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*Short Communication*

# Concerning the Absorption and Emission Properties of Phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*]perylene-7,14-dione

**H. Falk*** and **A. F. Vaisburg**

Institut für Chemie, Johannes Kepler Universität, Linz, A-4040 Austria

**Summary.** In contrast to hitherto published data, phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*]perylene-7,14-dione, the fundamental chromophoric system of hypericin type compounds, exhibits an absorption with a long wavelength band at 423 nm in aprotic solvents like dimethylsulfoxide ($\varepsilon \approx 7000$). Its fluorescence in these solvents is below the detection limit. In protic solvents like methanol, the long wavelength absorption is bathochromically shifted to 546 nm, and a fluorescence at 565 nm is observed. This behavior was interpreted from the reversal of $n - \pi^*$ and $\pi - \pi^*$ transitions. The data have not been recorded yet due to the very low solubility of this compound. Its monoprotonation in ground and excited states is characterized by $pK_a$ and $pK_a^*$ values of $-6$ and 2; diprotonation occurs at a $pK_a = -7$.

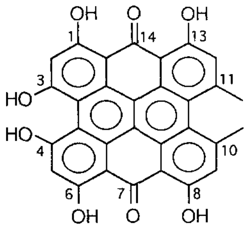
**Keywords.** Phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*]perylene-7,14-dione; Hypericin; Protonation; Absorption spectra; Fluorescence.

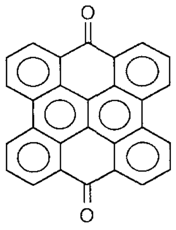
### Absorptions- und Emissions-Eigenschaften von Phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*] perylen-7,14-dion (Kurze Mitt.)

**Zusammenfassung.** Im Gegensatz zu bislang publizierten Daten zeigt Phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*] perylen-7,14-dion, das fundamentale chromophore System der Hypericintyp-Verbindungen, in aprotischen Lösungsmitteln wie Dimethylsulfoxid eine Absorption mit einer langwelligen Bande bei 423 nm ($\varepsilon \approx 7000$). In diesen Lösungsmitteln ist Fluoreszenz nicht nachweisbar. In protischen Lösungsmitteln wie Methanol wird die langwellige Bande bathochrom verschoben (546 nm) und bei 565 nm tritt Fluoreszenz auf. Dieses Verhalten wurde mit der Umkehr in der Reihenfolge von $n - \pi^*$ und $\pi - \pi^*$ Übergängen interpretiert. Die Daten wurden wegen der extremen Schwerlöslichkeit dieser Verbindung bislang nicht erhalten. Die Monoprotonierung im Grund- und Anregungszustand ist durch $pK_a$- und $pK_a^*$-Werte von $-6$ und 2 charakterisiert; die Diprotonierung tritt bei $pK_a = -7$ ein.

Hypericin (**1**) is a naturally occurring phenanthroperylene quinone [1], which became important recently due to its biological activity [2]. During our investigations of the chemistry [3], stereochemistry [4], and physical properties [5] of hypericin type pigments, the properties of the fundamental chromophoric system of this class of compounds, phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*]perylene-7,14-dione (**2**), seemed to be of interest. Recent communications [6, 7], which state that **2** does neither absorb nor emit in the region between 300 and 600 nm in dimethylsulfoxide prompted us to report on our results.

**1**





**2**

Phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*]perylene-7,14-dione (**2**) was prepared in four steps starting with the dimerization of anthrone with $FeCl_3$, basic isomerization of the resulting bianthronyl to the dihydroxy-bianthracenylidene, oxidation of the latter with benzoquinone, and finally photocyclization of the bianthrone to yield **2** according to Ref. [8]. It was recrystallized from nitrobenzene, carefully washed with acetone, and dried for 48 h at 80 °C and 0.1 HP; m.p.: not below 350 °C. Its identity was proven by its absorption spectrum in conc. sulfuric acid solution [8]. Moreover, its elemental analysis (C, H, N) gave satisfactory agreement between experimental and calculated values, and ensured the absence of nitrobenzene. The $^1H$ NMR spectrum of **2** could not be recorded due to its insolubility; however, the spectra of all precursor materials displayed only the signals corresponding to the respective structures. The solvents were of UVASOL grade (Merck) and distilled from NaH under argon protection before use. Absorption and emission spectra were measured on Hitachi U-3210 (path length 1 cm) and F-4010 instruments. The protonation constant $pK_a$ of **2** was estimated from the absorption spectra of a concentration series of aqueous sulfuric acid with varying $H_0$ values according to Ref. [9]. The corresponding excited state $pK_a^*$ was calculated by means of a *Förster* cycle [10].

The absorption spectrum of **2** in dimethylsulfoxide is shown in Fig. 1. It should be stressed that the absorption spectrum could be measured only after very carefully dissolving **2**, ensuring its complete dissolution (24 h storage in the dark at room temperature with frequent vigorous shaking). **2** was found to be extremely insoluble in common solvents when in pure form. Moreover, the spectrum had to be recorded under high gain conditions. The long wavelength band of the absorption spectrum of **2** was observed at 423 nm ($\varepsilon \approx 7000$) and thus was found to be hypsochromically shifted compared to the absorption of **1** by about 170 nm. This shift could be rationalized from the well known bathochromic effect exerted by the two methyl and six hydroxyl groups linked to the fundamental system **2** in **1**.

The fluorescence quantum yield of **2** was found to be less than the detection limit and accordingly negligible compared to the strong fluorescence of hypericin (**1**) in this solvent [11]. The same kind of behavior was found for other aprotic dipolar solvents; *e.g.* in dimethylformamide the long wavelength band was found at 422 nm, and virtually no fluorescence could be detected. Addition of up to 10 vol% *Hünig* base, phenol, or sulfuric acid did not change the absorption and emission characteristics of these solutions.

Upon dissolving **2** in protic dipolar solvents like methanol, the absorption shifted bathochromically to 546 nm and became strongly fluorescent at 565 nm

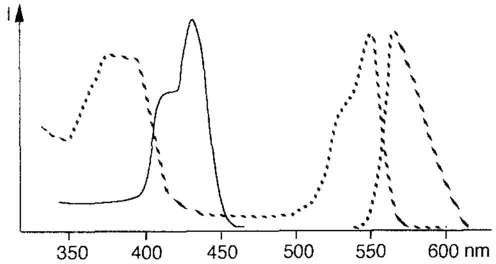


**Fig. 1.** Absorption and emission spectra of **2** in dimethylsulfoxide ( – ) and methanol (···); intensities in arbitrary units

(Fig. 1). Due to the extremely low solubility of **2** in this solvent, quantitative data could not be estimated.

Monoprotonation of **2** was found to be characterized by $pK_a$ and $pK_a^*$ values of $-6.0 \pm 0.5$ and $2.0 \pm 0.8$. The nonprotonated species (40% aqueous sulfuric acid as the solvent) absorbed at 426 nm and did not show fluorescence within the detection limit. The corresponding monoprotonated species (75% sulfuric acid) absorbed at 509 nm and exhibited fluorescence at 585 nm. For **1**, the monoprotonation $pK_a$ and $pK_a^*$ values have been deduced to amount to $-6.0$ and $-3.2$ [12]. In concentrated sulfuric acid, both carbonyl groups were mostly protonated. This diprotonated species was characterized by long wavelength absorption bands at 513 and 575 nm, and an emission at 586 nm as reported in Refs. [6, 8]. For this step, a $pK_a$ value of about $-7.1$ was estimated.

These results on the absorption properties of phenanthro[1,10,9,8,*o*,*p*,*q*,*r*,*a*]perylene-7,14-dione (**2**) in aprotic dipolar solvents like dimethylsulfoxide were found to be in contrast to the data reported in Ref. [6]. A base line from 600 nm downwards and a steeply rising absorption at about 280 nm have been presented in this paper. In methanol as the solvent the same type of absorption has been shown together with a marked fluorescence which was erroneously normalized to the steeply rising absorption at about 250 nm. These observations obviously have been due to the extremely low solubility of **2** in common organic solvents.

From the data deduced above it was concluded that the absorption properties of **2** corresponded to a quite "normal" extended condensed aromatic system. Thus, in aprotic dipolar solvents **2** exhibited a long wavelength absorption band, which was similar to the one of **1**. **2** is non-fluorescent in such solvents as is well known from similar compounds like benzophenone [13]. Due to a $n-\pi^*$ transition hidden in the long wavelength absorption edge of such compounds, fluorescence is entirely absent in favor of intersystem crossing. In methanol, the $\pi-\pi^*$ absorption of **2** became bathochromically shifted, whereas the $n-\pi^*$ transition was hypsochromically displaced due to hydrogen bonding solvatation at the lone pairs of the carbonyl groups. Accordingly, the long wavelength transition became the lowest energy transition and allowed for the usual fluorescence properties of highly condensed aromatic ring systems. The same interpretation held for the corresponding shifts upon protonation and upon substitution with hydroxyl groups as given for **1**. Protonation of **2** by pure methanol as speculated in Ref. [6] seemed to be unlikely due to the tremendous $pK_a$ difference ($\approx 22$) between methanol and **2**. Moreover, storage of such methanol solutions of **2** over $K_2CO_3$ did not change their absorption and emission properties. One should also note in this respect that for monoprotonation an aqueous sulfuric acid of at least 70% was needed! These findings on **2** will become fundamental for the interpretation of the photochemical and photophysical behavior of hypericin and its derivatives.

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