (MTHF) was distilled for purification.

Absorption spectra were recorded on a Shimadzu UV1600 spectrophotometer whereas emission was tried to measure with a Hitachi F-7000 fluorescence spectrophotometer. Steady state photolysis was carried out by using a xenon lamp (150 W) with a cut-off filter ($\lambda > 290$ nm) at 295 K. Third harmonics (355 nm) from a Nd:YAG laser system (9 mJ/pulse, Lotis-TII, LT-2137) was used as the excitation laser light sources. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere [22]. Transient absorption spectra were obtained using a Unisoku USP-T1000-MLT system, which provides a transient absorption spectrum with one laser pulse. The obtained transient spectral data were analyzed using the least-squares best-fitting method. ^{1}H NMR spectra were recorded on a Bruker ARX-500 (400 MHz) NMR spectrometer using Me_4Si as an internal standard.

3. Results and discussion

Fig.1 shows absorption spectra of compounds **1**, **2** and HC in benzene.

The maximum wavelengths (λ_{abs}) of the absorption bands for compounds **1** and **2** located in the longer wavelength region compared to that of HC due to expanded π-conjugation with the diene moiety and naphthyl rings. The λ_{abs} values and the absorptivities (ε) at λ_{abs} in benzene are listed in Table 1.

From the magnitude of the ε values, it is inferred that the electronic character of the absorption bands of **1** and **2** is of π,π^*. The shape of the absorption spectra was not influenced by the solvent properties such as polarity and protic or aprotic, indicating that intramolecular hydrogen bonding is strong in these compounds and free of the intermolecular hydrogen bonding with solvent molecules. The absorption spectra of compound **1** and **2** in benzene, acetonitrile and ethanol are compared and deposited in Supplementary Materials as Fig. S1. Emission from compound **1** and **2** was not obtained in benzene and the powder at 295 K, and in MTHF at 77 K. From the onsets of the absorption spectra, the S_1 energies (*E*s) of HC, **1** and **2** were estimated to be ca. 63, ca. 63 and ca. 57 kcal mol^{-1}, respectively, and listed also in Table 1. We carried out steady-state photolysis ($\lambda > 290$ nm) of compounds **1** and **2** in benzene for 3 h, and the absorption spectra showed no changes. These observations indicate that compounds **1** and **2** are substantially photostable, and efficiently convert the absorbed photon energy to heat in solution, which could deserve to be ideal sunscreens. We expected that the deactivation mechanism of excited states of compounds **1** and **2** are similar to that of HC although HC shows weak fluorescence from the S_1 state of the tautomer [16].

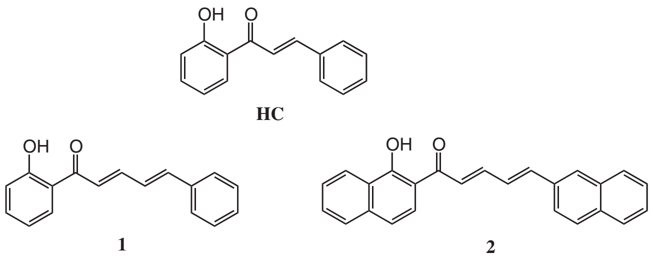

Chart 1. Molecular structures of 2′-hydroxychalcone (HC) and the related compounds studied in this work.

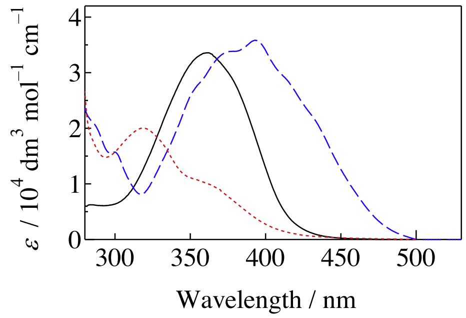

Fig. 1. Absorption spectra of compounds **1** (full black), **2** (broken blue), and **HC** (dotted red) in benzene.

Table 1
Photophysical parameters of HC, compounds **1** and **2** in benzene.

Compound	λ_{abs}/nm	ε/10^4 dm^3 mol^{-1} cm^{-1}	*E*s/kcal mol^{-1}
HC	315	2.00	~63
1	362	3.37	~63
2	393	3.59	~57

For understanding the photo-thermal conversion mechanism of compounds **1** and **2**, we carried out time-resolved transient absorption measurements using nanosecond laser photolysis techniques. Fig. 2 shows a transient absorption spectrum obtained upon 355 nm laser pulsing in Ar-purged benzene solution of compound **1**.

The absorption band at 470 nm decayed according to a single exponential function with a 1.2 µs lifetime (see inset in Fig. 2). The transient species for the observed absorption band was assigned to have triplet manifold because the transient signal was quenched by the amount of the dissolved oxygen. Laser flash photolysis of compound **2** in benzene provided no transient spectra in the wavelength region 420–680 nm. These experimental results indicate that compound **1** underwent intersystem crossing to the triplet state whereas compound **2** deactivates from the low-

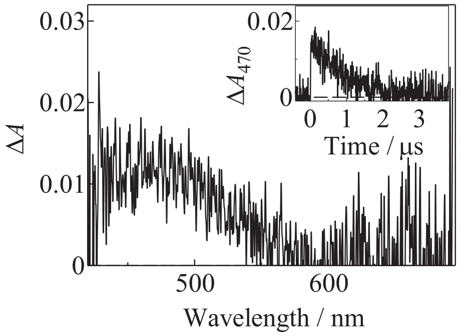

Fig. 2. Transient absorption spectrum at 100 ns upon 355 nm laser pulsing in Ar-purged benzene solution of compound **1**. Inset; a time profile at 470 nm in the microsecond time region.