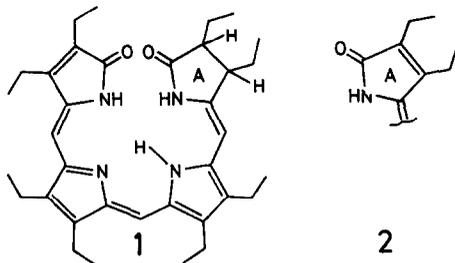


LONG-LIVED π -CATION RADICALS OF BILINDIONATO ZINC COMPLEXES*

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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 tool¹⁾, but the primary steps of these reactions have been investigated only recently^{2,3)}. They became in particular interesting⁴⁾ with the proposal, that the conversion of the plant photomorphogenetic pigment phytochrome from P_r to P_{fr} may involve oxidativ events^{5,6)}. The formal nucleophilic substitution proposed recently for this process⁷⁾ 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 π -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.



$\underline{\underline{1}}\text{-Zn}$ and $\underline{\underline{2}}\text{-Zn}$ were prepared from $\underline{1}$ and $\underline{2}$ ⁸⁾, 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 $\underline{1}$ ($\underline{\underline{1}}\text{-Zn}$, $10^{-4}M$) 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 $\underline{\underline{1}}\text{-Zn}$ 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

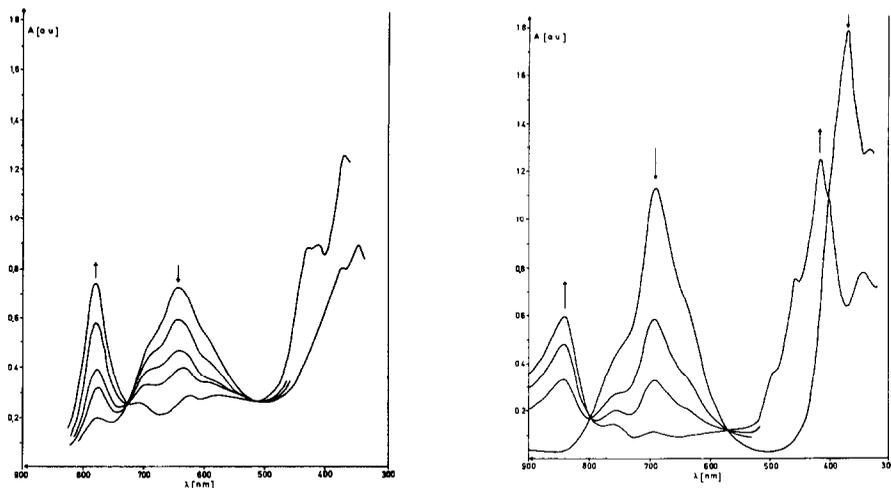


Fig. 1 a: Titration of $\underline{1-Zn}$ ($1 \times 10^{-4} M$) in benzene containing pyridine (2M), with iodine ($1.5 \cdot 10^{-3} M$) in benzene. The final concentration of I_2 was $2.5 \times 10^{-4} M$. The arrows denote increasing and decreasing absorptions, respectively.

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

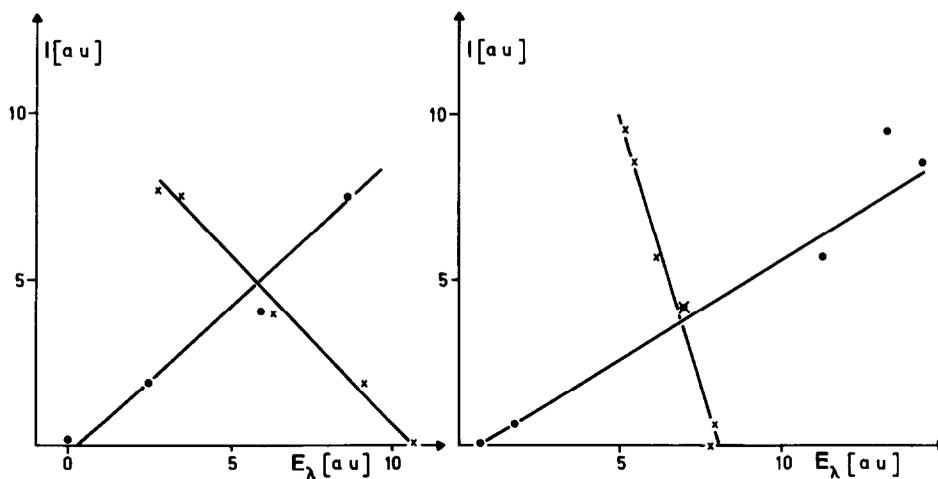


Fig. 2: Correlation of the uv-vis spectral absorptions ($E_\lambda [a.u.]$), with the doubly integrated intensities of the esr signal during the titration of $\underline{1-Zn}$ (a) and $\underline{2-Zn}$ (b) in benzene containing pyridine (2M) with iodine in a combined uv-vis/esr cell. a: Titration of $\underline{1-Zn}$ 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 $\underline{\underline{1-Zn}}$ ³⁾. 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-oxyl⁹⁾. 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 .

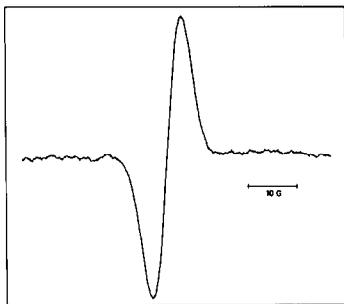


Figure 3:

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^{3,4,7)} increased reactivity of $\underline{\underline{1}}$ as compared to $\underline{\underline{2}}$.

A structureless esr signal with a similar linewidth has been reported¹⁰⁾ 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 complexes¹¹⁾. 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 π -cation radicals. To our knowledge, this is the first report of a long-lived π -cation radical derived from a bilindione (for paramagnetic metal complexes, see ref. 12). Bilindione radicals have been postulated as intermediates from electrochemical studies^{10,13)}, but only the 1-amino analogues gave radicals sufficiently long-lived to be observable by esr spectroscopy¹⁰⁾. 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 methanol¹⁴). There occurs even a gradual blue-shift (~ 10 nm) of the absorption of free 1 and 2 upon standing in pyridine-benzene containing iodine^{7,15}). 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, π -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 intermediates¹⁶). The possibility of such intermediates should also be considered when choosing the proper reference wavelength in double frequency spectroscopy.

Acknowledgements: This work was supported by the Deutsche Forschungsgemeinschaft, Bonn - Bad Godesberg. We thank Dr. H. Schlude for helpful discussions and the disposition of the esr spectrometer and Ms. H. Hinrichsen for the esr measurements.

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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(Received in UK 3 July 1979)