Inorganica Chimica Acta, 77 (1983) L13–L15

Porphyrins Appended with Podand Side Arm. Evidence for the Existence of Folded Conformer

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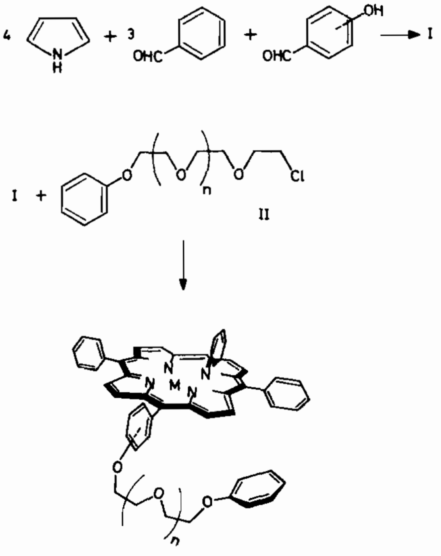
Received February 4, 1983

Recent years have witnessed the synthesis of porphyrins with peripheral substituents, essentially directed towards the development of models for the ligand binding affinities of heme moieties and cytochrome activity [1]. The design of organic substituents to the porphyrins must of necessity contain a potentially ligating terminal group, *viz.* a nitrogeneous base that can effectively coordinate to the metal centre thereby blocking one of the faces of the porphyrins for entry to other molecules. The driving force necessary to fold the side arm over the porphyrin ring has been the coordinative interaction between the terminal group and the metal centre. Our interest has been to induce conformational mobility to the side arm so as to promote intra-molecular interaction between the terminal group and the porphyrin chromophore. We present here information on the synthesis of porphyrins endowed with a side arm of variable length consisting of $-OCH_2CH_2O-$ groups appended to *meta* or *para* position of the phenyl group situated in one of the *meso* positions of the porphyrin and the side arm terminating with an aryl group. Optical and ESR data of the synthesised porphyrins provide evidence for the existence of folded conformers. The advantages of the ESR method include the fact that changes in the electronic manifold of the spin-free metal as a consequence of CT interaction can easily be reflected in the change in g values and hyperfine coupling constants. Besides, cyclic voltammetric studies of the synthesised porphyrins have been helpful in determining the ease of ring oxidation and difficulty in reduction as compared to the tetraphenylporphyrin.

The synthetic route begins with the normal porphyrin (I) functionalised with a hydroxyl group at either the *para* or the *meta* position of one of the aryl groups. This was then condensed with phenoxy derivatives of chloroglycols (II) in the presence of K_2CO_3 or KOH in DMF to yield the corresponding 'tail' porphyrins (Scheme).



M = 2H, Co(II), Cu(II), Zn(II)

n	para	meta
1	1a	2a
2	1b	2b
3	1c	2c

The divalent metal (Co^{2+}, Cu^{2+} and Zn^{2+}) derivatives of the porphyrins have been prepared according to the procedure described in the literature [2]. Structural integrity of these porphyrins relies heavily on the ^1H NMR data. The spectra of the free-base porphyrins and their Co(II) and Zn(II) derivatives are highly characteristic and all the resonances are suitably apportioned and assigned. Interestingly, the ethylenic proton resonances appeared as a non-degenerate AA′BB′ multiplet, (centred at 4.3, 4.1, 4.0 and 3.8 δ for n = 3) due to restricted rotation about O–C–C–O bonds and exist predominantly in all *gauche* conformation.

The optical absorption spectra of the free-base porphyrins are typical of the *etio* type. The reduced intensities of the Q bands as compared to that of the tetraphenylporphyrins are reminiscent of those observed for molecular complexes formed by TPP with π-acceptors [3]. Further, the singlet emission studies of the Zn(II) derivatives of the synthesised porphyrins reveal interesting results. It is found that fluorescence quantum yields (ϕ_F) of Q(0,0) emission are decreased by 20–30% when compared to ZnTPP, indicating the involvement of the terminal aryl group in the marginal quenching of the fluorescence.

The ESR spectra of Cu(II) derivatives of the synthesized porphyrins in frozen toluene solution were interpreted using a spin Hamiltonian for axial symmetry. The g values and hyperfine constants were calculated from the spectra, and are listed in Table I. The well resolved 18 line spectrum (Fig. 1) observed in the perpendicular region assures the relative accuracy of the magnitudes of hyperfine and super-

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0020-1693/83/$3.00

TABLE I. ESR Data of the Cu(II) Porphyrins with Podand Side Arm.[a]

Compound	$g_\parallel$	$g_\perp$	Cu $A_\parallel$ $\times 10^4$ cm^{-1}	Cu $A_\perp$ $\times 10^4$ cm^{-1}	N $A_\parallel$ $\times 10^4$ cm^{-1}	N $A_\perp$ $\times 10^4$ cm^{-1}	$-\Delta\alpha^2$
Cu1a	2.148	2.000	200.6	32.51	15.53	16.28	0.0781
Cu1b	2.158	2.012	209.5	32.04	14.53	16.02	0.3800
Cu1c	2.162	2.012	201.9	32.27	15.14	16.13	0.0553
Cu2a	2.171	2.023	202.7	32.21	13.78	16.10	0.0393
Cu2b	2.162	2.005	211.0	30.58	13.52	15.29	0.0330
Cu2c	2.164	2.018	200.0	33.23	13.30	16.61	0.0558
CuTPP	2.185	2.047	208.1	31.55	14.79	15.77	–

[a] α^2 values were calculated making use of the expression given by D. Kievelsen and S. K. Lee, *J Chem. Phys.*, *35*, 149 (1961).

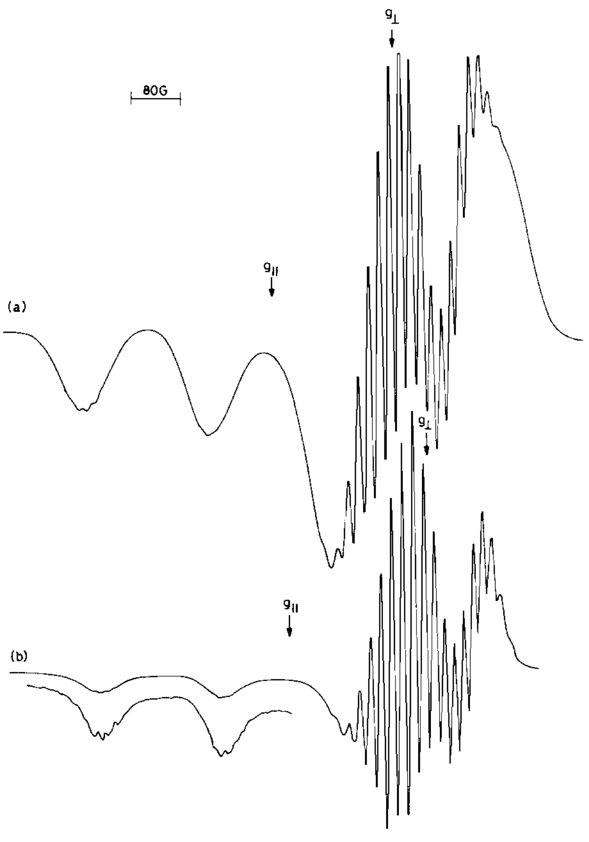

Fig. 1. ESR spectra of (a) CuTPP and (b) Cu–2a in toluene at 100 K.

TABLE II. Redox Potentials of Zn(II) Derivatives of Porphyrins with Podand Side Arm.[a]

Compounds	Potentials (Volts)			
	Oxidation		Reduction	
	$E^{I}_{1/2}$	$E^{II}_{1/2}$	$E^{I}_{1/2}$	$E^{II}_{1/2}$
Zn1c	0.79	1.09	−1.45	−1.73
Zn2c	0.83	1.14	−1.36	−1.53
ZnTPP	0.81	1.14	−1.32	−1.71

[a] Cyclic voltammetric measurements were carried out using a three electrode assembly with Pt-button (working electrode), Pt-wire (counter-electrode) and SCE reference electrode. Butyronitrile was used as the solvent with TBAP as supporting electrolyte. All potentials are reported *vs.* SCE.

hyperfine coupling constants. An inspection of Table I reveals a decrease in g and |A| values accompanied by an increase in $A^N_\parallel$ and $A^N_\perp$ values, similar to those observed for molecular complexes of Cu TPP with organic π-acceptors [3]. A justification that the π-electronic manifold of porphyrin macrocycle is changed upon the positioning of the remote aryl group nearer to the Cu(II) centre can be seen from the decrease in covalency factor α^2 as compared to TPP. The decrease in α^2 values signifies that the M–N bond is slightly more covalent. The origin of this can be traced to either an increase in the electronic charge on Cu(II) relative to CT complexes (thereby providing easier mixing of the metal d-orbital with ligand orbitals) or to an increase in the electron density of nitrogens, such that σ coordinative bonding becomes more covalent. In either of these cases, the necessary condition is to position an electron acceptor nearer to the porphyrin moiety. The present results indicate the possible existence of folded conformer.

Cyclic voltammetric studies of the Zn(II) derivatives of the 'tail' porphyrins reveal completely reversible one electron redox potentials. The magnitudes of the observed potentials are compared with TPP under the same experimental conditions (Table II). Despite the close similarity in the values of the potentials, it can be noted that the oxidation potentials are relatively more anodic and the reduction potentials are less cathodic for the *meta* substituted 'tail' porphyrins than for *para* substituted analogues. This is attributed to the π-complexation of the remote aryl group of the side arm with the porphyrin centre resulting in the alteration of the redox potentials. This is in line with the observations of Mashiko *et al.* [4], who in their structural studies on cytochrome *c* models demonstrated the perturbance of redox potentials as a consequence of the conformational changes of the side arm of the porphyrin. Molecular models were constructed making use of the structural parameters of MTPP [5] and a cation complex of a linear glycol [6]. Consideration of these models, along with the computer calculations of interatomic distances employing the CART program, reveal that the closest distance falls within the range of molecular interactions (4.9 to 6.7 Å) between the remote aryl ring and one of the pyrrole rings, indicating the possible existence of folded conformer. In view of the encouraging results obtained herein we are presently pursuing a study of the interaction of these porphyrins with cations in our laboratory.

Acknowledgement

One of authors (G.B.M.) is thankful to CSIR, New Delhi, for the award of a scholarship.

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