COMMUNICATION

5- and 10-Oxocorroles from β-octalkylcorroles

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The reaction of Zn ions with β-octaalkylcorroles leads to the air oxidation of the macrocycle, with the formation of a mixture of 5- and 10-oxocorroles. Spectroscopic characterization confirms the antiaromatic character of these macrocycles. A simple synthetic protocol opens the way for more detailed studies of oxocorrole chemistry.

A research bonanza driven by the interesting and peculiar properties shown by the corrole macrocycle has characterized corrole chemistry over the past two decades. As a result, the contracted porphyrinoid has been shown to be both different from the parent porphyrin and also interesting in diverse fields of applications.[1] For example, the coordination chemistry of corrole is characterized by the so-called non-innocent character of this macrocycle, which makes it challenging from one side to elucidate the electronic structure of the complexes, and from the other side, interesting from both catalysis and clinical applications of these metal derivatives.[2] The bright emissions of corroles have also been of interest for potential applications in solar cells or photodynamic therapy(PDT) of tumors.[3]

The increase of interest in corrole chemistry at the beginning of this century was possible due to the discovery of simple synthetic procedures for the preparation of 5,10,15-triarylcorroles, which made available this macrocycle for studies in several research groups.[4] For this reason, the research has been focused on triarylcorrole derivatives, while β-octa-alkylcorroles, the first examples reported for this porphyrinoid,[5] almost disappeared from the scene.[6] Apart from the simple synthetic approach, the bigger popularity of triarylcorroles has been motivated by their high stability under oxidative conditions, due primarily to the protective action of the *meso*-phenyl groups.

However, reactivity at the *meso*-positions of corroles has been sparsely explored[7] and not always devoted to macro ring opening. One interesting example is represented by the formation of 10-oxocorroles. These macrocycles were first described by Bröring as by-products of the oxidative ring closure of linear tetrapyrroles to give 5,15-diphenylcorroles,[8] while Guilard obtained them from the air oxidation of Ni complexes of corrole dyads.[9] More recently, Osuka and Tanaka reported their formation by oxidation of *meso*-unsubstituted 5,15-bis (pentafluorophenyl)corrole (Fig. 1).[10]

The nomenclature adopted by these groups for their macrocycles has been different, starting from the 10-oxocorroles used by Bröring to the 10-isooxocorrole used by Osuka. To avoid confusion, and because the term isocorrole has been used to indicate a corrole wherein the conjugation is interrupted by a sp^3 carbon, we prefer in this work to use the term oxocorrole.

Oxocorroles have been usually obtained by using strong oxidants, and we were surprised to obtain them upon attempting to coordinate Zn ion to a β-octaalkylcorrole, as indicated below.

In the past we observed the formation of the Zn corrole anion in pyridine,[11] but our recent reports on the formation of the neutral Zn complexes with the corrole radical species,[12] led us to investigate the reaction of corrole **1** with Zn ions in boiling methanol. The reaction was spontaneous with the disappearance of the corrole and the prompt formation of an orange product in good yield, which upon TLC analysis revealed the presence of two species. Preparative TLC allowed the complete separation of a first fraction, while the second band was incompletely separated. Our spectroscopic characterization of the first fraction gave interesting results; the UV-vis spectrum of

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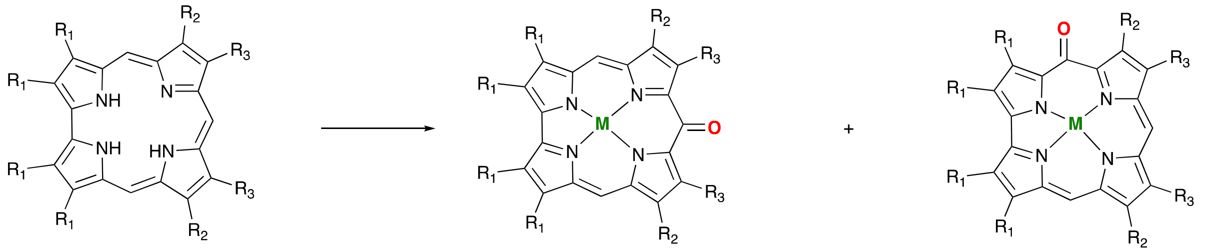

1. R_1 = Et; R_2 = Me; R_3 = methoxycarbonylethyl
2. $R_1 = R_2 = R_3$ = Et

3. R_1 = Et; R_2 = Me; R_3 = methoxycarbonylethyl; M = Zn
4. $R_1 = R_2 = R_3$ = Et; M = H_2

5. R_1 = Et; R_2 = Me; R_3 = methoxycarbonylethyl; M = Zn
6. $R_1 = R_2 = R_3$ = Et; M = H_2

Fig. 1. Synthetic pathway to 5- and 10-oxocorroles

the product showed a band centered at 420 nm, together with an absorption at 332 nm (Fig. 2). This spectrum was similar to what was reported for the corresponding oxo-vanadyl derivative.[13] ^{1}H NMR characterization confirmed the probable formation of an oxocorrole, as demonstrated by both the diamagnetic nature of the compound coupled with the lack of aromatic character. The spectrum (Fig. 3) showed the absence of resonances attributable to the *meso* protons of an aromatic corrole derivative.

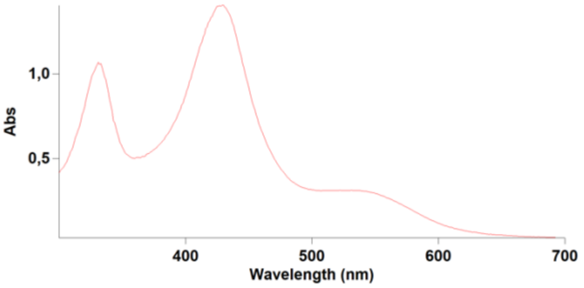

Fig. 2. UV-vis spectrum of **3** in CH_2Cl_2

A singlet around 5 ppm was instead present; this signal can be attributed to the 5,15-protons of the corrole macrocycle and the X-ray crystallographic characterization of a suitable crystal of this product revealed the formation of the Zn complex of the 10-oxocorrole **3**, as a penta-coordinated aquocomplex (Fig. 4).

The corrole has a dome conformation, with the four N atoms lying an average of 0.21 Å out of the best plane of the 19 carbon atoms. But the ketone does not conform to the overall dome shape, having its oxygen atom tilted out of plane by 0.49 Å to the same side as the N atoms. The Zn atom has square pyramidal coordination geometry, lying 0.50 Å out of the N_4 plane, with Zn-N distances 1.9879(11) – 2.0233(12) Å and $Zn-OH_2$ distance 2.0536(11) Å.

Although we failed to completely separate the second fraction, the ^{1}HNMR spectrum (Fig. S2) of the mixture showed the formation of a less symmetrical product, as indicated by the presence of two different singlets in the 5 ppm region, although the residual signals of **3** present as an impurity indicated the incomplete separation of the two products. X-ray analysis of a crystal obtained from the NMR tube indicated the formation of the 5-

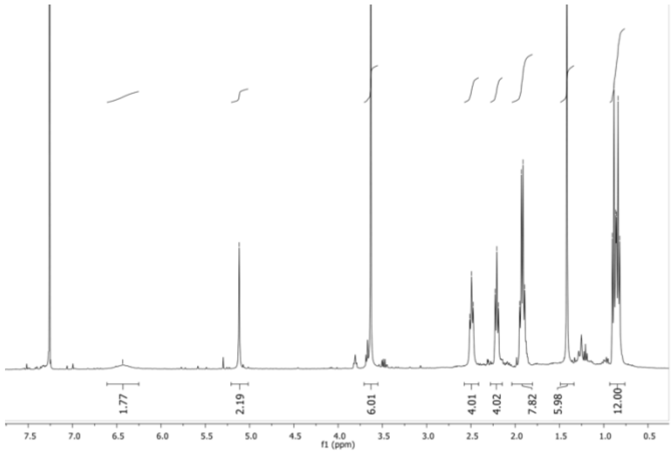

Fig. 3. ^{1}H NMR spectrum of **3** in $CDCl_3$

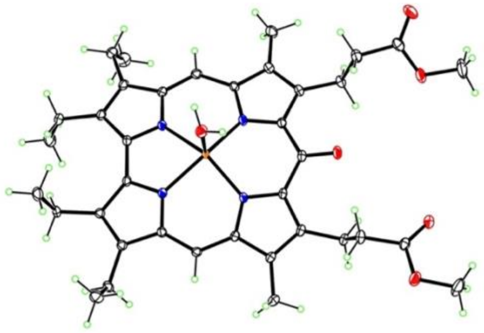

Fig. 4. Crystal structure of **3** with 50% ellipsoids

oxocorrole regioisomer **5** (Fig. S3), although also in this case contaminated with **3**. A crystal structure analysis (supplementary information) showed partially occupied carbonyls at the 5, 10 and 15 positions.

It is significant to note that the formation of the oxocorroles does not require the use of strong oxidants, as observed in the case of the previous examples for monomeric species, the presence of molecular oxygen was sufficient.[13]

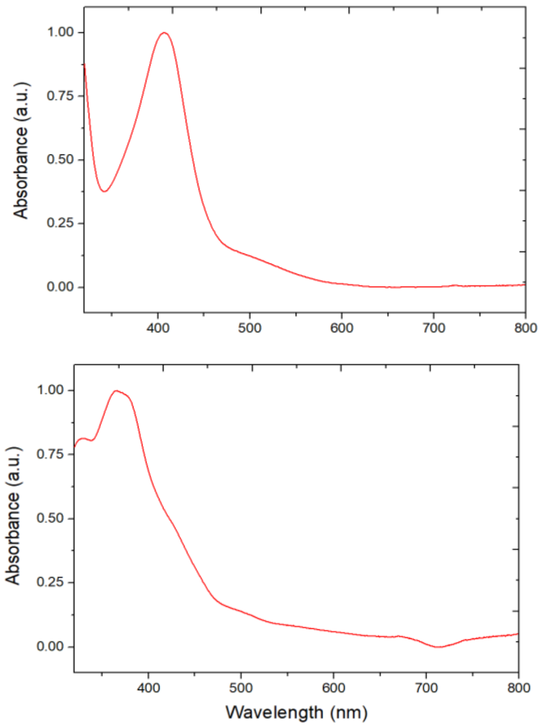

Fig. 5. UV-vis spectrum of: a) 10-oxocorrole **4** and b) 5-oxocorrole **6** in CH_2Cl_2

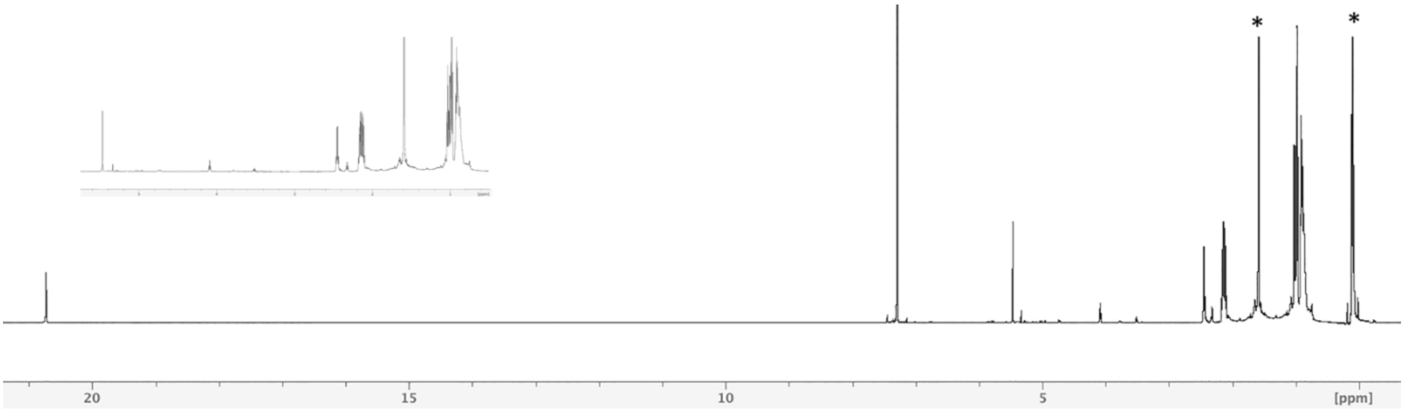

Fig. 6. ^{1}H NMR spectrum of **4** in $CDCl_3$ (inset shows the 0-6 ppm region)

As previously reported for corrole dyads,[9] the formation of the oxocorrole is probably due to the attack of molecular oxygen upon the Zn corrole complex, through the intermediate hydroperoxide isocorrole. To investigate the influence of the solvent, we repeated the same reaction in pyridine, observing again the formation of the Zn complex of the 5- and 10-oxocorroles, in similar yields.

With the aim to achieve the separation of the two regioisomers and to investigate the scope of the reaction, we tested octaethylcorrole in the reaction, obtaining again a mixture of 5- and 10-oxocorrole in an almost statistical ratio. However although the UV-visible monitoring of the reaction indicated the formation of the Zn complex, the complex was less stable and subsequent reaction work up led to demetalation of the product, affording the corresponding oxocorrole free bases. This demetalation was advantageous because we were able to separate the 5- and 10-oxocorroles, allowing characterization of the two regioisomers **4** and **6** (Fig. 1).

The UV-vis spectra indicated some important differences between the two regioisomers. While the regiosomer **4** shows a red shifted absorption, **6** possessed a blue shifted absorption centered below 400 nm (Fig. 5).

The ^{1}H NMR characterization of both isomers confirmed the anti-aromatic character of the macrocycles, with the inner core NH protons resonating above 20 ppm (Fig. 6 and Fig. S6).

It is interesting to note that the same complexes can be obtained by reaction of the corresponding *a,c*-octaethylbiladiene with Zn ions in refluxing methanol; following the progress of the reaction by UV-vis spectroscopy, we noted the initial formation of the corrole free base, followed by the formation of the oxocorrole products.

To explore a possible improvement in the reaction yields, we decided to test the reaction of the octaethylcorrole using an oxidant salt, such as Tl(III) acetate. Also in this case, the reaction afforded the same mixture of 5- and 10-oxocorrole, but it was possible also to isolate a further product of the reaction. Although this species was not stable, we were able to characterize it; the UV-vis spectrum (Fig. S7) shows both a Soret-like band below 400 nm, together a red shifted band above 700 nm.

The ^{1}H NMR (Fig. S8) indicated the absence of an aromatic ring current effect and was in agreement with the formation of **7**, which can be considered to be the ketal species of the 5-oxocorrole, which is an unprecedented example of an isocorrole (Fig. 7).

Unfortunately, the low stability of this intermediate did not allow us to obtain a crystal suitable for X-ray crystallographic characterization.

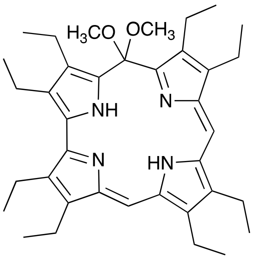

Fig. 7. Molecular structure of **7**

The electrochemical properties of **4** and **6** were investigated using cyclic voltammetry (CV) (Table 1 and Fig. S9). Both derivatives exhibited electrochemical reversibility at all measured scan rates for their first oxidation and reduction processes ($E_{ox1}^{1/2}, E_{red1}^{1/2,}$), indicating good chemical and thermal stability of the monoionic species. In comparison to 5-oxocorrole, 10-oxocorrole showed no significant changes in $E^{1/2}{}_{ox1}$ and $E^{1/2}{}_{ox2}$ values, whilst the $E^{1/2}{}_{red1}$ value is anodically shifted by 60 mV indicating the formation of a more electron-rich system, resulting in a widening of the ΔE_{CV} by 100 mV.

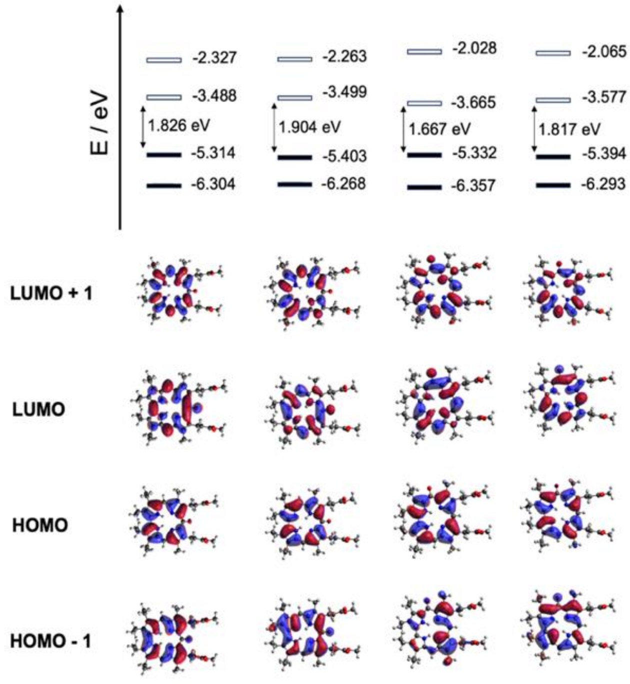

Fig. 8. MO diagrams for 10-oxo1, 10-oxo2, 5-oxo1, 5-oxo2

Table 1. Redox potentials(V), electrochemical- and optical gap values (eV). CV were measured in CH_2Cl_2 under N_2 with 0.1 M TBAP as the electrolyte, SCE as a reference electrode and a Pt wire as counter-electrode. Scan rate: 0.02 V s^{-1}. *Mean value of the two tautomers calculated energies.

Compound	$E^{1/2}{}_{red1}$	$E^{1/2}{}_{ox1}$	$E^{1/2}{}_{ox2}$	ΔE_{CV}	ΔE_{HL}
5-oxo	-0.58	0.98	1.33	1.56	1.74*
10-oxo	-0.64	1.02	1.31	1.66	1.86*

To provide further insight into the electronic transitions, density functional theory (DFT) calculations were performed at the b3lyp/6-311+g(d,p) level of theory. The *Kohn-Sham* representation of the frontier orbitals suggests a similar HOMO distribution between the free bases of **3** and **5** (Fig. 8, Table 1), consistent with the experimental data, as well as a lowering of the LUMO energy level observed for the 5-oxocorrole, probably due to the participation of oxygen within the orbital distribution.

At the same time, a destabilization of LUMO +1 was observed in the case of 5-oxocorrole. This computational finding aligns well with the experimentally observed blue shift of 5-oxocorrole in its UV-vis spectrum, given that the Soret band involves the transition of four main orbitals, namely HOMO-1, HOMO, LUMO, and LUMO+1 (the latter to a greater extent) (Table S1).

Conflicts of interest

There are no conflicts to declare.

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