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Short Communication

An Unusual Photoreaction of 3,4-Di-O-benzyl-hypericin

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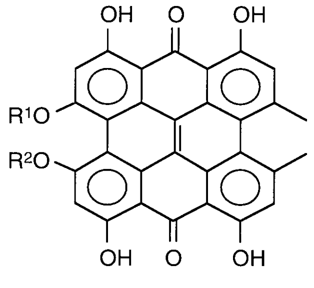
Summary. Upon irradiation of 3,4-di-O-benzyl-hypericin and proton sponge (*bis*-1,8-N,N-dimethyl-amino-naphthalene) in benzene solution, a stable radical ion pair formed which exhibited an intense absorption band around 800 nm. This was advanced by UV/Vis, NMR, and ESR spectroscopy. In presence of oxygen, irradiation of this photoproduct led to an activated oxygen species which then attacked the proton sponge.

Keywords. Radical; Hypericin; Electron transfer.

Introduction

Hypericin (**1**), the main pigment of *Hypericum* species, is well known for its photodynamic action. However, commonly **1** and its derivatives were never observed to become phototransformed themselves [1]. As a rare exception in the photochemistry of hypericin derivatives it has been found recently that 3-O-benzyl-hypericin (**2**) dissolved in benzene in the presence of proton sponge (*bis*-1,8-N,N-dimethylamino-naphthalene) displays a remarkable and unique photorearrangement leading to the blepharismin type chromophor [2]. We wish now to report on a second rather unusual photoreaction of a hypericin derivative, which was found fortuitously when the photoreaction mentioned above was performed on a sample of **2** contaminated with traces of 3,4-di-O-dibenzyl-hypericin (**3**).



1: $R^1 = R^2 = H$
2: $R^1 = Bz, R^2 = H$
3: $R^1 = R^2 = Bz$

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Results and Discussions

When **3** [3] is dissolved in benzene together with an excess of proton sponge and irradiated in presence or absence of oxygen within and above the absorption band of **3** at about 580 nm, the absorption spectrum changes dramatically. As shown in Fig. 1, an intense broad absorption band ($\varepsilon \approx 600000$) of the photoproduct **I** developed at 800 nm at the expense of the absorption bands of **3** (cf. the isosbestic point).

Attempts to isolate the resulting photoproduct **I** failed. However, the product solution remained unchanged when being kept for several days. Evaporation and redissolution in benzene also left the product absorption spectrum unchanged. In addition, the reaction was followed by means of ^{1}H NMR spectroscopy using benzene-d$_6$ as the solvent. Upon irradiation of the sample the signals [3] were considerably broadened, those of the hydroxyl protons between 14 and 15 ppm even disappeared, and a new signal at 2 ppm developed. In contrast to a solution of **3** together with proton sponge in benzene kept in the dark a strong, stable, and structureless ESR signal at $g = 2.0031$ was observed after irradiation of the sample with light of $\lambda > 500$ nm.

Treatment of the benzene solution of the resulting photoproduct **I** with oxidizing or reducing agents (*e.g.* Fe(III), Fe(II)) led to an immediate bleaching of the product absorption band with recovering the educt spectrum of **3** to most of its original extent.

The data presented above led to the conclusion that upon irradiation of **3** in presence of proton sponge an electron is transferred between **3** and the proton sponge, leading to the corresponding stable radical ion pair **I**. Upon further

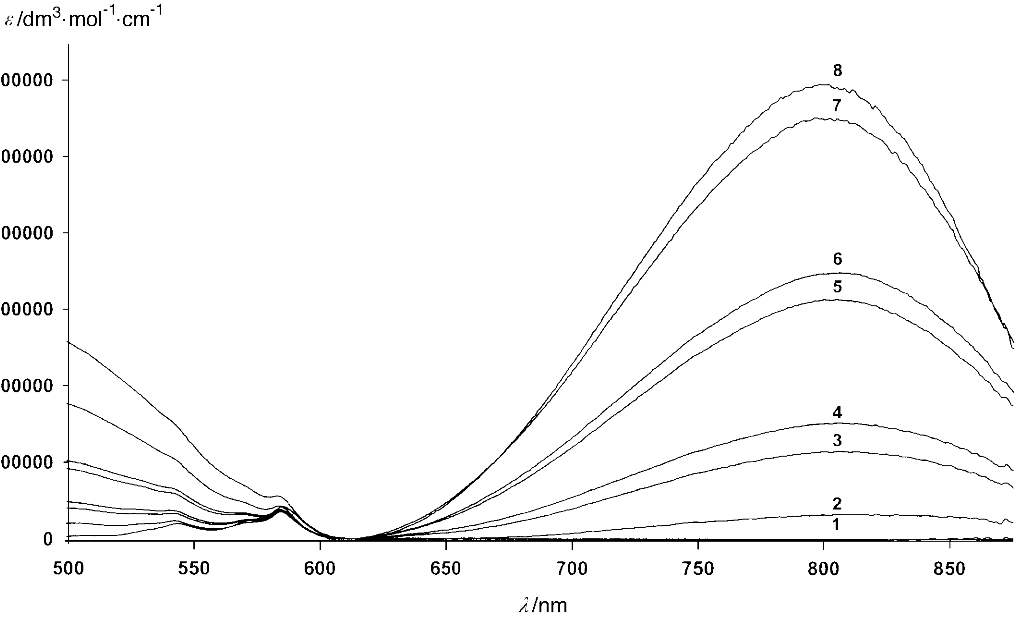

Fig. 1. UV/Vis spectra of a solution of **3** (10^{-5} mol · dm^{-3}) and proton sponge (10^{-4} mol · dm^{-3}) in benzene irradiated with light of $\lambda > 500$ nm for 0 (1), 4 (2), 12 (3), 17 (4), 22 (5), 75 (6), 90 (7), and 250 (8) min

irradiation of a benzene solution of **I** in presence of oxygen, the absorption band of **I** was diminished, that attributable to the proton sponge at 336 nm decreased, and a hypsochromically shifted band at 297 nm developed instead displaying an isosbestic point. Otherwise, when a highly dilute solution ($10^{-6}\,\mathrm{mol\cdot dm^{-3}}$) of **3** and an excess of proton sponge (10–100 mole equivalents) was irradiated, the absorption of **I** at about 800 nm could not be detected, but the spectrum changed in the low wavelength region as described above, leaving the absorption bands of **3** unchanged. Isolation of the thus formed secondary photoproduct **II** could be achieved by chromatography on Sephadex LH20 with methanol as the eluent. NMR spectroscopy of **II** indicated that it was consistent with a C_{2v}-symmetrical 1,8-disubstituted naphthalene system. The electrospray mass spectrum from a methanol/formic acid solution ($m/e = 245$ corresponding to $C_{14}H_{16}N_2O_2 \cdot H^+$) led to a molecular structure with two hydrogen atoms of the proton sponge replaced by two oxygen atoms added in a C_{2v}-symmetrical manner. It is not yet clear beyond this point what the detailed structure of this product is. Nevertheless, the radical ion pair **I** obviously catalytically activated molecular oxygen upon further irradiation, and the latter then attacked the proton sponge.

Experimental

3,4-Dibenzyloxy-1,6,8,13-tetrahydroxy-phenanthro[1,10,9,8-*opqra*]perylene-7,15-dione (3,4-Di-O-benzyl-hypericin, **3**) was prepared according to Ref. [3]. Irradiations were performed using a 300 W Philips tungsten lamp and a cut-off filter of $\lambda < 500$ nm at room temperature. Degassing was achieved by purging with a stream of Ar for 10 min; otherwise, the solution was bubbled with air. The proton sponge was of commercial origin (Fluka), solvents were of p.a. quality. NMR, UV/Vis, ESR, and mass spectra were recorded using Bruker DRX 500, Hewlett Packard 8453 UV/VIS, Bruker EMX 9.5 GHz, and Hewlett Packard 59987 quadrupole instruments.

Acknowledgements

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