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The First Annulated Porphyrazine Containing Four Endoperoxide Bridges

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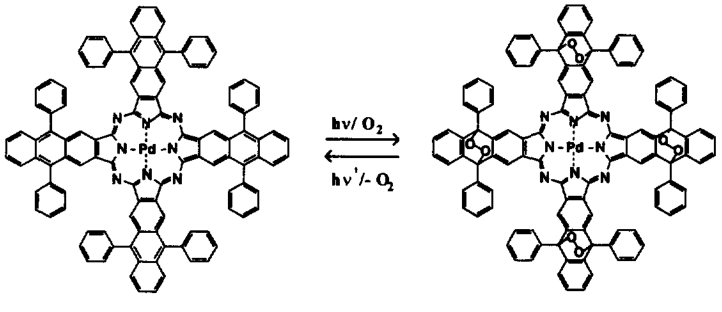
Abstract: Photooxygenation of palladium octaphenyltetraanthraporphyrazine **1** to **2**, which is the first example of a porphyrazine containing four endoperoxide bridges in the anthracene unit has a Q-band absorption maximum at 662 nm and exhibits photochromic properties. Irradiation of **2** into higher excited electronic states ($\lambda_{exc.} < 350$ nm) leads to a regeneration of the oxygen-free derivative with $\lambda^{max} = 846$ nm due to a cycloreversion. Copyright © 1996 Elsevier Science Ltd

Modified tetrapyrrolic compounds play an important part as potential photosensitizers in the laser tumor therapy (PDT)[1]. However, skin photosensitivity and oxygen depletion at the tumor during the PDT treatment are limitating factors to their application. To overcome these problems we have recently suggested new approaches involving higher excited states of photosensitizers.[2] Here we report the photochemical preparation of a tetraanthraporphyrazine **2** with four transannular endoperoxide bridges and its mass spectrometry behaviour. Because of the unusual photochromic properties of **2** such a system is not only of interest for PDT. Photochromic systems working in the red / near i. r. region are almost unknown.[3]

2 has been generated photochemically from **1** (scheme1). Compound **1** dissolved in benzene has a Q-absorption band at 846 nm.[4] When this solution (~5×10^{-5} M) saturated with oxygen is irradiated ($\lambda_{exc} > 750$ nm), the 846 nm band completely disappears and a stable photoproduct with $\lambda^{max} = 753$ nm is formed. Further irradiation of the 753 nm photoproduct leads to the stable compound **2** with a Q-band maximum at $\lambda^{max} = 662$ nm (Fig. 1).



1

2

Scheme 1

The purity of **2** was checked by HPLC[5]. Singlet oxygen is involved in a selfsensitized photoreaction. This was independently shown in other experiments with external singlet oxygen generators added to the benzene solution of **1**.

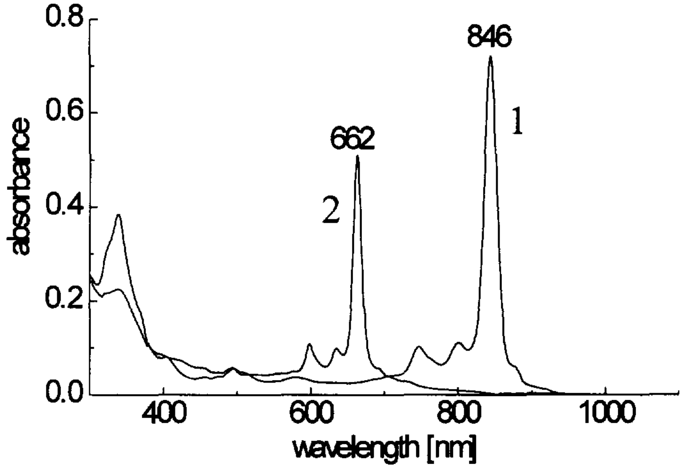


Figure 1: Absorption spectra of the tetraanthraporphyrazine **1** and its endoperoxide **2** in benzene.

The results can be understood as incorporation of oxygen as endoperoxide bridges in the middle part of the anthracene unit. Only in this case the absorption maximum of the Q-band corresponds to that of an alkyl-substituted phthalocyanine. The corresponding palladium tetra-*tert*-butylphthalocyanine complex synthesized by us, has a Q-band maximum at λ^{max} = 661 nm [6] (solvent: benzene).

Photooxygenation of aromatic hydrocarbons is well known and leads exclusively to the corresponding endoperoxides.[7]

The liquid secondary ion mass spectra (LSIMS)[8] obtained of **1** freshly dissolved in 3-nitrobenzyl alcohol exhibited the stable peak for the molecular ion M^+ at m/z 1626 (for ^{106}Pd) (Fig. 2). No peaks for heavier ion signals (m/z > 1700) were detectable in 3-nitrobenzyl alcohol. The peaks show multiplet character, owing to the presence of natural abundance of the palladium isotopes. The LSI mass spectra of **2** in 2-nitrophenyl octyl ether indicate the molecular ion peak at m/z 1754 (for ^{106}Pd) (Fig. 2). This result corresponds to an incorporation of eight oxygen atoms. In addition, the mass spectrum shows m/z 1722, m/z 1690, m/z 1658 and m/z 1626 ions. The mass difference between the ions formed in the fragmentation of **2** corresponds exactly to 32 n, where n is the number of the oxygen containing anthracene units in the compound: **2**, m/z = 1754, m/z (1754-32) = 1722, m/z (1722-32) = 1690, m/z (1690-32) = 1658; **1**, m/z (1658-32) = 1626. The final fragment ion at m/z 1626 corresponds to the molecular ion of **1**.

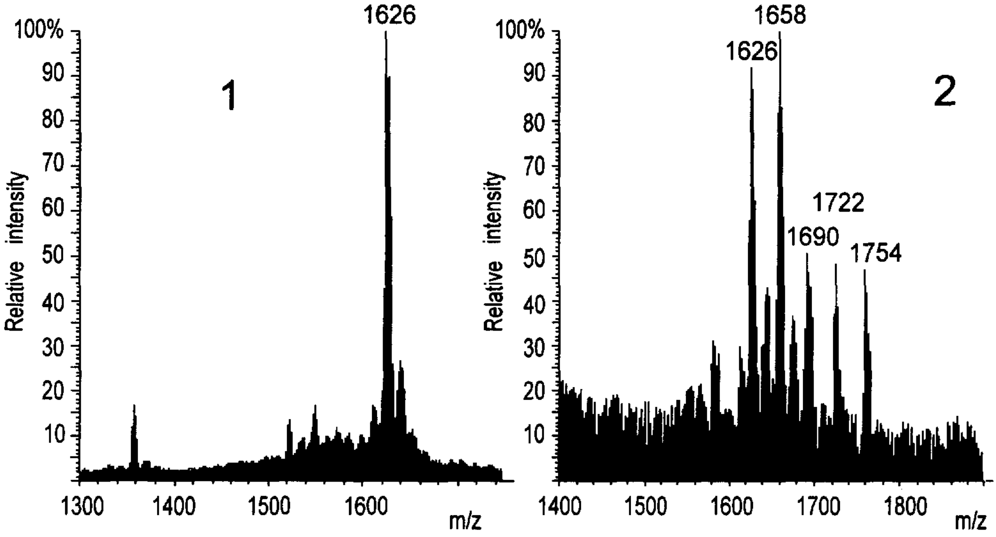


Figure 2: LSI mass spectra of the tetraanthrapophyrazine **1** and its endoperoxide **2**.

The most favoured fragmentation pathway involves a release of four molecules of oxygen. In the case of the above mentioned stable photoproduct (precursor of **2**) with λ^{max} = 753 nm the molecular ion peak at m/z 1690 indicates the incorporation of four oxygen atoms. The heavier ion signals as seen for **2** are absent but the peaks of the fragment ion at m/z 1658 and m/z 1626 reflect the loss of oxygen. The fragmentation behaviour of m/z 1690 is exactly the same as observed for **2**. The loss of oxygen represents one of the most favoured decomposition pathways. The related product ions are of high abundance.

The 9,10-endoperoxide of 9,10-diphenylanthracene exhibits an analogous behaviour. The LSI mass spectrum in 3-nitrobenzyl alcohol only shows a weak signal of the $[M+H]^+$ peak at m/z 363 (17 %) but a very intense and stable peak at m/z 330 (100 %). This explains the loss of oxygen from the endoperoxide. Endoperoxides of other aromatic hydrocarbons exhibit a similiar behaviour.[9]

When **2** dissolved in benzene is irradiated into the region of higher excited singlet states with a nitrogen laser ($\lambda_{exc.}$337 nm) the start molecule **1** is partly regenerated due to a release of molecular oxygen from the transannular endoperoxide. The release of O_2 ($^1\Delta_g$) from higher excited singlet states of simply aromatic hydrocarbons has been well demonstrated.[10] So the system **1**→**2** is a very interesting photochromic system working on the basis of a cycloreversion in the red / near i.r. region.

Tetrapyrrolic compounds with endoperoxide bridges may also act as photosensitizers with internal source of singlet oxygen for PDT.[2]

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4. **1** was obtained by reaction of 9,10-diphenyl-2,3-dicyanoanthracene (0.053 mmol) with K_2PdCl_4 (0.025 mmol) in the presence of urea (0.3 mmol) at 290°C. After treatment with hot 5% HCl and 5% NaOH solution the black solid was extracted several times with ethanol. For further purification the remaining solid was chromatographed on LiChrospher 100 RP-18 endcapped using DMF / toluene / H_2O (60/ 35/5) as eluent and then benzene / DMF (80 / 20). The yield of **1** was 20%.
   UV / VIS / NIR (benzene) λ^{max} (lg ε): 846 (5.36); 796 (4.54); 742 (4.54); 695sh (4.20); 575 (4.27); 500 (4.39); 475sh (4.34), 340 (5.16).
5. LiChrospher 100 RP-18 endcapped, eluent: toluene / acetonitrile (50 / 50) plus 4% H_2O. UV / VIS (benzene) λ^{max}: 662, 632, 595, 535, 410 sh, 340.
6. For a general synthesis see : Freyer, W. ; Minh, L.Q. *Monatsh. Chem.* **1986,** 117, 475-489.
   UV / VIS (benzene) λ^{max} (lg ε): 661 (5.39); 630 (4.62); 593(4.64); 555sh (4.11); 395sh (4.11); 346 (4.88); MS (3-nitrobenzyl alcohol) m/z: 843 $[M+H]^+$ for ^{106}Pd.
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8. Low resolution LSI mass spectra were recorded on a double- focusing mass spectrometer VG Autospec using a Cs ion gun with 32 kV anode voltage and 0.5 uA heater current.
   3-Nitrobenzyl alcohol and 2-nitrophenyl octyl ether were used as matrices. Ion intensity for **2** increased by using 2-nitrophenyl octyl ether instead of 3-nitrobenzyl alcohol as matrix whereas **1** gives more intensity with 3-nitrobenzyl alcohol. Spectra were acquired over a mass range from m/z 1100 to m/z 2050. Tuning and calibration were performed using CsI.
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