

Short Chain Basket Handle Porphyrins : Ground and Excited State Dynamics

M. RAVIKANTH, DAMODAR REDDY and T. K. CHANDRASHEKAR*

Department of Chemistry, Indian Institute of Technology, Kanpur-208 016

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The effect of porphyrin ring distortion on the ground and excited state dynamics of short chain basket handle porphyrins has been investigated. The covalent attachment of phenyl ring of meso-5,10,15,20-tetraphenylporphyrin (H_2TPP) by short bridging groups of varying nature and length induces distortion in the porphyrin ring. The optical absorption bands and emission bands exhibit significant red-shifts with reduction in intensity relative to corresponding planar porphyrin due to ring distortion. On protonation both optical and emission bands experience blue-shift due to lack of expected resonance interaction. Metallation does not alter the degree of distortion. The Zn^{II} derivatives showed emission from both S_1 and S_2 excited state with quenching of fluorescence. Redox potential data suggest easier oxidations and harder reductions both in the ground and first singlet excited states relative to corresponding planar porphyrins. Zero field splitting parameters D and E of basket handle porphyrins evaluated from photoexcited triplet esr show small but significant differences attributed to distortion of the porphyrin plane. The calculated structures reveal the expected distortion in the porphyrin plane caused by short bridging groups and offers an explanation for the unusual spectral and electrochemical shifts observed in basket handle porphyrins relative to planar porphyrins.

The occurrence of porphyrin rings in nature as ligands in such crucial and multiple roles as those spanned by the heme proteins¹, chlorophyll², vitamin B_{12} ³ etc. are well documented. One reason for the richness of the porphyrin chemistry in biological systems is its ability to exist in various nonplanar conformations due to flexibility of the porphyrin ring^{4,5}. For example, the domed porphyrins present in several heme proteins¹ are involved in oxygen transport, peroxide reduction and disproportionation, the mitochondrial electron transport chain and drug metabolism. The nickel tetrapyrrole cofactor F_{430} present in methyl-reductase⁶ enzyme which catalyses the production of methane is also in domed conformation. Nonplanar conformational distortion of tetrapyrrole pigments of photosynthetic reaction centres² has been suggested to control their photophysical properties. The highly puckered and distorted corrin ring of vitamin B_{12} ³ helps in weakening of the cobalt-carbon bond to generate a 5'-deoxyadenosyl radical. The above examples highlight the influence of nonplanar conformation on the electronic structure of the porphyrin ring systems.

Because of the biochemical significance of nonplanar porphyrins in the recent past, there has been considerable interest in synthesising and

studying physicochemical properties of various nonplanar porphyrins⁷. In the process of our investigations in this direction, we found that one of the way of introducing distortion is the bridging of phenyl groups present at the periphery of the porphyrin ring with variety of short bridging groups^{8,9}. This article reviews the effect of porphyrin ring distortion on ground and excited state properties of short chain basket handle porphyrins synthesised in the authors' laboratory. The following types (Fig. 1) of short chain basket handle porphyrins are studied : (a) simple alkyl chain bridged porphyrins, (b) simple aryl (*para*- and *meta*-xylyl) bridged porphyrins, (c) porphyrins with electron-withdrawing substituents on bridged phenyl groups and (d) porphyrins with electron-withdrawing substituents of β -pyrrole as well as on bridged phenyl groups.

The synthesis and characterisation of basket handle porphyrins studied here are reported elsewhere^{10a-c}. Three kinds of isomers were formed by condensation of desired dialdehyde with pyrrole in propionic acid medium : cross-*trans*-linked, adjacent-*trans*-linked and adjacent-*cis*-linked (Fig. 1). In all three, the nature of bridging is different and magnitude of deformation present in the porphyrin ring depends on the nature of the isomer.

Results and Discussion

Ground state dynamics :

Visible absorption studies : The absorption spectral characteristics of the free bases along with the corresponding dications generated by addition of a drop of trifluoroacetic acid in a benzene solution is shown in Fig. 2. The absorption spectral data are listed in Table 1. A comparison of this with the unstrapped H₂TPP reveals the following interesting features : (i) a considerable red-shift of the Soret band and Q-bands, (ii) a drastic reduction in the intensity of both Soret and Q-bands; the magnitude of red-shift and intensity decrease

depend on the nature of the isomer and maximum effects are observed for cross-*trans*-linked isomer, (iii) upon protonation, the Q-bands experience a blue-shift in contrast to the large red shift observed for protonation of H₂TPP, (iv) substitution of electron-withdrawing groups on bridging phenyl leads to further red-shift with reduction in intensity, (v) β-substitution results in gradual red-shift of all the bands and the magnitude of red-shift depends on the number of bromines substituted. However, a plot (Fig. 3a) of magnitude of red-shift versus the number of bromines substituted is nonlinear suggesting that the magnitude of shifts is non-additive.

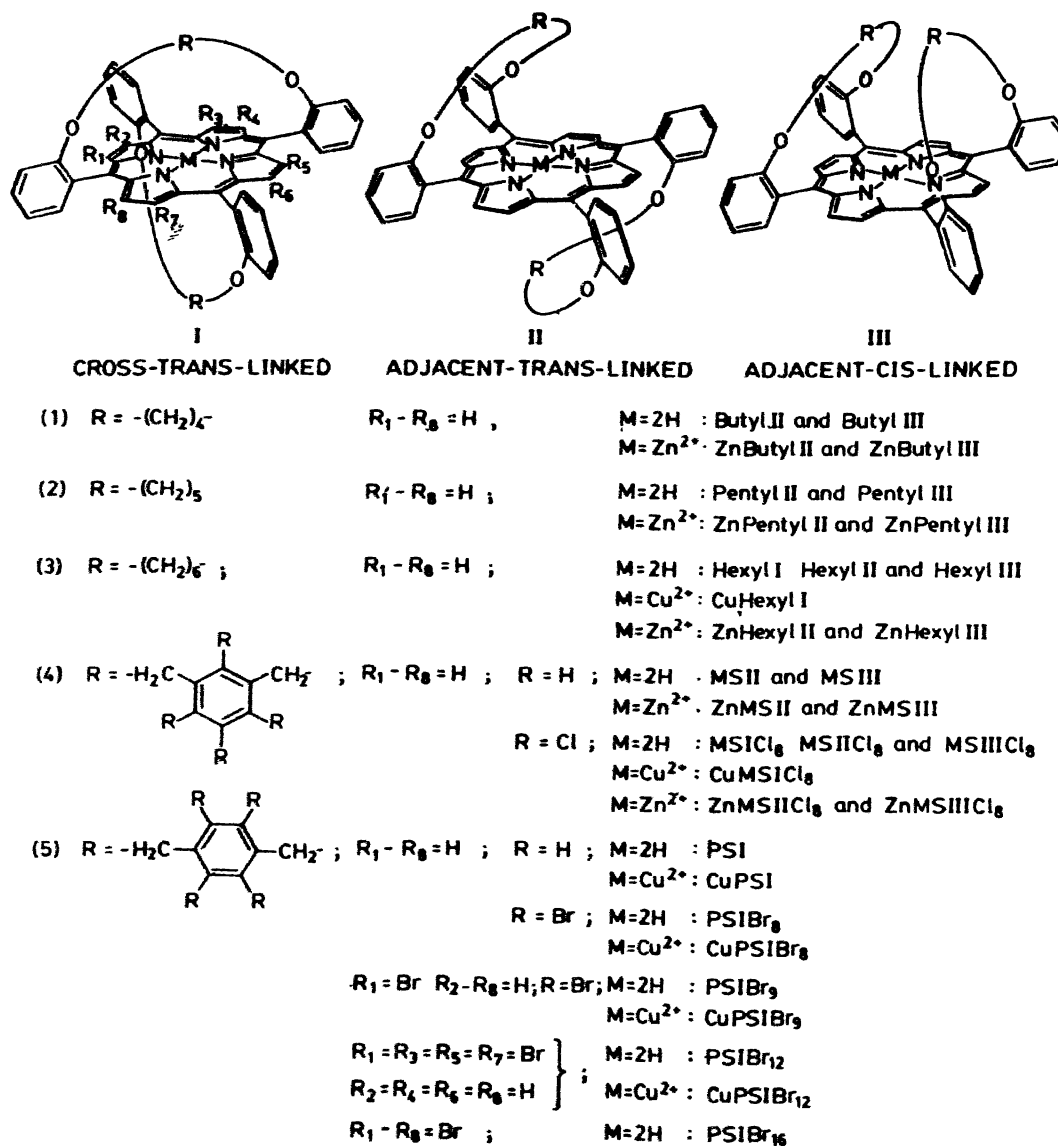


Fig. 1. Structures of various short chain basket handle porphyrins.

We prepared Cu^{II} derivatives of most interesting cross-*trans*-linked isomer of various basket handle porphyrins^{10b,c} to observe the deformation effect on geometry around the metal ion. The absorption data of copper(II) derivatives (Table 2) reveal significant bathochromic shifts and broadening of all the *Q*- and Soret-bands with drastic reduction in intensity indicating the existence of deformation in the porphyrin ring of metallo derivatives. However, the magnitude of the band shifts for these derivatives relative to CuTPP is comparable to the shifts observed for the free bases relative to their corresponding unstrapped derivatives suggesting that the introduction of the Cu^{II} ion does not alter the degree of distortion. The effect of electron-withdrawing substituents on bridging phenyl and pyrroles resulted in further red-shift of the absorption bands. It has been observed that the magnitude of red-shifts of both Soret and *Q*-bands relative to the corresponding unstrapped derivatives for basket handle porphyrins described here depends on the chain length of the bridging group. A plot (Fig. 4) of the magnitude of the shifts observed for the Soret and *Q*-bands for various free

bases and copper(II) derivatives versus the number of atoms in the bridging chain is linear suggesting that the magnitude of the red-shifts can be directly related to the degree of distortion.

Protonation of unsubstituted or *para*-substituted free-base tetraaryl porphyrins¹¹ generally results in a large red-shift of the *Q*-bands while the free base tetraalkyl porphyrins¹² show blue-shift. This difference in behaviour is attributed to the increased resonance interaction between the aryl group and the porphyrin ring in tetraarylporphyrins due to the coplanarity of the phenyl ring and porphyrin plane. However, in the basket handle porphyrins restricted rotation around the porphyrin-phenyl bond may forbid any extension of conjugation between the phenyl groups and the porphyrin ring, preventing resonance interaction. A similar effect was observed for the *ortho*-substituted tetraphenylporphyrins upon protonation¹².

Electrochemistry : The distortion effects on the electrochemical behaviour were monitored by cyclic voltammetry. A comparison of the cyclic voltammograms of the copper(II) derivatives with that of CuTPP in CH_2Cl_2 is made in Fig. 5. All the free bases and copper(II) derivatives exhibit two separate one-electron porphyrin ring centred oxidations corresponding to the formation of mono- and dications respectively. Both the oxidations are reversible [$\Delta(E_a - E_c) = 55\text{--}65\text{ mV}$] with the ratio of peak currents close to unity. The first oxidation potentials were found to be shifted to less positive values (180–260 mV) relative to H_2TPP and CuTPP respectively, indicating easier oxidation. However, electrochemical data (Table 3) reveal harder oxidations for β -substituted derivatives. The one-electron reductions of the porphyrin ring were observed in both the free bases and the copper(II) derivatives suggesting formation of monoanions. Furthermore, the first reduction potentials in both metal and free base derivatives are shifted to more negative values (280–390 mV) suggesting harder ring reductions relative to CuTPP and H_2TPP . In contrast, the reductions are found to be easier for β -substituted derivatives. Fig. 5 and Table 3 indicates an additional couple for tetrabromo-*p*-xylyl and tetrachloro-*m*-xylyl bridged porphyrin and metalloporphyrin derivatives. These are reversible in all cases when scanned separately and is assigned to the reduction of the bridging phenyl ring containing electron-acceptor substituents.

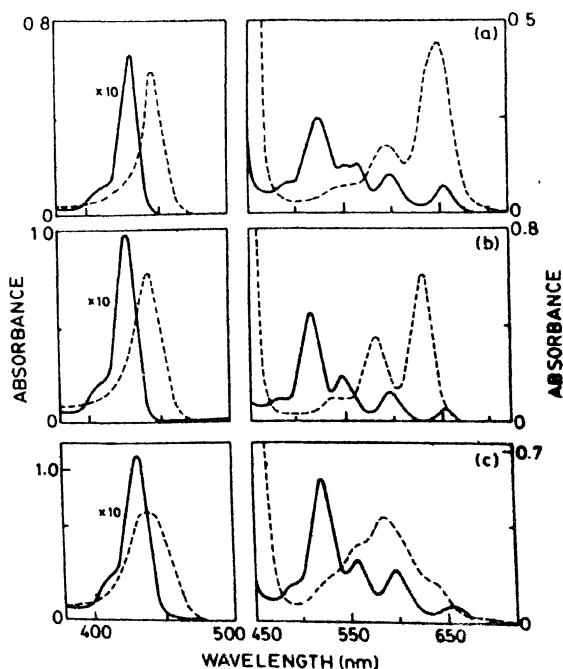


Fig. 2. Electronic absorption spectra of (a) MSII, (b) MSIII and (c) PSI in benzene and their corresponding dications. Concentration for *Q*-bands $\sim 10^{-5}M$ and for the Soret band $\sim 10^{-6}M$ (solid line corresponds to neutral form and dotted line to dications).

TABLE I—ELECTRONIC SPECTRAL DATA OF VARIOUS BASKET HANDLE PORPHYRINS AND THEIR DICATIONS IN CHCl₃

Compd.	Soret band λ_{\max} , nm ($\epsilon \times 10^{-4}$, dm ³ mol ⁻¹ cm ⁻¹) B (0,0)	Q-bands λ_{\max} , nm ($\epsilon \times 10^{-3}$, dm ³ mol ⁻¹ cm ⁻¹)			
		$Q_y(1,0)$	$Q_y(0,0)$	$Q_x(1,0)$	$Q_x(0,0)$
		H ₂ TPP	419 (46.4)	515 (18.7)	548 (8.6)
H ₄ TPP ²⁺	448 (43.6)			608 (9.0)	659 (50.9)
MSII	432 (31.72)	526 (12.09)	566 (6.42)	601 (5.14)	657 (3.74)
H ₄ MSII ²⁺	446 (23.8)			599 (6.98)	648 (17.62)
MSIII	428 (34.03)	520 (16.09)	552 (6.88)	602 (4.79)	661 (2.54)
H ₄ MSIII ²⁺	442 (21.54)		544sh (2.44)	586 (9.78)	634 (17.08)
PSI	433 (22.21)	529 (11.72)	566 (5.16)	605 (4.33)	663 (1.24)
H ₄ PSI ²⁺	440 (14.67)		566sh (6.34)	592 (8.51)	646sh (3.07)
Hexyl I	428 (22.8)	526 (11.5)	562 (5.2)	602 (4.5)	658 (1.9)
MSICl ₈	440 (14.7)	537 (11.7)	576 (5.4)	610 (4.8)	667 (1.8)
MSIICl ₈	428 (23.7)	524 (11.92)	562 (6.20)	596 (5.24)	650 (3.68)
MSIIICl ₈	426 (22.6)	520 (12.01)	549 (6.23)	595 (4.96)	651 (3.62)
PSIBr ₈	436 (23.21)	532 (12.3)	568 (4.1)	606 (4.4)	663 (0.8)
PSIBr ₉ [▼]	440.5 (19.8)	536.5 (12.2)	571 (3.6)	610 (4.5)	667 (1.4)
PSIBr ₁₂	450 (19.6)	544 (13.1)	579 (3.3)	616.5 (5.0)	674.5 (2.4)
PSIBr ₁₆	453.5 (12.8)	546.5 (10.9)	583 (4.3)	620.5 (5.5)	676.5 (2.2)

The easier oxidations are interpreted in terms of loss of coplanarity resulting in decreased electron delocalisation¹³ and the harder reductions are attributed to the destabilisation of anions due to steric hindrance of the strapping group to approach of the solvent. The direction of electrochemical potential shifts upon substitution of bromines is completely reversed and the magnitude of shifts are non-additive both for oxidation and reduction. The optical absorption red-shifts also follow the same trend. This has been ascribed in part to antagonistic

inductive effects of substitution on the lone-pair of the pyrrolic nitrogens¹⁴. The steric effect also contributes to this trend. Substitution of bulky bromine at the β -pyrrole position results in the steric hindrance between β -substituent and the *meso*-phenyl rings. Successive addition of more bromines enhances the steric hindrance thus increasing the non-planarity of the porphyrin ring. Thus, the combined steric and antagonistic induction effects accounts for the non-linear nature of the plots shown in Figs. 3(a) and 3(b).

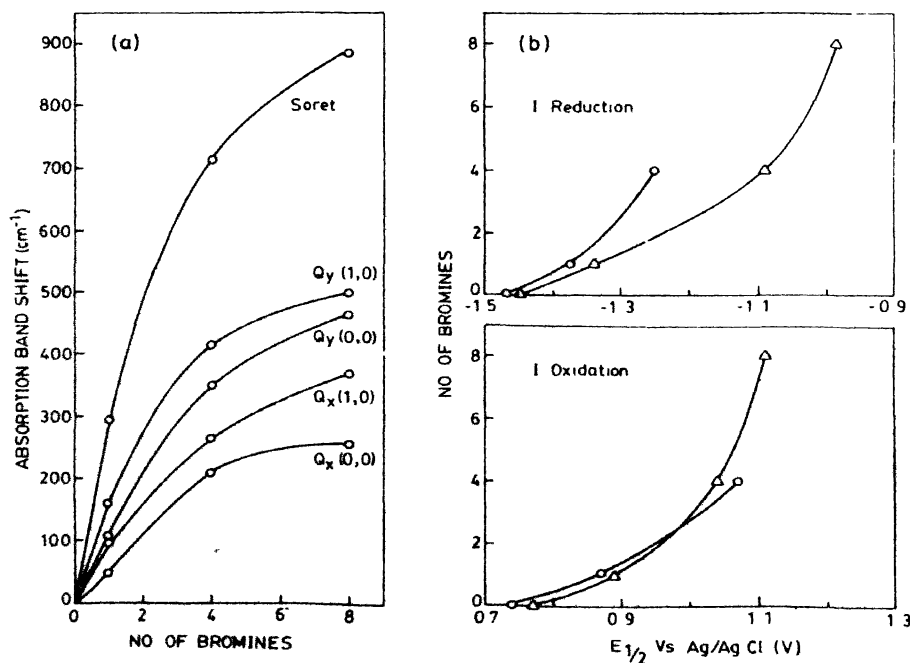


Fig. 3. Plots of (a) absorption band shift and (b) $E_{1/2}$ versus number of bromines of pyrrole brominated short chain basket handle porphyrins : (Δ) free base porphyrins and (O) copper(II) derivatives.

Esr spectral studies : A representative esr spectrum obtained at room temperature (CuHexylI) in chloroform-toluene (1 : 1) and a frozen glass of CuPSIBr₈ at -140° are displayed in Fig. 6. All the room temperature spectra were composed of four resolved copper lines with superhyperfine structure for two high field copper lines¹⁵. The low temperature spectra suggest an axial symmetry with resolved hyperfine couplings both in parallel and perpendicular fields.

TABLE 2—ELECTRONIC SPECTRAL DATA OF Cu^{II} DERIVATIVES OF VARIOUS CROSS-*trans*-LINKED BASKET HANDLE PORPHYRINS

Compd.	Soret band	Q-band	
	λ_{\max} , nm ($\epsilon \times 10^{-4}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) B (0.0)	λ_{\max} , nm ($\epsilon \times 10^{-3}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) Q(0.0)	Q(0.1)
CuTPP	417 (41.69)	540 (19.50)	585
CuHexylI	427 (31.26)	556 (13.07)	594 (2.29)
CuPSI	432 (14.82)	562 (6.97)	600 (1.46)
CuMSICl ₈	440 (12.61)	569 (5.80)	611 (1.55)
CuPSIBr ₈	435 (21.53)	563 (10.52)	603 (2.06)
CuPSIBr ₉	437 (23.11)	566 (14.17)	605 (3.29)
CuPSIBr ₁₂	444 (20.99)	573 (13.82)	613 (5.11)

The esr data (Table 4) indicate that the principal tensor components of superhyperfine interaction between the pyrrole nitrogens and the unpaired electron in the metal are almost equal in parallel and perpendicular regions, suggesting a predominantly isotropic interaction as expected for a CuN₄ moiety in the approximately tetragonal crystal field^{15,16}. Furthermore, the equally spaced hyperfine lines indicate that the nonplanarity of the porphyrin ring has little influence on the esr spectra and the unpaired electron is coupled equally to the four pyrrole nitrogens. This is not surprising as the nonplanarity observed in the X-ray structural work on CuTPP was not reflected in the esr spectrum.

Literature reports^{16,17} on structurally well characterised Cu²⁺ complexes with N,O,S donors ligands reveal inverse relationship between g_{\parallel} and $A_{\parallel}^{\text{Cu}}$ parameters. Generally, g_{\parallel} increases and $A_{\parallel}^{\text{Cu}}$ decreases upon increasing distortion. Even though g_{\parallel} values does not show any such trend, the $A_{\parallel}^{\text{Cu}}$ and A_0^{Cu} decrease gradually with increasing distortion relative to CuTPP probably indicating the expected nonplanarity around Cu²⁺ ion.

The α^2 value calculated from the spin Hamiltonian parameters represents the bonding

coefficient of b_1 molecular orbital and gives a qualitative idea about the strength of the Cu-N σ -bond¹⁸. The stronger the inplane σ -bond between Cu^{II} and nitrogen, the higher is the energy of the b_1 molecular orbital because of its antibonding character¹⁹. Thus the gradual decrease observed here (Table 4) indicates a lowering of the energy of the b_1 molecular orbital relative to that CuTPP and a weaker Cu-N interaction in the brominated distorted derivatives. A similar conclusion was arrived at to explain the higher value of α^2 for copper-phthalocyanine ($\alpha^2 = 0.79$) compared to CuTPP based on the X-ray crystal data which indicated a shorter Cu-N bond (by 0.05 Å) in the copper-phthalocyanine relative to CuTPP.

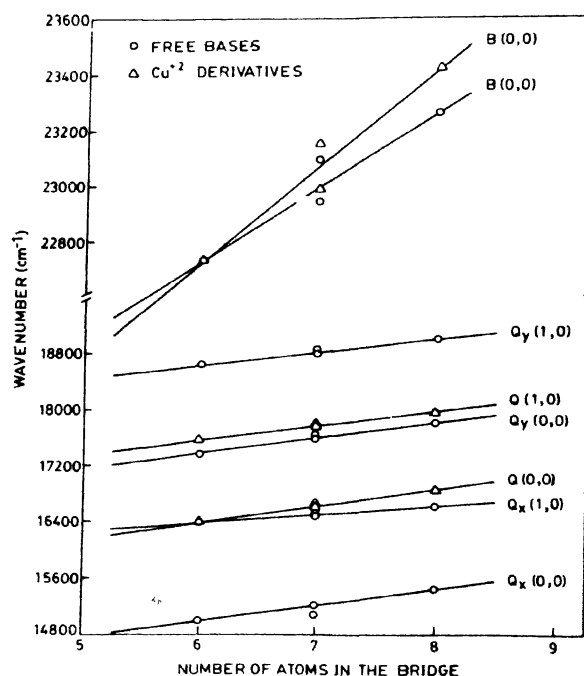


Fig. 4. Plots of absorption band shifts in Soret and Q-band region for various free base and Cu^{II} derivatives versus the number of atoms (6 for MSICl₈ and CuMSICl₈, 7 for PSI, PSIBr₈, CuPSI and CuPSIBr₈, 8 for Hexyl I and CuHexyl I) in the bridging chain

Excited state dynamics :

Emission spectra : An inspection of the emission data (Table 5) for all free base basket handle porphyrins indicates the following : (i) both Q(0,0) and Q(0,1) emission bands are shifted to higher wavelengths relative to H₂TPP, (ii) there is broadening of the emission bands with significant (60–90 %) quenching of the fluorescence intensity

leading to a decrease in the quantum yields relative to H₂TPP, (iii) presence of electron-withdrawing groups on pyrroles resulted in further red-shift of the bands with reduction in intensity, (iv) magnitude of red-shifts and reduction in fluorescence yields are dependent on the nature of the isomer, bridging chain-length and nature of substituents, (v) maximum red-shifts and intensity quenching of fluorescence bands are observed for the cross-*trans*-linked derivatives in the order alkyl bridged porphyrin < unsubstituted aryl bridged porphyrins < porphyrin with electron-withdrawing substituents in pyrroles and bridging aryl group, (vi) all distorted porphyrins excluding β -halogen substituted porphyrins are found to be better oxidants and reductants in the singlet excited state and cross-*trans*-linked isomers exhibit better donating ability among all isomers and (vii) substitution of electron-withdrawing groups on pyrroles resulted in reduction of electron density in the porphyrin ring and becomes poor donors compared to H₂TPP in the singlet excited state.

TABLE 3—ELECTROCHEMICAL REDOX DATA (V) OF FREE BASE AND COPPER(II) DERIVATIVES OF SHORT-CHAIN BASKET HANDLE PORPHYRINS

Compd.	Ring oxidation			Bridge phenyl reduction	Ring reduction	
	I	II	III		I	II
H ₂ TPP	1.03	1.30	—	—	-1.23	-1.55
MSII	0.84	1.20	—	—	-1.32	-1.67
MSIII	0.90	—	—	—	-1.34	-1.67
MSICl ₈	0.85	1.32	—	-1.13	-1.45	—
MSIICl ₈	0.92	1.25	—	-1.14	-1.34	-1.69
MSIIICl ₈	0.95	—	—	-1.13	-1.34	-1.68
PSI	0.85	1.23	—	—	-1.39	-1.78
PSIBr ₈	0.77	1.32	—	-1.14	-1.45	—
PSIBr ₉	0.89	1.32	—	-1.05	-1.34	—
PSIBr ₁₂	1.04*	1.28*	1.37	-0.92	-1.09	-1.44
PSIBr ₁₆	1.11	—	—	-0.74	-0.99	-1.39
CuTPP	1.06	1.31	—	—	-1.14	-1.74
CuHexylII	0.81	1.25	—	—	-1.50	—
CuPSI	0.85	1.30	—	—	-1.45	—
CuMSICl ₈	0.76	1.26	—	-1.14	-1.51	—
CuPSIBr ₈	0.74	1.30	—	-1.14	-1.48	—
CuPSIBr ₉	0.87	1.35	—	-1.05	-1.38	—
CuPSIBr ₁₂	1.07	1.43	—	—	-1.23	-1.7

* Irreversible

The Zn^{II} derivatives of the porphyrins show emission from both the S₁ and S₂ excited states. The

room temperature S₁ and S₂ emission spectra of the Zn^{II} derivatives together with planar ZnTPP are shown in Fig. 7. The excitation spectra were recorded, in particular, for the S₂ emission and the inset in Fig. 7 shows a comparison of the emission and excitation spectra for the ZnMSII isomer. The mirror image relationship between the Soret fluorescence and the Soret absorption is obvious. The salient features of the emission data (Table 6) for the Zn^{II} derivatives are as follows: (i) a red-shift in both S₁ and S₂ emission maxima relative to ZnTPP, (ii) a reduction in S₁ and S₂ fluorescence yields, and (iii) a small reduction in energy gap between S₂ and S₁ excited states in the distorted porphyrins relative to ZnTPP. The redox potential data indicate that the Zn^{II} derivatives are poor oxidants and reductants than free bases, both in the ground and excited states.

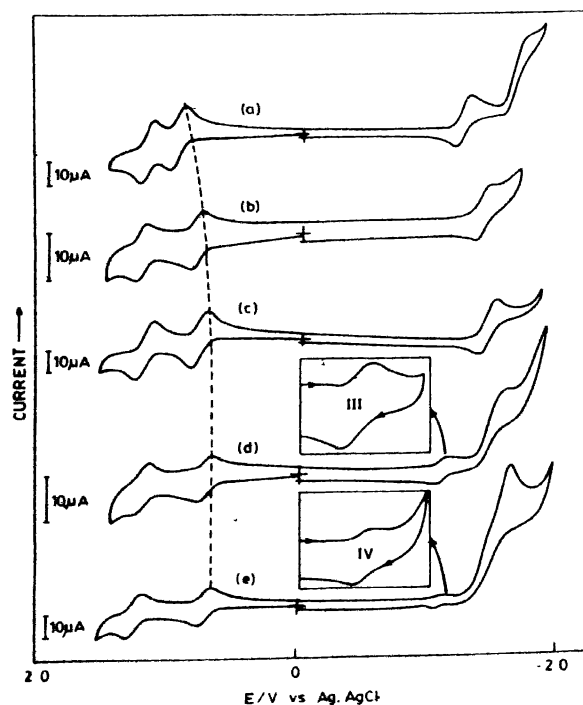


Fig. 5. Cyclic voltammograms of (a) CuTPP, (b) CuPSI, (c) CuHexylII, (d) CuMSICl₈ and (e) CuPSIBr₈; concentrations $\approx 5 \times 10^{-4}M$, scan rate 100 mV s^{-1} . Inset shows the reversible nature of bridging phenyl ring reduction. The potentials are versus Ag/AgCl with TBAP as the supporting electrolyte.

The red-shifts observed for emission bands for the distorted derivatives are consistent with absorption data. An inspection of the quantum yield data (Table 5) indicates significant quenching of the

TABLE 4—ESR DATA FOR Cu^{II} DERIVATIVES OF CROSS-*trans*-LINKED SHORT-CHAIN BASKET HANDLE PORPHYRINS IN CHCl₃ : TOLUENE(1 : 1)

Compd.	g_{\parallel}	g_{\perp}	$A_{\parallel}^{\text{Cu}}$ $\times 10^4 \text{ cm}^{-1}$	A_{\perp}^{Cu} $\times 10^4 \text{ cm}^{-1}$	A_{\parallel}^{N} $\times 10^4 \text{ cm}^{-1}$	A_{\perp}^{N} $\times 10^4 \text{ cm}^{-1}$	α^2	g_{iso}	A_0^{Cu} $\times 10^4 \text{ cm}^{-1}$	A_0^{N} $\times 10^4 \text{ cm}^{-1}$
CuTPP	2.187	2.067	218	32.80	14.5	16.40	0.7500	2.107	97.70	15.90
CuHexyl I,	2.155	2.057	205	32.50	n.r.	16.25	0.7239	2.090	90.00	16.30
CuPSI	2.159	2.054	202	32.88	n.r.	16.44	0.7212	2.089	89.51	15.85
CuMSICl ₈	2.161	2.042	200	30.22	14.0	15.11	0.7234	2.081	86.96	16.30
CuPSIBr ₈	2.161	2.056	205	32.00	14.9	15.99	0.7332	2.091	89.70	15.85
CuPSIBr ₈	2.159	2.029	190	31.62	14.3	15.81	0.6485	2.081	87.8	15.80
CuPSIBr ₁₂	2.180	2.021	187.6	31.23	14.0	15.61	0.6347	2.082	86.2	15.20

n.r. = not resolved

TABLE 5—EMISSION WAVELENGTH (nm) AND EXCITED STATE POTENTIAL (V) OF FREE BASE SHORT-CHAIN BASKET HANDLE PORPHYRINS IN BENZENE

Compd.	$Q(0.0)$	$Q(1.0)$	ϕ_{T}	${}^*E^0(P^+/P^*)$	${}^*E^0(P/P^-)$
H ₂ TPP	653 (683)	717	0.110	-0.870	0.670
Hexyl I	678 (643)	734	0.057	-0.979	0.429
Hexyl II	654 (647)	719	0.100	-0.946	0.556
Hexyl III	654 (653)	717	0.086	-0.966	0.576
Pentyl II	657 (649)	724	0.043	-0.977	0.547
Pentyl III	659 (666)	724	0.060	-0.971	0.521
Butyl II	667 (670)	—	0.040	-0.949	0.589
Butyl III	662 (671)	—	0.041	—	—
PSI	672 (663)	739	0.012	-0.995	0.445
MSII	665 (665)	727	0.039	-1.024	0.544
MSIII	663 (649)	727	0.032	-0.970	0.530
MSICl ₈	679 (659)	745	0.028	-0.976	0.496
MSIICl ₈	658 (662)	723	—	-0.964	0.544
MSIIICl ₈	656 (644)	723	0.023	-0.940	0.540
PSIBr ₈	669 (665)	736	0.010	-1.083	0.353
PSIBr ₉	673	736	—	-0.952	0.502
PSIBr ₁₂	682	—	—	-0.778	0.728
PSIBr ₁₆	686	—	—	-0.697	0.833

Numbers in parenthesis represent the absorption maxima or corresponding dications.

emission bands relative to planar H₂TPP. The important factors which contribute to the quenching are : (i) *ortho*-substituent effect^{11a,20} on the *meso*-phenyl ring of H₂TPP decreases the quantum yield by about 10% relative to the unsubstituted porphyrins, (ii) the heavy atom effect of the substituted halogens decreases the quantum yield by about 60% by increasing the rate of intersystem crossing, and (iii) the decay of the S₁ state through internal conversion leads to a decrease in the quantum yield. Generally, internal conversion accounts for about 20% decay in porphyrins²¹. It is difficult to apportion the individual contributions of the above effects to the fluorescence quenching in

the absence of quantitative data such as ϕ_{T} and ϕ_{IC} . Thus, it is reasonable to attribute the decrease in the quantum yields to their combined effect. The changes in the singlet excited state potentials estimated from the ground state redox potentials and the singlet excited state energy reveal that the distorted porphyrins are better oxidants and reductants in the excited state relative to planar H₂TPP. Of the three isomers, *cross-trans*-linked isomers are relatively strong donors. Substitution of electron-withdrawing groups in pyrroles leads to decrease of electron density in the porphyrin ring and becomes poor donors in the excited state compared to H₂TPP.

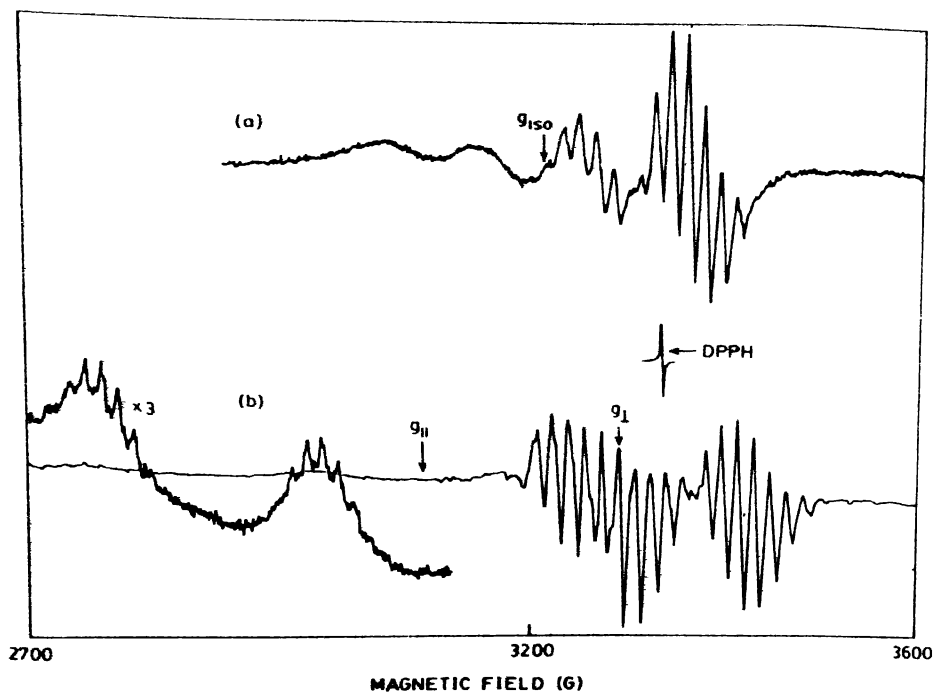


Fig. 6. Esr spectra in chloroform-toluene (1 : 1) of a CuHexyl I at 27° and (b) CuPSIBr₈ at -140°.

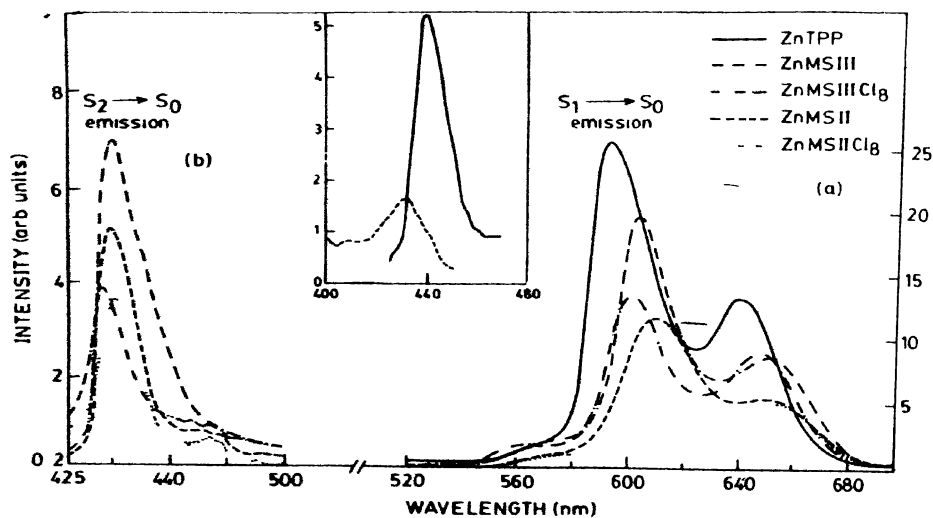


Fig. 7 Fluorescence spectra in benzene of various Zn^{II} derivatives of basket handle porphyrins and ZnTPP (a) emission from S₁ excited state $\lambda_{exc} = 431$ nm and (b) emission from S₂ excited state $\lambda_{exc} = 415$ nm, concentrations $\sim 2 \times 10^{-6}$ M The inset shows the emission (—) ($\lambda_{exc} = 415$ nm) and excitation (- - -) ($\lambda_{exc} = 460$ nm) spectra of ZnMSII.

In addition to S₁ emission, all the Zn^{II} derivatives of basket handle porphyrins showed emission from S₂ state. In all the cases, the S₂ emission spectrum is a mirror image of the Soret absorption band which is characteristic of S₂ emission in metalloporphyrins²². Furthermore, the fact that the S₂ emission is only observed when excited through the Soret absorption rules out any

thermal repopulation of S₂ from S₁. The effect of distortion is reflected in the slight red-shift of the emission bands and the reduced quantum yields relative to ZnTPP. The fact that the S₂ emission is observed for this class of molecules suggests the following : (i) the two common ¹(π, π^*) excited state configurations ¹(a_{1u}e_g) and ¹(a_{2u}e_g) are accidentally degenerate and the energy surfaces of the S₁ and S₂

TABLE 6—EMISSION DATA (nm) OF ZINC DERIVATIVES OF BASKET HANDLE PORPHYRINS IN BENZENE

Compd.	S_2 emission		S_1 emission			$\Delta E_{(S_2-S_1)}$ $\times 10^3 \text{ cm}^{-1}$
	$\beta(0.0)$	$\phi_F \times 10^4$	$Q(0.0)$	$Q(0.1)$	ϕ_F	
ZnTPP	432	3.9	598	647	0.032	6.69
ZnHexyl II	436	3.7	599	647	0.078	6.24
ZnHexyl III	437	3.1	603	646	0.024	6.30
ZnPentyl II	440	3.5	613	653	0.023	6.23
ZnPentyl III	442	2.6	609	652	0.024	6.15
ZnButyl II	448	3.2	626	—	0.019	6.35
ZnButyl III	444	3.0	620	—	0.021	6.39
ZnMSII	443	3.4	618	660	0.022	6.39
ZnMSIII	444	—	610	660	—	6.13
ZnMSIICl ₈	443	2.9	612	654	0.019	6.23
ZnMSIIICl ₈	439	—	602	649	—	6.17

excited states are parallel and (ii) there is no triplet excited state between the S_1 and S_2 excited states. Furthermore, it can be seen from Table 6 that the energy gap ΔE between S_2 and S_1 , decreases slightly for the distorted isomers relative to ZnTPP. Kurabayashi *et al.*^{22b} studied the S_2 fluorescence for various metallo-tetraphenylporphyrins and have observed that the rate of $S_2 \rightarrow S_1$ internal conversion, which is the main source of decay from the S_2 state, is a function of the energy gap between the S_2 and S_1 excited states. The decreased quantum yields of S_2 fluorescence for AlClTPP, ZnTPP and CdTPP correlate linearly with the energy gap between S_2 and S_1 . Thus, the decrease in the energy gap in the distorted Zn^{II} porphyrins relative to ZnTPP indicates an increased rate of $S_2 \rightarrow S_1$ internal conversion and qualitatively accounts for the decreased quantum yield. It is pertinent to note that the decreased oscillator strength of the Soret band in the distorted Zn^{II} porphyrins relative to ZnTPP may also contribute to decreased quantum yield. The excited state potential data of the Zn^{II} derivatives of deformed porphyrins suggest that they are poor donors than free bases in the singlet excited state.

Triplet *esr* spectra : Fig. 8 shows the low-temperature *esr* spectra of triplets of PSI, MSII and MSIII randomly oriented in toluene : CHCl_2 (1 : 2). Table 7 lists the values of the D and E parameters derived from the spectra. As can be seen in Table 7, the D values for all the short-chain basket handle porphyrins are lower (4–19%) than the value

obtained for the parent H_2TPP . The magnitude of the decrease varies with the structure of the isomer.

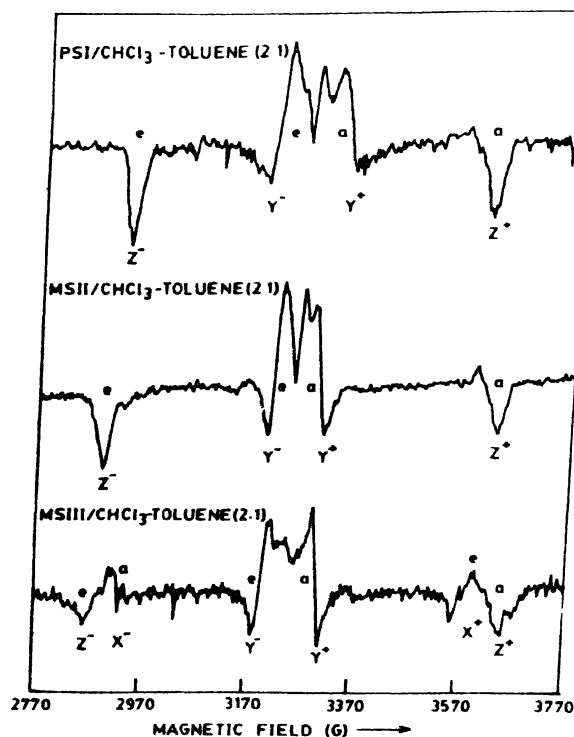


Fig. 8. Triplet *esr* spectra of PSI, MSII and MSIII in CHCl_3 -toluene (2 : 1) at 100 K; microwave power 5.0 mW, field modulation 20 G (100 kHz), excitation with square wave modulated (83 Hz) light of an argon ion laser (514.5 nm, 0.5 W); (a) absorption and (e) emission peaks. Approximately $\sim 1 \times 10^{-4} M$ solution was used for recording the spectra.

D for MSIII is comparable to the value observed for tetraphenyl chlorin (H_2TPC)²³ while for MSII and PSI the values differ substantially.

The E values for MSII and MSIII are slightly larger than the value found for the parent compound H_2TPP while for the PSI isomer a slight decrease is observed. The spin polarisation pattern of all the isomers is the same (eaeaea) as that observed for H_2TPP .

TABLE 7—ZERO FIELD SPLITTING PARAMETERS (10^{-4} cm^{-1}) OF VARIOUS BASKET HANDLE PORPHYRINS

Compd.	D	E	X	Y	Z
H_2TPP	383	78	205	60	-255
MSII	347 (36)	90	206	25	-231
MSIII	369 (14)	91	214	32	-246
PSI	317 (66)	66	171	40	-211

An inspection of D values (Table 7) shows that, in general, there is a decrease in D values for all basket handle porphyrins relative to that of parent H_2TPP suggesting an increase in the average separation between the unpaired electrons. This observed reduction in D is probably due to the fact

becomes noncoplanar. 1H nmr studies of these porphyrins have indicated that the *meso*-phenyl ring is under considerable strain at least in the PSI isomer because of the tension imposed by the bridging chain^{10a}. This might reduce the dihedral angle between the phenyl and porphyrin plane, thus allowing increased spin delocalisation into the phenyl rings. The large red-shifts of both the Soret and Q -bands in the optical spectrum relative to H_2TPP , support this possibility. Thus it is likely that, at least in the PSI isomer, spin delocalisation into the phenyl ring is increased, which would account in part for the observed reduction in the D value. The calculated structures clearly reveal the distortion of the ring upon introducing short-chain and this structural change upon introduction of a short-bridging chain and the spin-delocalisation into the phenyl groups accounts for the reduction in D values.

Table 7 indicates small differences in the magnitude of E values for the different isomers relative to H_2TPP . Thus the observed small decrease and increase in E values for PSI and MSII, MSIII respectively, suggest a smaller deviation of the axial symmetry for PSI relative to MSII and MSIII.

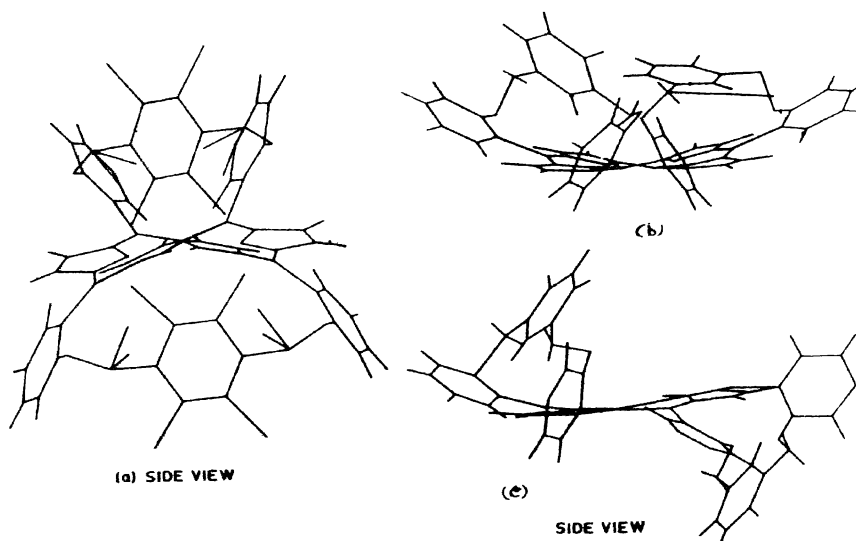


Fig. 9. Energy optimised calculated structures of (a) PSIBr₈, (b) MSII, (c) MSIII.

that the porphyrin ring is not a rigid structure so that its geometry can be modified by intermolecular interactions. In TPP systems, as pointed out by van der Waals *et al.*²⁴, a lowering of the D value is expected on (i) delocalisation of the π -electrons into the phenyl groups and (ii) when the porphyrin ring

The intersystem crossing (ISC) process generating the triplets and the triplet decay process are known to be spin-selective²⁴. For porphyrins, at 100 K in dilute frozen solution, the relative magnitudes of the triplet lifetime and electron spin relaxation time (T_1) are such that, even under steady

state illumination, thermal equilibrium is not established. With light modulation coupled with synchronous detection using a lock-in amplifier the spin-polarisation effect is enhanced strongly. This accounts for the observation of absorption (*a*) as well as emission (*e*) signals in the esr spectra. The spin-polarisation pattern observed in the spectra of all the three isomers, eaeaea, corresponds to that found in the parent H₂TPP. Even H₂TPC shows a similar polarisation pattern. The pattern shows that the middle (*y*) zero-field spin level is the most active (following the convention; the order of energy levels chosen, $T_x > T_y > T_z$) in the triplet state. $T_1 \rightarrow S_0$ intersystem crossing in the basket handle porphyrins relative to the other two states.

Calculated structures : An attempt has been made to generate energy optimised structures using MOBY²⁶ software to estimate qualitatively the magnitude of distortion present in various isomers of basket handle porphyrins. Fig. 9 reveals the expected distortion for all the three isomers by linking the phenyl groups present at the *meso*-position of porphyrin with various short-bridging chains. Thus the calculated structures are in conformity with the unusual spectral and electrochemical behaviour observed in short-chain basket handle porphyrins.

Conclusion : The short-bridging chain enforces considerable distortion in the porphyrin skeleton of basket handle porphyrins described here as evidenced by their ground and excited state dynamics. The magnitude and direction of optical and redox potential shifts compared to unstrapped porphyrin derivatives suggest a significant changes in the electronic structure of the porphyrin ring in these porphyrin systems. The excited state properties also can be significantly altered in the nonplanar conformation relative to its planar conformation. The geometry optimised structures are in conformity with the anomalous ground and excited state properties observed for short-chain basket handle porphyrins.

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