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Photocleavage of dimers of coumarin and 6-alkylcoumarins

Thomas Wolff[a], Helmut Görner[b,*]

[a] Technische Universität Dresden, Physikalische Chemie, D-01062 Dresden, Germany
[b] Max-Planck-Institut für Bioanorganische Chemie, D-45413 Mülheim an der Ruhr, Germany

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ABSTRACT

The cleavage of four coumarin dimers, the *syn*-head-to-tail (ht) dimer of parent coumarin (*syn*-ht-CC**1**), the *anti*- and *syn*-hh dimers of 6-methylcoumarin (*anti*-hh-CC**2** and *syn*-hh-CC**2**, respectively) and the *anti*-hh dimer of 6-dodecylcoumarin (*anti*-hh-CC**3**), was studied by UV–vis and IR spectroscopy and HPLC upon direct 254 nm irradiation as well as sensitized excitation. The quantum yield of dimer splitting is $\Phi_{sp} = 0.1–0.3$ in various solvents and the effects of structure and solvent polarity are small. In certain solvents some of the dimers produced CO_2 along with the monomers in the splitting reaction. Electron transfer from dimers to the triplet state of sensitizers, such as benzophenone or 9,10-anthraquinone, was observed in acetonitrile.

1. Introduction

The photodimerization properties of parent coumarin (C**1**) in solution as well as in solid systems have been intensively investigated [1–9]. Four photodimers (CC), *syn*-head-to-head (*syn*-hh), *anti*-hh, *syn*-head-to-tail (ht) and *anti*-ht, were identified for C**1** and a series of 6-alkyl coumarins, e.g. 6-methylcoumarin (C**2**) and 6-dodecylcoumarin (C**3**) [10], see Scheme 1. Essentially *syn*-hh and *anti*-hh dimers and virtually no *anti*-ht dimers are formed upon direct excitation of C**1** in solution. The *anti*-hh dimers of C**1** and C**2** were found after benzophenone sensitization in both polar and non-polar solvents and *anti*-hh dimers are favoured in solvents of low polarity, but *syn* dimer formation is enhanced in polar solvents and micellar solutions of cationic cetyltrimethylammonium bromide and anionic sodium dodecyl sulfate [10].

The photophysical properties of coumarins are in favour of an overall triplet mechanism rather than of separate singlet and triplet pathways for the non-sensitized and sensitized photodimerizations of coumarins, respectively [11–16]. Fluorescence and phosphorescence of C**1** were detected at −196 °C, but virtually no emission appears in fluid solution, the quantum yield of fluorescence is $\Phi_f < 10^{-3}$ [13]. The triplet state is observable at room temperature [14–16], the T–T absorption spectra of C**1**, C**2** or C**3** have maxima at 410–430 nm and the influence of substitution on the quantum yield of intersystem crossing Φ_{isc} in a given solvent is small at room temperature. $\Phi_{isc} = 0.054$ for C**1** in water [15], smaller for C**1** and C**2** in most other solvents and largest in 2,2,2-trifluoroethanol (TFE) [13]. The dimerization quantum yield (Φ_{dim}) upon irradiation at 300–350 nm is very low in most cases, e.g. for C**1** (0.3 M) in dichloromethane and acetonitrile (for *syn*- and *anti*-hh) $\Phi_{dim} = 1 \times 10^{-3}$ and 9×10^{-4}, respectively [5,8]. On the other hand, Φ_{dim} is large, up to 0.8, for the BF_3/OEt_2 catalyzed reaction [9]. Recently, several points in the mechanism of photodimerization were addressed, e.g. the roles of the sensitizer, solvent and molecular structure, and reasons for the differing triplet reactivities were discussed [12]. The dimers are photocleaved into monomers upon irradiation at 200–300 nm (Scheme 1). The dimer splitting of coumarins is efficient [12,17–20] and for dimers of C**1**, which were prepared by benzophenone-sensitized irradiation in 2-propanol, a quantum yield of $\Phi_{sp} = 0.2$ has been reported upon irradiation at 266 nm [17].

Photoswitched storage and release of guest molecules in the pore void of coumarin-modified MCM-41 nanoparticles has been reported [21]. Reversible photocleavage and crosslinking was achieved when 4-methylcoumarin was functionalized in polyester [22]. With respect to the wavelength dependence of photodimerization versus photocleavage, the features of coumarins appear to be analogous to the thymine and other pyrimidine moieties. The photosensitized splitting of thymine dimers has been achieved by using a variety of sensitizers, mostly electron acceptors, such as

* Corresponding author.
E-mail address: goerner@mpi-muelheim.mpg.de (H. Görner).

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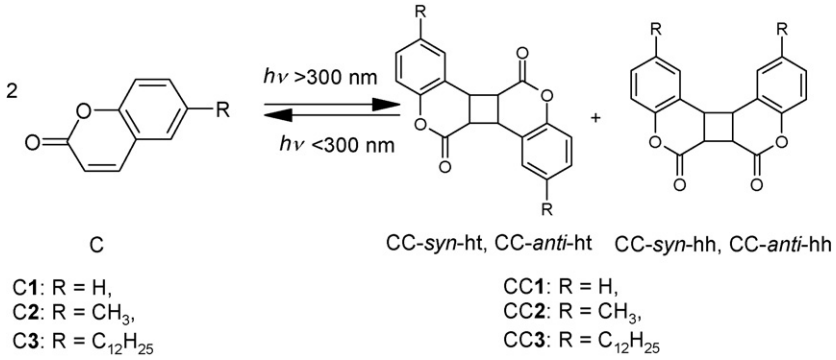

Scheme 1.

quinones or flavins [23–30]. Photoinduced DNA repair and splitting of pyrimidine model dimers can also be initiated by electron transfer [23]. The photoinduced electron transfer of monomers has been reviewed [31]. For cyanine dyes it has been shown that the triplet state of both, monomer and dimer, can be quenched by electron donors and acceptors [32].

Here, we aim at a deeper insight with regard to the photochemical dimer splitting of parent C**1** and alkylcoumarins. For these purposes, *syn*-ht-CC**1**, *anti*-hh-CC**2**, *syn*-hh-CC**2** and *anti*-hh-CC**3** dimers were studied by both UV and IR spectroscopy in the absence and presence of appropriate sensitizers using illumination at 248/254 and 308 nm, respectively. As sensitizers benzophenone, 4-carboxybenzophenone, duroquinone (Me_4BQ), chloranil (Cl_4BQ) and 9,10-anthraquinone (AQ) were used.

2. Experimental details

The coumarins were from previous work [12] and the sensitizers as commercially available. The solvents (Merck) were checked for impurities. For irradiation at 254 and 280/366 nm a Hg lamp and a 1000 W Hg–Xe lamp with a monochromator was used, respectively. The UV–vis spectra were recorded on a diode array (HP 8453). They are presented for 0.5 mm pathlength, otherwise performed in 1 cm cells. The quantum yield Φ_{sp} was measured using the absorption at the maximum versus irradiation time. As reference uridine in water was used, $\Phi_d = 0.002$ [33]. For HPLC analyses a 125×4.6 mm Inertsil ODS-3 5 μm column was used with MeOH–water 1:2 or 2:1 as eluents. Redimerization can be excluded since the monomer concentrations derived from dimer splitting are as low as 0.2 mM. Photoproduct analyses after 366 nm irradiation of AQ or Cl_4BQ, in acetonitrile–water (1:1) in the presence of *syn*-ht-CC**1** in using HPLC were performed, but not further carried out since they revealed several peaks related to quinone photochemistry and overlapping with the coumarin monomer and dimer signals. The molar absorption coefficient of monomeric C**1** in acetonitrile at 310 nm is $\varepsilon_{310} = 5.2 \times 10^3\ M^{-1}\ cm^{-1}$ [20]. The value of C**2** in several solvents at the maximum is typically $\varepsilon_{275} = (0.8–1.2) \times 10^4\ M^{-1}\ cm^{-1}$ and for the dimers *anti*-hh-CC**2** and *syn*-hh-CC**2** in chloroform $\varepsilon_{280} = 3.1 \times 10^3$ and $\varepsilon_{280} = 2.5 \times 10^3\ M^{-1}\ cm^{-1}$, respectively [10]. The IR spectra were recorded on a FTIR spectrometer (Bruker IFS66); the concentrations were adjusted to $A_{exc} = 0.1–2$ in 0.05 cm CaF_2 cells. The molar absorption coefficient of *anti*-hh-CC**2** in methylcyclohexane (MCH) was estimated as $\varepsilon_{1722} = 5 \times 10^3\ M^{-1}\ cm^{-1}$. For photolysis with UV–vis detection two excimer lasers ($\lambda_{exc} = 248$ and 308 nm, rise time 10–20 ns), two transient digitizers (Tektronix 7912AD and 390AD) and an Archimedes 440 computer for data handling were used as in previous work [11]. The measurements refer to 25 °C.

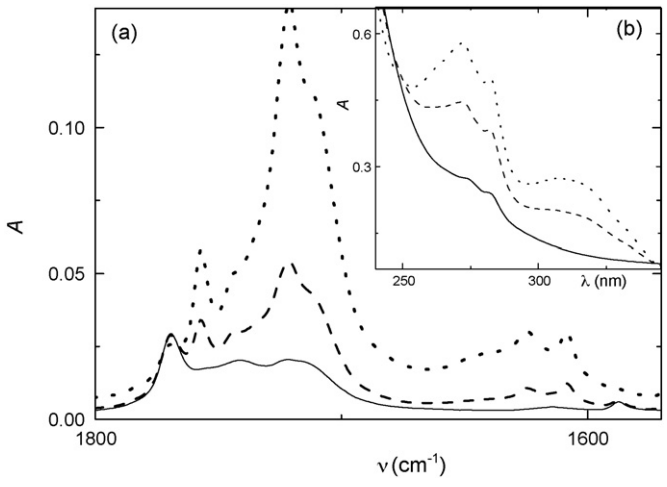

Fig. 1. (a) IR and (b) corresponding UV spectra of *syn*-ht-CC**1** in air-saturated MCH prior to (full) and after 2 (dashed) and 10 min (dotted) irradiation at 254 nm.

3. Results and discussion

3.1. Direct photocleavage of dimers

The absorption spectrum of *syn*-ht-CC**1** in MCH (Fig. 1b), carbon tetrachloride or more polar solvents has a maximum at 275 nm and no band above 300 nm. Continuous UV irradiation results in an absorption increase at 250–350 nm and an isosbestic point at 248 nm. The spectral changes with stronger absorbance at a major maximum around 275 nm and minor maximum at 312 nm are due to monomer formation. Corresponding spectra were obtained in solvents of low and large polarity for the other coumarin dimers, the changes are shown for *anti*-hh-CC**2** in acetonitrile and *anti*-hh-CC**3** in MCH, Figs. 2b and 3b, respectively.

The IR spectra of monomeric C**1** and dimeric *syn*-ht-CC**1** in MCH exhibit major peaks at $\tilde{\nu}_m = 1730\ cm^{-1}$ and $\tilde{\nu}_d = 1757\ cm^{-1}$, respectively (Fig. 1a). *Anti*-hh-C**2** in air-saturated MCH shows a major dimer peak at 1780 cm^{-1}, an isosbestic point at 1769 cm^{-1} and the monomer band centered at $\tilde{\nu}_m = 1722\ cm^{-1}$ (not shown). Additional monomer peaks appear at 1575, 1497, 1170, 1125 and 1044 cm^{-1}. The main absorption peak of *anti*-hh-CC**2** in carbon tetrachloride is similar and shifted to $\tilde{\nu}_d = 1768\ cm^{-1}$ in more polar solvents, acetonitrile (Fig. 2a). For *anti*-hh-CC**3** in MCH the peak at $\tilde{\nu}_d = 1779\ cm^{-1}$ converts to the monomer peak with $\tilde{\nu}_m = 1722\ cm^{-1}$ (Fig. 3a). Corresponding spectra were obtained for other cases (Table 1). The peak to peak ratio $2 \times \varepsilon_m/\varepsilon_d$ of monomers at $\tilde{\nu}_m$ (after complete cleavage) to dimers at $\tilde{\nu}_d$ of 0.4–0.9 was obtained. The photoproduct of *anti*-hh-CC**2** in carbon tetrachloride and dichloromethane, however, is not fully in line with the