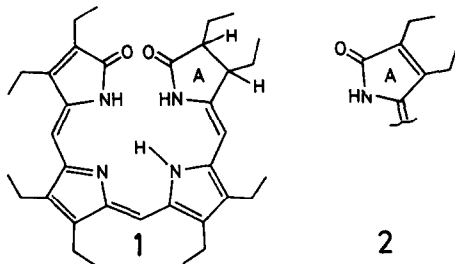


LONG-LIVED  $\pi$ -CATION RADICALS OF BILINDIONATO ZINC COMPLEXES\*

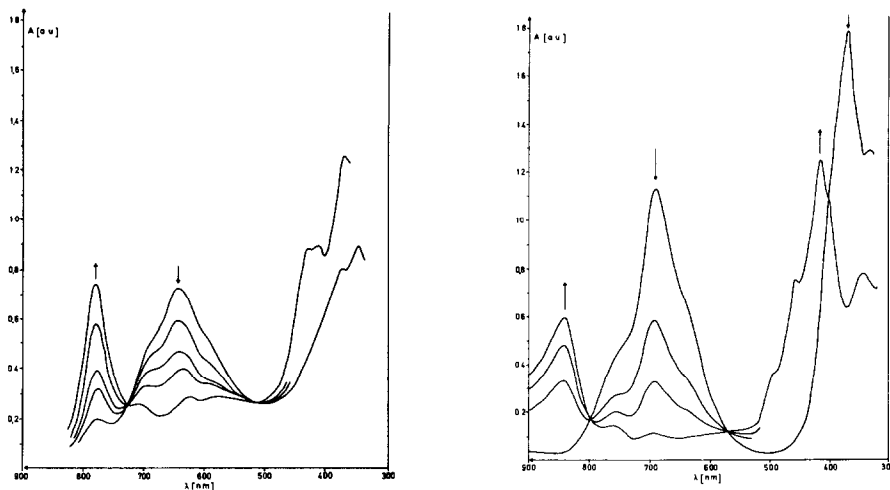
C. Krauss and H. Scheer, Institut für Botanik der Universität,  
Menzinger Str. 67, 8000 München 19, West Germany

**Summary:** The title compounds have been prepared by  $I_2$ -oxidation in benzene-pyridine solutions and characterized by uv-vis and esr spectroscopy.

The oxidation of bilindiones has long been used as an analytical tool<sup>1)</sup>, but the primary steps of these reactions have been investigated only recently<sup>2,3)</sup>. They became in particular interesting<sup>4)</sup> with the proposal, that the conversion of the plant photomorphogenetic pigment phytochrome from  $P_r$  to  $P_{fr}$  may involve oxidativ events<sup>5,6)</sup>. The formal nucleophilic substitution proposed recently for this process<sup>7)</sup> has been suggested to arise from an oxidation-addition reaction, but no intermediates could be identified. We now wish to report the observation of long-lived  $\pi$ -cation radicals by uv-vis and esr spectroscopy in the reaction mixture, by using zinc-complexes of bilindiones rather than the free bases as educts.

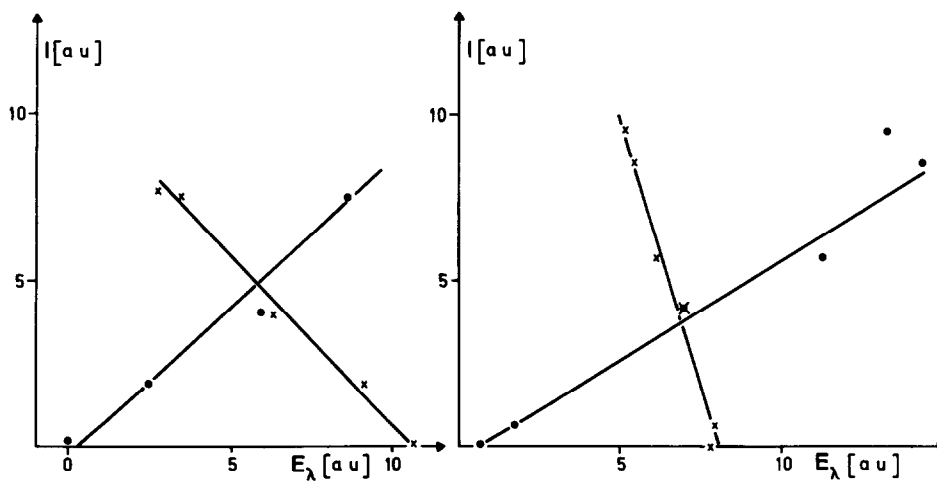


$\underline{\underline{1-Zn}}$  and  $\underline{\underline{2-Zn}}$  were prepared from  $\underline{1}$  and  $\underline{2}$ <sup>8)</sup>, respectively, by adding equimolar amounts of  $Zn^{++}$ -acetat in methanol. Parallel measurements of uv-vis and esr spectra were performed in a custom made combination cell, which allowed additions of the iodine stock solution in benzene under  $N_2$ -atmosphere. Uv-vis spectra were recorded with a DMR-22 and PMQ-2 spectrophotometer (Zeiss, Oberkochen), esr spectra with a E4 instrument (Varian, Darmstadt). A solution of the zinc complex of  $\underline{1}$  ( $\underline{\underline{1-Zn}}$ ,  $10^{-4}M$ ) in benzene containing pyridine (2M) was titrated with  $I_2$  ( $1.5 \cdot 10^{-3}M$ ) dissolved in benzene. The titration (fig. 1 a) results in a rapid conversion of  $\underline{\underline{1-Zn}}$  into a product absorbing at 780 nm (P 780), with only minor (further oxidized) by products absorbing below 600 nm being formed. A similar species had



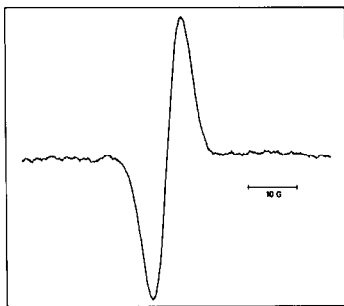
**Fig. 1 a:** Titration of  $\underline{1-Zn}$  ( $1 \times 10^{-4} M$ ) in benzene containing pyridine (2M), with iodine ( $1.5 \cdot 10^{-3} M$ ) in benzene. The final concentration of  $I_2$  was  $2.5 \times 10^{-4} M$ . The arrows denote increasing and decreasing absorptions, respectively.

**b:** Titration of  $\underline{2-Zn}$ . All concentrations as before, but the final concentration of  $I_2$  was  $6 \times 10^{-4} M$ .



**Fig. 2:** Correlation of the uv-vis spectral absorptions ( $E_\lambda [a.u.]$ ), with the doubly integrated intensities of the esr signal during the titration of  $\underline{1-Zn}$  (a) and  $\underline{2-Zn}$  (b) in benzene containing pyridine (2M) with iodine in a combined uv-vis/esr cell. a: Titration of  $\underline{1-Zn}$  monitored at  $\lambda = 780$  (oo) and 650 nm (xx). b: Titration of  $\underline{2-Zn}$  monitored at  $\lambda = 840$  (oo) and 680 nm (xx).

been observed earlier as an intermediate during the oxygenation of  $\underline{\underline{1-Zn}}$ <sup>3)</sup>. The correlation (fig. 2 a) between the absorption increase at  $\lambda_{\max} = 780$  nm, and the increase of the esr signal (fig. 3) demonstrate, that the 780 nm product is itself a radical, or is in equilibrium with a radical having no strong absorption bands in the visible and near infrared spectral region. Calibration with a weighed amount of diphenylpicrylhydrazyl gave 0.67 moles of spins formed per mole of  $\underline{\underline{1-Zn}}$  oxidized. Allowing for some further oxidation and taking into account the extinction coefficients of free bilins in the range of 15-30,000, this favors P 780 being a cation radical itself. The esr signal (fig. 3) exhibits no fine structure, it has a peak-to-peak linewidth of 6 G, and a g-factor of 2,0080 as determined with 2,2,6,6-tetramethylpiperidine-1-oxyl<sup>9)</sup>. P 780 is stable in the presence of the latter even after exposure to light, but destroyed in the presence of air in the dark. A weak signal can already be observed in freshly prepared solutions of  $\underline{\underline{1-Zn}}$  in benzene/pyridine in the absence of iodine. It increases (probably due to the presence of residual  $O_2$ ) by irradiation with visible light to a level reaching 10-15 % of that obtained with  $I_2$ .



**Figure 3:**

Esr spectrum of  $\underline{\underline{1-Zn}}$  oxidized with  $I_2$  in benzene containing pyridine (2 M). Modulation amplitude = 0.5 G.

A similar paramagnetic species ( $\lambda_{\max} = 840$  nm (fig. 1 b), peak-to-peak linewidth = 6 G) is formed from  $\underline{\underline{2-Zn}}$  upon titration with  $I_2$ . In this case, the amount of iodine required for saturating oxidation is 2-3 times higher than for the oxidation of  $\underline{\underline{1-Zn}}$  (fig. 1a,2a), which correlates with the well known<sup>3,4,7)</sup> increased reactivity of  $\underline{\underline{1}}$  as compared to  $\underline{\underline{2}}$ .

A structureless esr signal with a similar linewidth has been reported<sup>10)</sup> for the cation radical of a 1-aminobilin-19-onato zinc complex, and signals of this type are typical for the cation radicals of octaalkylporphinato- and chlorinato zinc and magnesium complexes<sup>11)</sup>. In the latter, they are due to anisotropic line broadening and only moderate spin densities at hydrogen bearing C-atoms and N-atoms. From this analogy and from the basic solvent system used, the species formed from  $\underline{\underline{1-Zn}}$  and  $\underline{\underline{2-Zn}}$  are assigned as  $\pi$ -cation radicals. To our knowledge, this is the first report of a long-lived  $\pi$ -cation radical derived from a bilindione (for paramagnetic metal complexes, see ref. 12). Bilindione radicals have been postulated as intermediates from electrochemical studies<sup>10,13)</sup>, but only the 1-amino analogues gave radicals sufficiently long-lived to be observable by esr spectroscopy<sup>10)</sup>. The stabilization in the solvent system used may be due to the aprotic environment, or to the formation of complexes with either solvent or iodine. The long-wavelength bands of  $\underline{\underline{1-Zn}}$  and  $\underline{\underline{2-Zn}}$  dissolved in pyridine-benzene have some fine structure (fig. 1), as compared

to the single banded spectra, e.g. in methanol<sup>14</sup>). There occurs even a gradual blue-shift ( $\sim 10$  nm) of the absorption of free 1 and 2 upon standing in pyridine-benzene containing iodine<sup>7,15</sup>). In both cases, unchanged 1-Zn and 2-Zn, or 1 and 2, respectively, can be isolated back from the reaction mixture almost quantitatively.

No intermediates with similar long-wavelength absorptions ( $\lambda_{\max} > 650$  nm) have been identified as yet during oxidative reactions of free bilins. As at least partly the same products are obtained from oxidation of both 1 and 1-Zn, however,  $\pi$ -cation radicals are likely intermediates, too, during the reaction of free bases. If these cation radicals have similar long-wavelength absorption bands as those derived from metal complexes, this region may warrant an inspection for phytochrome intermediates<sup>16</sup>). The possibility of such intermediates should also be considered when choosing the proper reference wavelength in double frequency spectroscopy.

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**Footnote:\*)** Studies on Plant bile pigments. 8.Part 7 : W. Kufer and H. Scheer, Hoppe-Seyler's Z. Physiol. Chem., in press.

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