Brominated Short-chain Basket-handle Porphyrins and their Copper(II) Derivatives: Spectral and Electrochemical Studies on the Effect of β-Substitution *versus* Distortion†

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Pyrrole-brominated short-chain basket-handle porphyrins and their copper(II) derivatives have been synthesized and characterized. These porphyrins are significantly distorted and the β-substitution by bromines further enhances the degree of distortion. Optical absorption and electrochemical studies reveal considerable shifts in the energies of absorption maxima and electrode potentials. An analysis of these shifts indicates significant changes in the energies of the highest-occupied (HOMO) [$a_{1u}(\pi)$ and $a_{2u}(\pi)$] and lowest-unoccupied molecular orbitals (LUMOs) [$e_g(\pi^*)$] of the porphyrin ring upon β-substitution and distortion. Specifically: (*a*) both distortion and β-substitution decreases the energy gap between the HOMO and LUMO due to different stabilization/destabilization mechanisms and (*b*) the magnitude of separation between $a_{1u}(\pi)$ and $a_{2u}(\pi)$ is large for β-substitution while it is small for distortion relative to the corresponding planar unsubstituted derivative. The absorption and redox potential shifts show a non-linear behaviour with the number of bromine substituents and this is ascribed to the combined effect of antagonistic inductive interactions and steric hindrance. ESR spectral studies indicate weakening of the Cu–N σ bond without much change in the electronic structure of Cu^{2+}.

The role of synthetic metalloporphyrins as catalysts in epoxidation and hydroxylation reactions of organic substrates in the presence of an oxygen donor is well documented in the literature.[1] The catalytic property of a metalloporphyrin can be effectively modulated by a suitable introduction of electron-withdrawing groups on the porphyrin periphery. Recent studies have indicated that the substitution of halogens on β-pyrrole and *meso*-phenyl positions of metallotetraphenylporphyrins affords catalysts with high turnover numbers and that the porphyrin ring is robust and resilient to attack by strong oxidizing agents generated as intermediates.[2–4] The peripheral substitution affects the electronic structure of the porphyrin ring by altering the energies of highest-occupied (HOMOs) and the lowest-unoccupied molecular orbitals (LUMOs) which in turn affects the energies of Q and B transitions and the redox potentials.[5,6]

Recent studies from this laboratory have shown that the optical and redox properties of metal derivatives of 5,10,15,20-tetraphenylporphyrin (H_2tpp) can be significantly influenced by inducing distortion in the porphyrin plane by covalent attachment of short bridging chains across the porphyrin periphery.[7] β-Pyrrole substitution of these distorted porphyrins by halogens is expected to further alter the π-electron delocalization.[8] Furthermore, this offers an opportunity to understand the combined effects of distortion and β-substitution on the electronic structure of the porphyrin ring. In view of this, we wish to report the synthesis, spectral and electrochemical characterization of a series of bromine-substituted short-chain basket-handle porphyrins and their copper(II) derivatives (Fig. 1). It has been shown that both distortion and β-substitution leads to optical absorption red shifts and a decrease in hyperfine couplings of copper and nitrogen. However, the redox potential shifts show opposing trends between distortion and β-substitution. Distortion results in easier oxidations and harder reductions while β-substitution leads to harder oxidations and easier reductions. An attempt has been made to explain these shifts in terms of perturbation of energies of the HOMOs and LUMOs following the recent treatment of Crossley and co-workers.[9]

Results

Proton NMR spectroscopy and fast atom bombardment (FAB) mass spectral data were used to confirm the number of bromines substituted on the β-pyrrole positions of H_2L^1. As expected H_2L^2 exhibits a multiplet for the pyrrole protons while H_2L^3 shows a singlet with integrated intensity corresponding to four protons. However, no pyrrole signal was observed for H_2L^4. The *m*/*z* peaks in the FAB mass spectra further confirm the number of bromines incorporated in the porphyrins.

(*a*) *Electronic Spectral Studies*.—A comparison of the absorption spectra of the copper(II) derivatives of H_2L^1, H_2L^2 and H_2L^3 in the Soret- and Q-band regions are shown in Fig. 2 and the absorption data are listed in Table 1. It is apparent that β-substitution results in a gradual red shift of all the bands with reduction in intensity. However, a plot of the magnitude of red shift *versus* the number of bromines substituted [Fig. 3(*a*)] is non-linear suggesting that the magnitude of red shifts are not additive.

(*b*) *Electrochemical Studies*.—Cyclic voltammograms of [CuL^1] **4** and [CuL^3] **6** in CH_2Cl_2 containing 0.1 mol dm^{-3} NBu_4ClO_4 are shown in Fig. 4. Differential pulse voltammograms were also recorded for a precise measurement of $E_{\frac{1}{2}}$ values. Generally, the cyclic voltammograms revealed two ring oxidations and three reductions. The first reduction is assigned to the reduction of the bridging phenyl group based on our earlier work.[7c] The remaining two reductions correspond to porphyrin-ring reductions due to the formation of mono- and di-anions.[10] The electrochemical data tabulated in Table 2 reveal harder oxidations and easier reductions for β-substituted derivatives relative to H_2L^1 or [CuL^1]. However, the shifts in redox potentials are non-additive and the specific potential shift induced [Fig. 3(*b*)] per bromine decreases as the number of bromines on the porphyrin ring increases as observed by Callot and co-workers[8c] for β-substituted cyanoporphyrins.

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† *Non-SI units employed:* eV ≈ 1.6 × 10^{-19} J, G = 10^{-4} T.

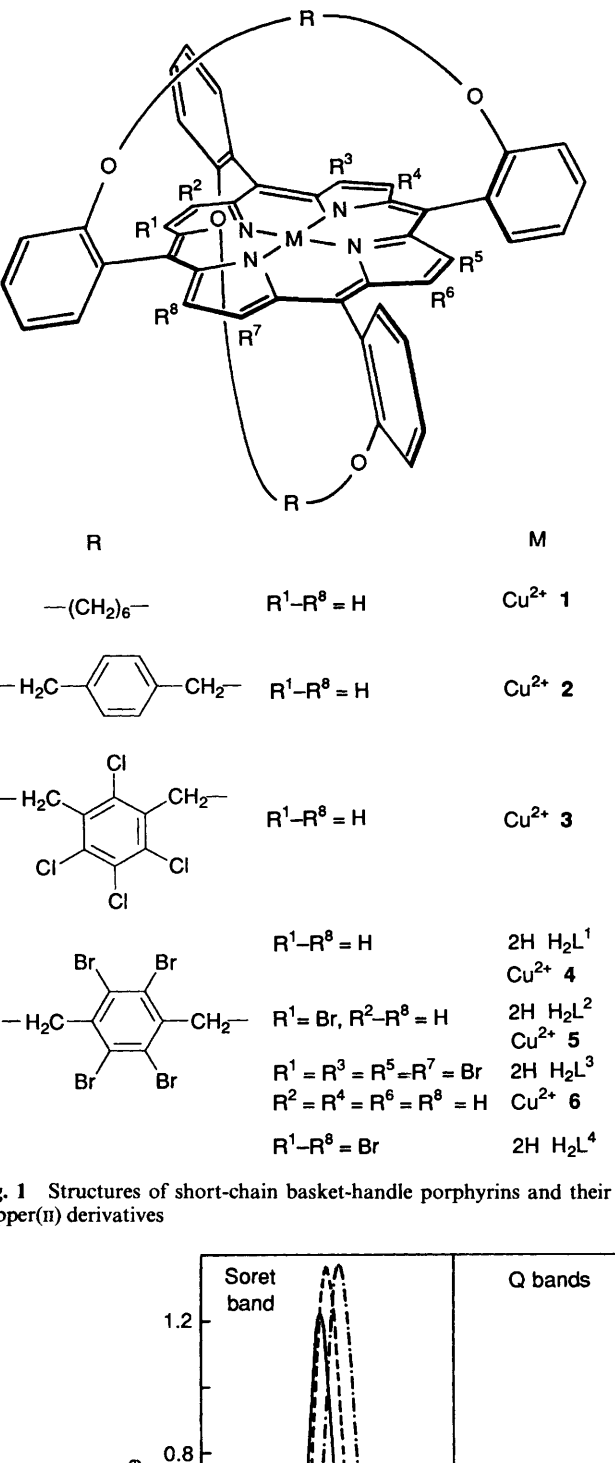

Fig. 1 Structures of short-chain basket-handle porphyrins and their copper(II) derivatives

(*c*) *Analysis of Spectral and Electrochemical Shifts*.—The absorption and electrochemical shifts upon β-substitution were analysed following the treatment of Crossley and co-workers.[9] Essentially, the method relates the shifts observed in the centre of gravity of the Q and B bands[11] in the absorption spectra (δE^{cg}/eV) and the redox potentials ($\delta E_{\frac{1}{2}}^{red\,I}$ and $\delta E_{\frac{1}{2}}^{ox\,I}$) resulting from incorporation of substituents (s) to the energy shifts of the HOMO [$a_{1u}(\pi)$ and $a_{2u}(\pi)$] and LUMO [$e_g(\pi^*)$] orbitals [equations (1)–(4)]. Here $\delta\varepsilon_k$ corresponds to shifts in the energy

$$\delta E_{\frac{1}{2}}^{red\,I}(s) = -\delta\varepsilon_k(s) \tag{1}$$

$$\delta E_{\frac{1}{2}}^{ox\,I}(s) = -\delta\varepsilon_j(s) \tag{2}$$

$$\delta E^{cg}(s) = \delta\varepsilon_k - [\tfrac{1}{2}(\delta\varepsilon_i + \delta\varepsilon_j)] \tag{3}$$

$$\delta\varepsilon_i = 2(-\delta E^{cg} + \delta\varepsilon_k - \tfrac{1}{2}\delta\varepsilon_j) \tag{4}$$

of the doubly degenerate e_g orbital and $\delta\varepsilon_i$ and $\delta\varepsilon_j$ correspond to shifts in the energies of the a_{2u} and a_{1u} levels upon β-substitution relative to the unsubstituted derivative. The various spectroscopic energy shifts and the redox potentials calculated for the copper(II) derivatives are tabulated in Table 3. Thus, a plot of $\delta\varepsilon_i$ and $\delta\varepsilon_j$ *versus* $\delta\varepsilon_k$ should give changes in the separation between the a_{1u} and a_{2u} orbitals upon β-substitution and distortion. Such a plot, shown in Fig. 5, clearly indicates a reduced energy separation upon distortion while β-substitution by bromines results in a larger separation relative to [Cu(tpp)].

(*d*) *ESR Spectral Studies*.—In order to evaluate the changes in the electronic structure of Cu^{2+} upon β-substitution and distortion, ESR spectra of copper(II) derivatives were recorded at room and low temperature (Fig. 6) and the ESR data are tabulated in Table 4. The room-temperature spectra display four resolved copper lines with superhyperfine structure observed for high-field lines.[12] The low-temperature spectra suggest an axial symmetry with resolved hyperfine couplings both in parallel and perpendicular fields. The data analyses were essentially the same as described earlier.[7c]

Discussion

Theoretical iterative extended Hückel calculations on relative effects of electron-withdrawing β-substituents on *meso*-aryl porphyrins predict stabilization of both HOMO [$a_{1u}(\pi)$ and $a_{2u}(\pi)$] and LUMO [$e_g(\pi^*)$] orbitals.[8a,b] However, the LUMO is stabilized slightly more relative to the HOMO. These stabilizations are attributed to weak 'inductive' interactions

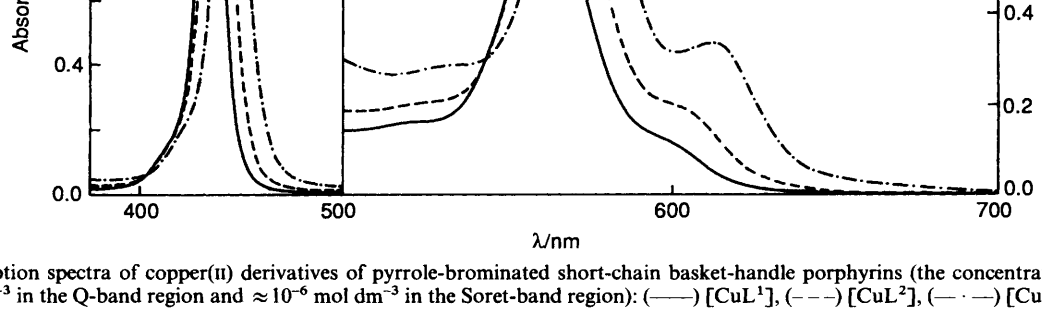

Fig. 2 Absorption spectra of copper(II) derivatives of pyrrole-brominated short-chain basket-handle porphyrins (the concentrations used were ≈ 10^{-5} mol dm^{-3} in the Q-band region and ≈ 10^{-6} mol dm^{-3} in the Soret-band region): (——) [CuL^1], (– – –) [CuL^2], (— · —) [CuL^3]

Table 1 Electronic spectral data [λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})] for brominated short-chain basket-handle porphyrins and their copper derivatives in benzene

		Q bands			
	Soret band	Q_y (1, 0)	Q_y (0, 0)	Q_x (1, 0)	Q_x (0, 0)
H_2L^1	436 (232.1)	532 (12.3)	567.5 (4.1)	606.5 (4.4)	665.0 (0.8)
H_2L^2	440.5 (198)	536.5 (12.2)	571.0 (3.6)	610.0 (4.5)	667.0 (1.4)
H_2L^3	450.0 (196)	544.0 (13.1)	579.0 (3.3)	616.5 (5.0)	674.5 (2.4)
H_2L^4	453.5(128)	546.5 (10.9)	583.0 (4.3)	620.5 (5.5)	676.5 (2.2)
[Cu(tpp)]	417 (416.9)	540 (19.5)		580	
[CuL^1]	435 (215.3)	563 (10.52)		603 (2.06)	
[CuL^2]	437 (231.1)	566 (14.17)		605 (sh) (3.29)	
[CuL^3]	443.5 (209.9)	572.8 (13.82)		612.8 (5.11)	

Table 2 Electrochemical redox data ($E_{\frac{1}{2}}$/V) *vs.* Ag–AgCl for brominated short-chain basket-handle porphyrins and their copper(II) derivatives in CH_2Cl_2

	Ring oxidation			Bridging phenyl	Ring reduction	
Porphyrin	I	II	III	reduction	I	II
H_2L^1	0.77	1.32	—	−1.14	−1.45	—
H_2L^2	0.89	1.32	—	−1.05	−1.34	—
H_2L^3	1.04*	1.28*	1.37*	−0.92	−1.09	−1.435
H_2L^4	1.11	—	—	−0.74	−0.985	−1.385
[Cu(tpp)]	1.06	1.31	—	—	−1.14	−1.74
[CuL^1]	0.74	1.30	—	−1.14	−1.48	—
[CuL^2]	0.87	1.348	—	1.05	−1.378	—
[CuL^3]	1.07	1.43	—	—	−1.227	−1.7

* Irreversible.

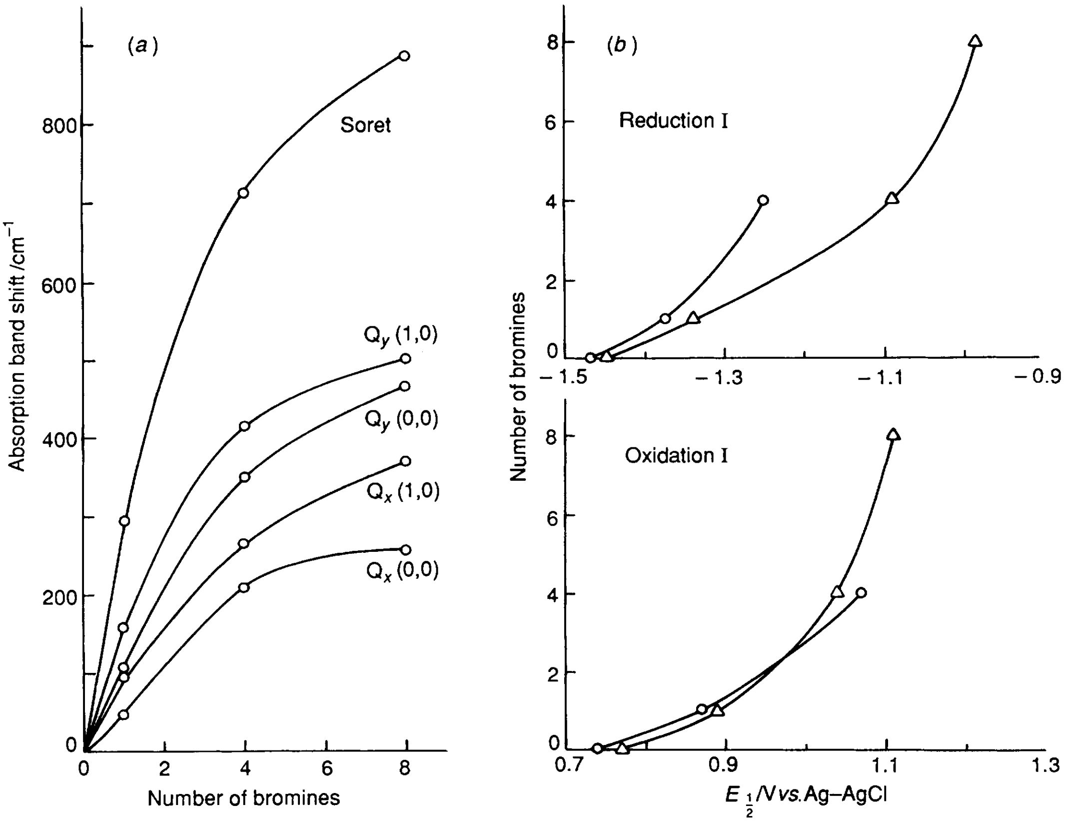

Fig. 3 Plot of (*a*) absorption band shift and (*b*) $E_{\frac{1}{2}}$ *versus* number of bromines incorporated into the pyrrole-brominated short-chain basket-handle porphyrins [Δ corresponds to free-base porphyrins and O to the copper(II) derivatives]

with the HOMO and strong ‘resonance’ interactions with the LUMO. Thus, the net result is a decrease in the energy gap between the HOMO and the LUMO. Intermediate neglect of differential overlap (INDO) calculations on a series of non-planar porphyrins predict destabilization of the porphyrin π system upon distortion such that the HOMO level is primarily affected with only a smaller perturbation on the LUMO so again decreasing the energy gap relative to the planar deriv-

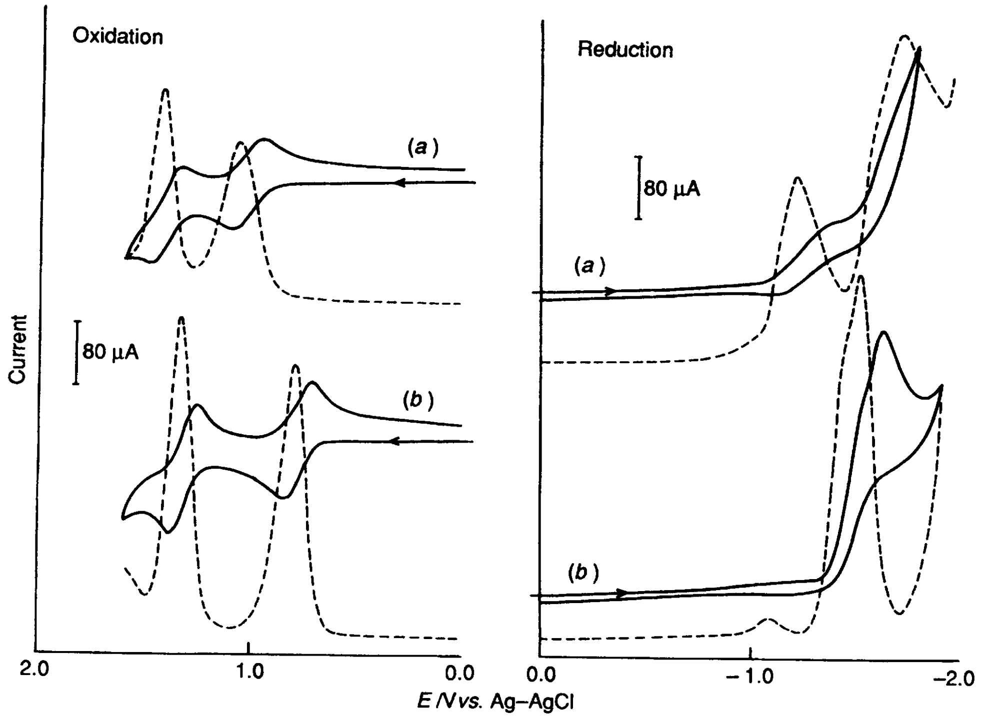

Fig. 4 Cyclic voltammograms of (*a*) [CuL^3] **6** (6.3 × 10^{-4} mol dm^{-3}) and (*b*) [CuL^1] **4** (7.6 × 10^{-4} mol dm^{-3}) in CH_2Cl_2 containing 0.1 mol dm^{-3} NBu_4ClO_4 at room temperature (scan rate: 200 mV s^{-1}). Dotted lines correspond to differential pulse voltammograms (scan rate: 10 mV s^{-1})

Table 3 Spectroscopic energy shifts *vs.* redox potentials

	δE/eV			$\delta\varepsilon$/eV		
	Electronic centre of gravity (E^{cg})	Oxidation	Reduction	$\delta\varepsilon_i$	$\delta\varepsilon_j$	$\delta\varepsilon_k$
[Cu(tpp)]	0	0	0	0	0	0
1	−0.060 01	−0.25	−0.36	0.590	0.25	0.36
2	−0.087 25	−0.21	−0.31	0.585	0.21	0.31
4	−0.102 28	−0.32	−0.340	0.565	0.32	0.34
3	−0.128 84	−0.30	−0.37	0.698	0.30	0.37
5	−0.112 21	−0.19	−0.238	0.510	0.19	0.238
6	−0.146 1	0.01	−0.087	0.476	−0.01	0.087

Table 4 ESR data * for the copper(II) derivatives of brominated short-chain basket-handle porphyrins in chloroform–toluene (1 : 1)

	$g_\parallel$	$g_\perp$	$A_\parallel^{Cu}$	$A_\perp^{Cu}$	$A_\parallel^{N}$	$A_\perp^{N}$	α^2	g_{iso}	A_0^{Cu}	A_0^{N}
[Cu(tpp)]	2.187	2.067	218	32.80	14.5	16.4	0.7500	2.17	97.7	15.90
[CuL^1]	2.161	2.056	205	32.00	14.9	15.99	0.7332	2.091	89.7	15.85
[CuL^2]	2.159	2.029	190	31.62	14.3	15.81	0.6485	2.081	87.8	15.80
[CuL^3]	2.160	2.021	187.6	31.23	14.0	15.61	0.6347	2.082	86.2	15.20

* A values in 10^{-4} cm^{-1}

ative.[13] These effects are clearly reflected in the spectroscopic and electrochemical energy shifts listed in Table 3. Thus, on going from **2** to **3**, the relative energies in $\delta\varepsilon_k$, $\delta\varepsilon_j$ and $\delta\varepsilon_i$ increase suggesting destabilization upon increasing distortion. On the other hand, there is a gradual decrease in $\delta\varepsilon_k$, $\delta\varepsilon_j$ and $\delta\varepsilon_i$ energies upon bromine substitution indicating relative stabilization of these orbitals. Assuming that the β-substituent effect is approximately proportional to the β-density,[9] the larger decrease in $\delta\varepsilon_j$ and $\delta\varepsilon_k$ relative to $\delta\varepsilon_i$ can be rationalized provided that $\delta\varepsilon_j$ and $\delta\varepsilon_i$ are identified respectively with a_{1u} and a_{2u} orbital shifts. This is in conformity with the fact that $a_{2u} > a_{1u}$ in *meso*-aryl porphyrins.[14] Thus, this clearly suggests that the red shifts observed upon β-substitution and distortion are due to different stabilization/destabilization mechanisms of the HOMO and the LUMO.

The plot in Fig. 5 is quite revealing. It is inferred from the plot that β-substitution by bromines increases the relative separation between a_{1u} and a_{2u} orbitals relative to [Cu(tpp)] and the magnitude of increase is proportional to the number of bromines substituted. The free-base derivatives also show the same trend. A similar conclusion was arrived at by Krishnan and Bhyrappa[6] from their studies on metallooctabromotetraphenylporphyrins. It has been shown that the relative separation between a_{1u} and a_{2u} increases in octabromo derivatives relative to the corresponding unsubstituted tpp derivatives and the energy of the a_{2u} orbital is found to be dependent on the electronegativity of the metal while the energy of a_{1u} remains independent of the nature of the metal ion. It is pertinent to point out here that their data analysis was based on a different method developed by Shelnutt and Ortiz.[5] On the other hand, the relative increase in energy separation between a_{1u} and a_{2u} is considerably smaller upon distortion of the

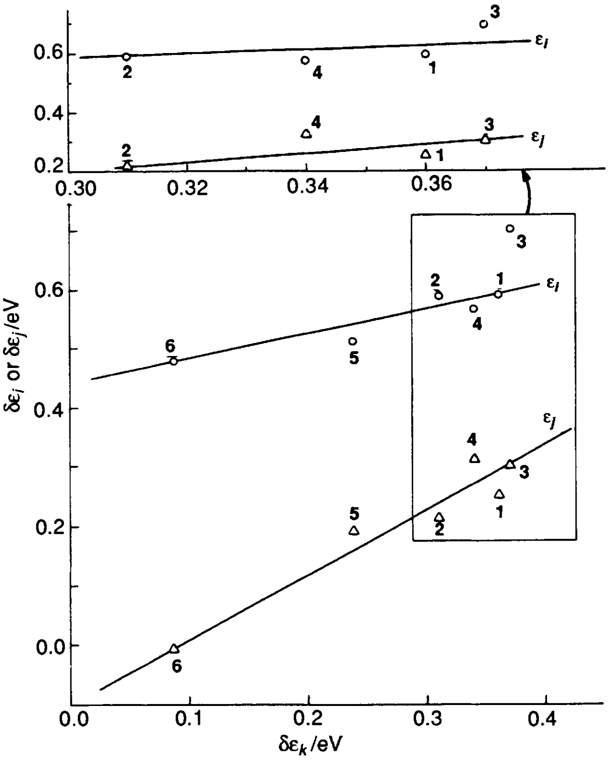

Fig. 5 Shift of the highest-occupied π-level energies [(△) $\delta\varepsilon_j$ and (○) $\delta\varepsilon_l$] plotted against corresponding shifts for the lowest unoccupied level [$\delta\varepsilon_k$]. Inset shows the separation between a_{1u} and a_{2u} on distortion

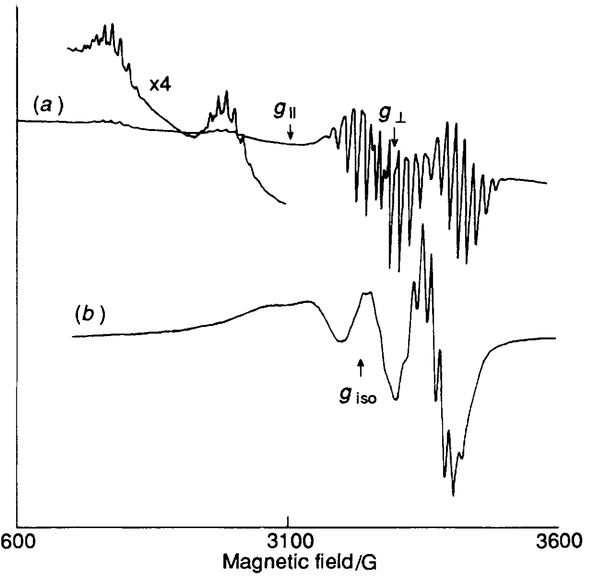

Fig. 6 ESR spectra of [CuL^2] **5** in toluene–chloroform (1 : 1): (*a*) at 100 K and (*b*) at room temperature

porphyrin plane (Fig. 5 inset). This is not surprising considering the fact that the distortion is a steric effect while β-substitution directly affects the porphyrin conjugation through a strong resonance interaction.[8c]

The direction of electrochemical potential shifts upon substitution of bromines is in agreement with the large body of the literature data on the substituent effects of porphyrins.[8,10] However, the magnitude of shifts are not additive [Fig. 3(*b*)] both for oxidation and reduction. The optical absorption red shifts also show similar behaviour [Fig. 3(*a*)]. This has been ascribed in part to antagonistic inductive effects of substitution on the lone pair of the pyrrolic nitrogens.[8c] The steric effect also contributes to this trend. The attachment of short chains across the periphery makes the porphyrin plane non-planar with a reduced dihedral angle between the porphyrin plane and the *meso*-phenyl rings.[7b] Substitution of bulky bromine at the β-pyrrole positions results in steric hindrance between the 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. Strong evidence for this conclusion comes from the X-ray crystal structure of 2,3,7,8,12,13,17,18-octabromoporphyrin in which the porphyrin ring is found to be puckered relative to H$_2$tpp.[6] Thus, the combined steric and antagonistic inductive effects account for the non-linear nature of the plots in Figs. 3(*a*) and 3(*b*).

The ESR data (Table 4) indicate that the principal tensor components of superhyperfine interaction between the pyrrolic 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 CuN$_4$ moiety in an approximately tetragonal crystal field.[12,15] Furthermore, the equally spaced nitrogen hyperfine lines (Fig. 6) indicate that the non-planarity 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 non-planarity observed in X-ray structural work on [Cu(tpp)] was not reflected in the ESR spectrum.[12]

Literature reports[15,16] on structurally well characterized copper(II) complexes with N, O and S donor ligands reveal an inverse relationship between $g_{\parallel}$ and $A_{\parallel}^{Cu}$ parameters. Generally, $g_{\parallel}$ increases and $A_{\parallel}^{Cu}$ decreases upon increasing distortion. Even though $g_{\parallel}$ values do not show any such trend, the $A_{\parallel}^{Cu}$ and A_0^{Cu} values decrease gradually with increasing distortion relative to [Cu(tpp)] probably indicating the expected non-planarity around the Cu^{2+}.

The α^2 value calculated from the spin-Hamiltonian parameters represents the bonding coefficient of the b_1 molecular orbital and gives a qualitative idea about the strength of the Cu–N σ bond.[17] The stronger the in-plane σ bond between Cu^{2+} and nitrogen, the higher is the energy of the b_1 molecular orbital because of its anti-bonding character.[18] Thus, the gradual decrease observed (Table 4) here indicates a lowering of the energy of the b_1 molecular orbital relative to that of [Cu(tpp)] and a weaker Cu–N interaction in the distorted brominated derivatives. A similar conclusion was arrived at to explain the higher value of α^2 for copper(II) phthalocyanine (α^2 = 0.79, Cu–N 1.93 Å) compared to [Cu(tpp)] (α^2 = 0.75, Cu–N 1.98 Å).[18,19]

In summary, it has been shown that a distinction between the effects of β-substitution and distortion on the energies of the frontier orbitals of the porphyrin ring is possible by study of spectral and electrochemical data.

Experimental

Porphyrin H$_2$L^1 and the copper(II) porphyrin complexes **1–4** were prepared as reported earlier by us.[7a,c]

Syntheses.—H$_2$L^2. Porphyrin H$_2$L^1 (60 mg, 0.0396 mmol) and *N*-bromosuccinimide (nbs) (8 mg, 0.455 mmol) were refluxed in chloroform (20 cm^3) for 3 h. The reaction mixture was evaporated and the residue was washed with methanol to remove a green material. The product was purified over a silica gel (60–120 mesh) column using benzene as the eluent, and a reddish green band separated was identified as H$_2$L^2 (yield: 62 mg, 98%). Mass spectrum (FAB): *m*/*z* 1593 (calc. for C$_{60}$H$_{33}$Br$_9$N$_4$O$_4$ 1593). ^{1}H NMR (CDCl$_3$): δ 8.84 (m, 4 H, *ortho* H of *meso* phenyls), 8.71–8.44 (complex m, 7 H, pyrrole), 7.49 (m, 8 H, *meta* H of *meso* phenyls), 6.69 (m, 4 H, *para* H of *meso* phenyls), 4.56 (m, 8 H, bridge CH$_2$), −0.51 (m, 2 H, NH).

H$_2$L^3. Porphyrin H$_2$L^1 (60 mg, 0.0396 mmol) and nbs (30 mg, 0.175 mmol) were refluxed in chloroform (30 cm^3) for 3 h. Work-up and purification as above gave H$_2$L^3 (yield: 63 mg, 86%). Mass spectrum (FAB): *m*/*z* 1830 (calc. for C$_{60}$H$_{30}$Br$_{12}$-

N_4O_4 1830). ^{1}H NMR ($CDCl_3$): δ 8.82 (m, 4 H, *ortho* H of *meso* phenyls), 8.69 (s, 4 H, pyrrole), 7.56 (m, 8 H, *meta* H of *meso* phenyls), 6.77 (m, 4 H, *para* H of *meso* phenyls), 4.64 (m, 8 H, bridge CH_2) and −1.0 (s, 2 H, NH).

H_2L^4. To a stirred solution of H_2L^1 (25 mg, 0.0165 mmol) in $CHCl_3$–CCl_4 (10 cm^3, 1 : 1) was added liquid bromine (84.5 mg, 0.027 cm^3, 0.528 mmol) dissolved in the same solvent (4 cm^3) over a period of 30 min at 30 °C. Stirring was continued for a further 4 h. Pyridine (0.075 cm^3) in 4 cm^3 solvent was added dropwise over a period of 30 min and the solution stirred for 12 h. The reaction mixture was treated with 20% aqueous $Na_2S_2O_5$ (20 cm^3) to destroy the excess bromine. The organic layer was separated and washed with water (3 × 100 cm^3) and dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to obtain the green product. The crude product was purified over a silica gel (60–120 mesh) column using benzene as the eluent, the single dark green band was identified as H_2L^4 (yield: 9 mg, 26%). Mass spectrum (FAB): *m/z* 2145 (calc. for $C_{60}H_{26}Br_{16}N_4O_4$ 2145). ^{1}H NMR ($CDCl_3$): δ 8.89 (m, 4 H, *ortho* H of *meso* phenyls), 7.57 (m, 8 H, *meta* H of *meso* phenyls), 6.79 (m, 4 H, *para* H of meso phenyls) and 4.75 (m, 8 H, bridge CH_2).

The copper(II) derivatives of H_2L^2 and H_2L^3 were prepared by the reported method.[7c] The details of the instrumentation are the same as reported earlier.[20]

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