Stepwise Oxidations and Reductions of a Physiologically Active Chlorin: Voltammetric and Spectroelectrochemical Studies on Bonellin Dimethyl Ester

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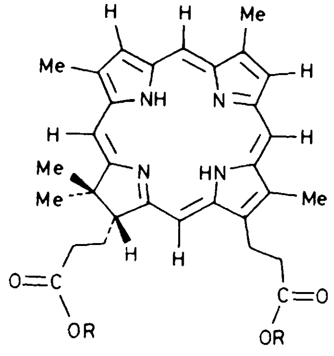
A.c. and cyclic voltammetric studies have established the occurrence of stepwise one-electron reductions and oxidations of the title compound (H_2Bn), and of octaethylchlorin. The absorption spectra (350—850 nm) of electrogenerated H_2Bn^- and H_2Bn^+ in CH_3CN are reported and the reduction is shown to pass through an intermediate, possibly [$H_2Bn{\cdot}H_2Bn^-$].

Bonellin (1; R = H) is the green pigment responsible for masculinisation of the indifferent larvae of the marine worm *Bonellia viridis*. It is also used as a defence chemical by the adult female. The pigment is structurally unique among naturally occurring chlorins in possessing a *gem*-dimethyl grouping, and no substituents on C-3, C-8, or the bridging methine C-15.[1] It is also the first tetrapyrrole macrocycle to be found which has no co-ordinated metal ion in the natural state. Nonetheless, in common with other porphyrin and chlorin derivatives, its biochemical action is known to involve a photo-redox mechanism.[2]

We report here an examination of the thermally equilibrated electron-transfer processes of bonellin dimethyl ester, detected voltammetrically, and of the changes in absorption spectrum accompanying its oxidation and reduction.



(1)

Results

As shown in Figure 1, bonellin dimethyl ester (1; R = Me), henceforth referred to as H_2Bn,† exhibits two reversible one-electron reductions and a reversible one-electron oxidation in CH_3CN. A further well defined oxidation, located by a.c. voltammetry at +0.86 V, is not fully characterised at present but coincides with the second reversible one-electron oxidation observed in a parallel study of *trans*-octaethylchlorin (H_2OEC). These electrode processes are summarised in equation (i).

$$H_2Bn^{2+\cdot a} \xleftarrow[-e^-]{} H_2Bn^+ \underset{-e^-}{\rightleftharpoons} H_2Bn \overset{+e^-}{\rightleftharpoons} H_2Bn^- \overset{+e^-}{\rightleftharpoons} H_2Bn^{2-} \qquad \text{(i)}$$

[a] Inferred product; see text.

A complementary examination of H_2Bn over a more limited range in strictly non-polar liquid 1-methylnaphthalene at 150 °C shows that the first reduction and first oxidation are unaltered in this medium, and are clearly simple electron-transfer processes uncomplicated by subsequent rearrangement or solvent interactions.

Consideration of the Table shows that the influence of the characteristic bonellin substitution pattern is to shift the array of electrode potentials by *ca.* +0.2 V relative to octaethylchlorin, while leaving the internal separations essentially unchanged. In comparison with porphyrins, oxidation of both chlorins is characteristically easy, and $E_{ox}(1) - E_{red}(1)$ 2.0 V; *cf.* 2.25 V for H_2OEP. (The first reductions of H_2OEC and H_2OEP are virtually coincident.) The electrochemically defined separation between donor and acceptor orbitals of bonellin is seen to match closely the prominent π to π^* transition energy in the absorption spectrum (1.94 eV),[3] suggesting that for bonellin and for chlorins in general the two experiments map the same levels of the molecular orbital manifold. This feature is shared by porphyrins but not, for example, by phthalocyanines.[4]

The fully reversible voltammetric behaviour found for bonellin implies that the simple electrode products already noted might persist as independent stable entities suited to electrosynthesis in bulk at controlled potentials. Thus there is the possibility of characterising the absorption spectra associated with H_2Bn^- and H_2Bn^+, which are possible intermediates in reductive and oxidative quenching, respectively, of photoactivated H_2Bn.

Spectroscopic monitoring *in situ* of the electrochemical generation of H_2Bn^- in CH_3CN was undertaken in a chilled optically transparent thin-layer cell mounted in the spectrophotometer beam. A remarkable sequence is observed during electrolysis at the plateau potential for the first reduction. Initially the progressive collapse of the π to π^* 639 nm H_2Bn band is accompanied by simultaneous growth of a band of similar appearance at 725 nm, together with a very broad and less obvious absorption between these peaks. However, as the reduction proceeds, with further depletion of neutral bonellin, the 725 nm band unexpectedly collapses so that the final

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† We follow porphyrin electrochemical usage here by indicating the two displaceable (N–H) hydrogen atoms of the free base; thus H_2OEP indicates octaethylporphyrin and CuOEP its copper salt. Likewise, H_2TPP is *meso*-tetraphenylporphyrin and H_2TPC its related chlorin.

Table. Stepwise electrode potentials for bonellin dimethyl ester and related macrocycles ($E_{\frac{1}{2}}$/V *vs.* Ag/Ag^{+} [a,b])

	ox. 2	ox. 1	red. 1	red. 2	$E_{ox}(1) - E_{red}(1)$	Solvent, temp.
H_2Bn		+0.35	−1.64		1.99	$C_{10}H_7Me$, 443 K
H_2Bn	+0.86	+0.37	−1.63	−2.08	2.00	MeCN, 293 K
H_2OEC	+0.74	+0.23	−1.81	−2.27	2.04	MeCN, 293 K
H_2OEP	+0.95	+0.46	−1.79	−2.26	2.25	Bu^nCN, 293 K

[a] Values quoted are by a.c. voltammetry on Pt and differ negligibly from cyclic voltammetry on Pt or, where accessible, a.c. voltammetry on Hg. [b] These strictly non-aqueous reference electrodes lie at *ca.* +0.35 V *vs.* SCE.

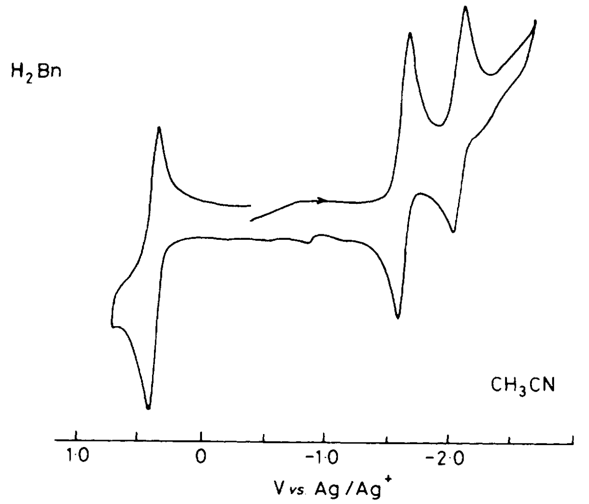


Figure 1. Typical cyclic voltammogram of bonellin dimethyl ester (scan rate 100 mV s^{-1}, [H_2Bn] = 4 × 10^{-4}M, in CH_3CN/0.1M-$TBABF_4$)

spectrum is dominated by a broad, strong band centred at 680 nm, together with sharper characteristic bands at 524 and 486 nm (Figure 2). The two-stage nature of the process is confirmed by the existence of two independent sets of isosbestic points, one relating H_2Bn with the intermediate, and the other relating the intermediate with the final product. It is stressed that all these changes take place at the potential appropriate for the first H_2Bn reduction, as determined voltammetrically, and are fully reversible. The neutral chlorin is wholly recovered by electroregeneration, which is accompanied by the appropriate spectroscopic regression, and the overall cycle is apparently unaltered in electrolyses performed at +10 and −35 °C. The spectroelectrochemical observations are consistent with an equilibrium association of H_2Bn^- and H_2Bn to form a dimer anion radical with a characteristic absorption band, as shown below. The present data do not determine whether H_2Bn^- is monomeric or reversibly dimerised in the final solution.

Parallel studies establish the same sequence of spectroscopic changes upon reduction of H_2OEC (but not H_2TPC) in CH_2Cl_2, CH_3CN, and $HCONMe_2$ between −35 and +10 °C. Thus, regardless of temperature, the two alkylated chlorins share a common cell reaction which is not subject to solvent participation. Porphyrin monoanions have been reported to undergo slow disproportionation in the presence of traces of water, ultimately yielding phlorins.[5] Analogous rearrangements are ruled out in our study since coulometry establishes that exactly one electron is consumed overall per molecule of chlorin, and since the voltammogram of the electrogenerated monoanion coincides with that of the starting material apart from inversion of current.

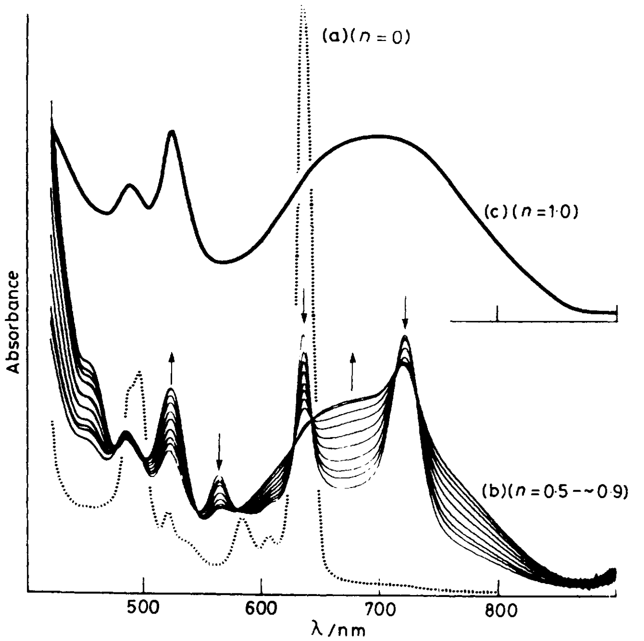
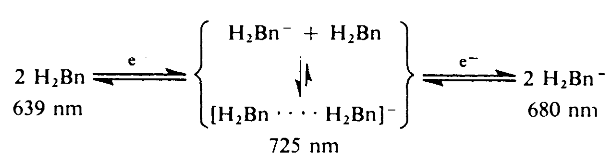


Figure 2. Electronic spectrum of electrogenerated bonellin dimethyl ester anion in acetonitrile:[a] (a) initial spectrum of H_2Bn (4 × 10^{-4}M, in electrolyte solution); (b) progression[b] linking the intermediate with H_2Bn^-; (c) ultimate spectrum[c] of H_2Bn^-, offset for clarity

[a] *n* is the inferred value of the charge accepted in Faraday mol^{-1} (see text). [b] Isosbestic points are at 545, 628, 712, and 730 nm in the stage shown, and at 478, 505, 585, 620, and 645 nm in the preceding stage. [c] Band maxima (and apparent ε values) are 486 (8 800), 524 (12 600), and 680 nm (12 200)



Scheme. Suggested electrode reactions

In contrast to these reductions, one-electron oxidation of H_2Bn leads to a generally featureless visible spectrum. Similar behaviour is reported for chlorophyll *a* and other metallochlorins,[6,7] and is observed in our study of H_2OEC. Although some anodic degradation of the chlorin was encountered, true isosbestic points are observed during electroregeneration of H_2Bn from H_2Bn^+. It follows that H_2Bn^+, like H_2Bn^-, is reversibly interconvertible with H_2Bn and long-lived under suitable conditions.

Although bonellin possesses a unique substitution pattern, the present spectroelectrochemical studies suggest that its electronic structure does not differ materially from that of symmetrically alkylated chlorins. There is now the prospect of exploring the reactivity patterns conferred on the redox-activated species, and the influence of co-ordinated metal ions on the chlorin systems.

Experimental

H_2Bn was isolated as previously described,[2] and sub-milligram quantities for electrochemical use were manipulated as 1% homogeneous dispersions in compressed pellets of the electrolyte, tetrabutylammonium tetrafluoroborate ($TBABF_4$). H_2Bn, H_2OEC, H_2OEP, and $TBABF_4$ were recrystallised and analytically pure. For voltammetric studies a Metrohm E505 cell station and three-electrode configuration were employed, interfaced with Metrohm E506/E612 or PAR 170 electrochemistry systems, with resistance compensation and phase-sensitive detection in the a.c. mode. The dropping mercury electrode functioned at electronically controlled drop times (normally 0.5 s); for other voltammograms Pt wire or microdisc working electrodes were used. Cell solutions [CH_3CN/0.2M-$TBABF_4$ at 20 °C and 1-methylnaphthalene/1.0M-$TBABF_4$ at 150 °C (ref. 4)] were degassed with argon.

For spectroelectrochemical studies an optically transparent (Pt or Au minigrid) working electrode in a jacketted Teflon and quartz cell, controlled by the Metrohm E506 and mounted in a Pye-Unicam SP 8-400 spectrometer, was used, as previously described.[8] The light was screened except during intermittent optical scans.

Acknowledgements

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