Tetrapyrroles. Part 1. Substituent Effects on Porphyrin Electronic Spectra

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The *B* and *Q* electronically excited states maintain a roughly constant energy separation in a wide range of porphyrins and porphyrin dications. An empirical scale, based upon this observation, has been used to discuss the magnitude of the substituent effects in various cases. The results lead to an alternative explanation of the green colour of *meso*-tetra-arylporphyrin dications.

Two main electronic states have been recognised[1,2] in the visible spectrum of most porphyrins, the B state, responsible for an intense absorption near 400 nm, and the Q state(s), responsible for a series of weaker bands originating near 600 nm. These states may be considered to arise from the splitting of pairs of nearly degenerate π,π^* states constructed *via* the four-orbital model.[3] In agreement with this view the $B - Q$ energy difference remained largely constant in a series of metal complexes of tetraphenylporphyrins[1] and of mesoporphyrin IX dimethyl ester.[4]

An alternative interpretation of these spectra has been advanced.[5]

The spectrum of neutral metal-free porphyrins resembles that of the *normal*[6,7] metal complexes except that the degenerate Q state of the metal complexes is clearly split into separate x- and y-polarised components. This reflects the loss of local four-fold symmetry when the central metal ion is replaced by two protons. The majority of data on the visible absorption spectra of substituted porphyrins refers to neutral, metal-free porphyrins with spectra of this type. The effects of substituents upon such spectra were discussed by Gouterman[1] with the aid of a model based upon substituent-induced mixing of the four states B_x, B_y, Q_x, and Q_y. The magnitude of the $Q_x - Q_y$ energy splitting was well described, but discussion of the absolute energies of the Q and B states was hampered by lack of experimental data. We have therefore re-examined this latter aspect in the light of the extensive data[8-10] now available for substituted metal-free porphyrins in both neutral and dicationic forms. In the case of the dications, addition of two further protons restores the local four-fold symmetry and thus the degeneracy of the Q states.

EXPERIMENTAL

Porphyrins were synthesised by established methods[11,12] and satisfactory elemental analytical results were obtained after sublimation *in vacuo*. meso-*Tetrakis-*(3-*methoxyphenyl*)*porphyrin* seems not to have been reported previously. It was prepared by reaction between pyrrole (3.5 ml) and 3-methoxybenzaldehyde (6 ml), and purified by chromatography in chloroform on alumina (grade II) followed by sublimation *in vacuo* (Found: C, 78.25; H, 5.2; N, 7.5. $C_{48}H_{38}N_4O_4$ requires C, 78.45; H, 5.2; N, 7.6%); decomp. >300 °C.

Spectra were recorded in spectrograde benzene (Fisons) containing a few drops of trifluoroacetic acid for the dications in 1 cm cuvettes on Unicam SP 1800 and SP 600 series 2 spectrophotometers.

RESULTS

Our principal result is that the $B - Q$ energy splitting, previously shown to be roughly constant in two series of metal complexes, also remains roughly constant in the majority of metal-free porphyrins examined (Figure 1 and Table). (The average of the Q_x and Q_y energies was used in the case of the neutral compounds.) The effects of substituents upon the band positions were consistent with previous results.[1,9,13]

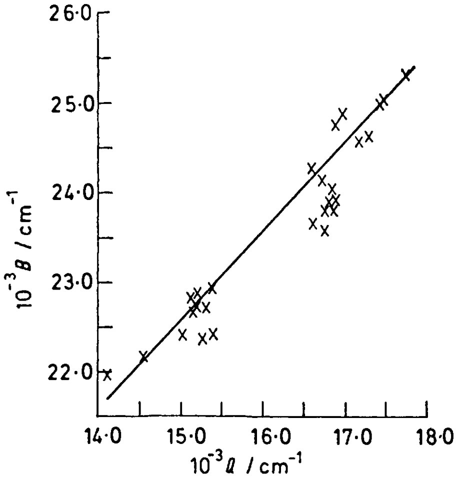

FIGURE 1 Q Band energies *versus* B band energies for 35 metal-free porphyrins (Table). The line runs from the point for porphin and has unit slope

DISCUSSION

The implication of Figure 1 is that the effect of a wide range of substituents (including protons) upon the B and Q state energies of metal-free porphyrins may be represented by a single empirical parameter. A convenient choice is the distance (δ/cm^{-1}) between the B,Q point for the substituted porphyrin and that for porphin itself, measured along the line of unit slope through the point for porphyrin (Figure 1). The perpendicular displacement (ε/cm^{-1}) of the point from the line gives an indication of the accuracy of the result. Simple expressions for these quantities may be given in terms of ΔB, the difference between the B band energy of porphin and that of the substituted porphyrins, and the analogously defined ΔQ [equations (1) and (2)]. A negative value of ε implies a smaller $B - Q$ energy separation than that in porphin. Ideally, of course, $\varepsilon = 0$. Values of δ and ε

$$\delta = (\Delta Q + \Delta B)/\sqrt{2} \qquad (1)$$

$$\varepsilon = (\Delta Q - \Delta B)/\sqrt{2} \qquad (2)$$

for those porphyrins appearing in Figure 1 are listed in the Table.

It is apparent from the Table that the *meso*-tetra-arylporphyrin dications conform particularly closely to Gouterman's prediction of the constancy of the $B - Q$ energy gap. This is perhaps surprising from two points of view. First, these compounds do not show the large intensity difference between the B and Q absorption bands assumed in Gouterman's analysis. And second, their pyrrole rings are known [14] to be far from coplanar. It is therefore tempting to attribute some of the protonation-induced enhancement of Q band intensity in these dications to their lack of pyrrole ring coplanarity.

Porphyrin visible band energies and substituent parameters

Porphyrin *	$10^{-3}B$/cm^{-1}	$10^{-3}(B - Q)$/cm^{-1}	$10^{3}\delta$/cm^{-1}	$10^{-3}\varepsilon$/cm^{-1}	Ref.
(1) Porphin	25.32	7.58	0.00	0.00	10
(2) Octaethylporphyrin	25.00	7.56	0.43	−0.02	10
(3) X = ethyl †	24.13	7.41	1.56	−0.12	9
(4) X = phenyl	23.92	7.10	1.62	−0.35	8
(5) X = 4-hydroxyphenyl	23.66	7.04	1.96	−0.39	9
(6) X = 4-methoxyphenyl	23.58	6.83	1.92	−0.53	8
(7) X = 4-tolyl	23.87	7.08	1.69	−0.36	8
(8) X = 4-fluorophenyl	24.04	7.19	1.53	−0.28	8
(9) X = 4-chlorophenyl	23.87	7.04	1.66	−0.39	8
(10) X = 4-bromophenyl	23.81	7.03	1.74	−0.39	8
(11) X = 3-methoxyphenyl	23.81	6.95	1.68	−0.45	8
(12) X = 3-tolyl	23.81	7.05	1.75	−0.38	8
(13) X = 3-fluorophenyl	23.92	7.04	1.58	−0.39	8
(14) X = 3-chlorophenyl	23.92	7.02	1.57	−0.40	8
(15) X = chloro	22.42	7.02	3.70	−0.40	10
(16) Dication of (4)	22.83	7.68	3.58	0.07	8
(17) Dication of (5)	21.96	7.83	4.92	0.18	9
(18) Dication of (6)	22.17	7.60	4.45	0.01	8
(19) Dication of (7)	22.42	7.38	3.95	−0.14	8
(20) Dication of (8)	22.88	7.66	3.50	0.06	8
(21) Dication of (9)	22.68	7.52	3.69	−0.04	8
(22) Dication of (10)	22.73	7.53	3.62	−0.04	8
(23) Dication of (11)	22.37	7.10	3.83	−0.34	8
(24) Dication of (12)	22.78	7.60	3.60	0.01	8
(25) Dication of (13)	22.94	7.53	3.33	−0.04	8
(26) Dication of (14)	22.73	7.41	3.54	−0.12	8
(27) Mesoporphyrin IX dme	25.00	7.57	0.44	−0.01	10
(28) Deuteroporphyrin IX dme	25.03	7.55	0.38	−0.03	10
(29) Coproporphyrin III tme	25.00	7.55	0.42	−0.02	10
(30) Uroporphyrin III ome	24.63	7.33	0.79	−0.18	10
(31) Protoporphyrin IX dme	24.57	7.39	0.92	−0.14	10
(32) Dication of (27)	24.75	7.86	0.99	0.20	10
(33) Dication of (28)	24.88	7.91	0.86	0.23	10
(34) Dication of (29)	24.75	7.86	0.99	0.20	10
(35) Dication of (31)	24.27	7.66	1.53	0.05	10

* As solutions in benzene (1)—(26) and aqueous detergent (27)—(35): Q band energies are an average of Q_x(0–0) and Q_x(0–0) where these differ. † In *meso*-X_4-porphyrin.

Meot-Ner and Adler [9] have shown that the substituent dependence of both neutral and dicationic *meso*-tetra-aryl porphyrin band energies correlate well with a mixed Hammett constant in which the resonance contribution dominates. Our results (Figure 2) largely confirm this view although we obtained satisfactory correlation with the ' pure ' resonance parameter [8,15] σ^+. Moreover the correlation lines intersect near $\delta = 0$, the value for porphin. This suggests that the substituent-induced shifts in the B,Q state energies are largely due to modulation of the electron density at the porphyrin *meso*-positions. And, moreover, that these modulations are transmitted across the aryl–porphyrin bond roughly twice as efficiently in the dications as in the neutral porphyrins. This could be a result of the protonation-induced changes in geometry [14] which would increase the π–π overlap between the porphyrin ring and its *meso*-aryl substituents in the diprotonated form.

There is, moreover, a further implication of Figure 2. A hypothetical aryl substituent of extremely great electron-withdrawing power (σ^+ *ca.* 4.0) would abolish the red-shift between the substituted porphyrin and porphin itself. It would also abolish any protonation-induced shift in B,Q state energies. This suggests that protonation-induced spectroscopic changes are magnified by electron-donating substituents at the *meso*-positions. The B,Q state energies are linked to the observed band intensities *via* the four orbital theory.[3] Hence the well known green colour of *meso*-tetra-aryl-porphyrin dications (due to an unusually large increase in Q band intensity on protonation) may be attributable to the electron-releasing power of the *meso*-substituents. An alternative explanation,[14] based upon the changes in conjugation following rotation into coplanarity of the *meso*-aryl substituents (which accompanies protonation of the pyrrole rings), is rendered less attractive by the observation (ref. 9 and unpublished results of J. D. and

L. R. M.) that a similar effect is shown by *meso*-tetra-alkylporphyrins.

Finally, the present data (Table) allow a correlation of the type of Figure 2 to be investigated in a preliminary way for substituents (H, Et, Ph, Cl) directly bonded to the porphyrin *meso*-positions. The result (δ: H < Et ~ Ph < Cl) seems inconsistent with the usual measures of substituent electron-releasing powers. If substantiated by further data, this possibly reflects the order of electron release by the substituent into the electronically-excited state of the porphyrin ring. In general this would differ from that established by ground-state measurements. For example, substituent polarisability could well play a larger role in view of the electronic rearrangements on excitation. The correlations of Figure 2 would then imply that the aryl rings and their substituents largely retained their ground-state electron distributions on excitation of the porphyrin ring system. Thus transmission of *para*- and *meta*-substituent effects around the aromatic ring to C(1) would be essentially a ground-state process. But the C(1)–C(*meso*) interaction (separately constant in the correlations of Figure 2A and B) would reflect the excited-state effects mentioned above.

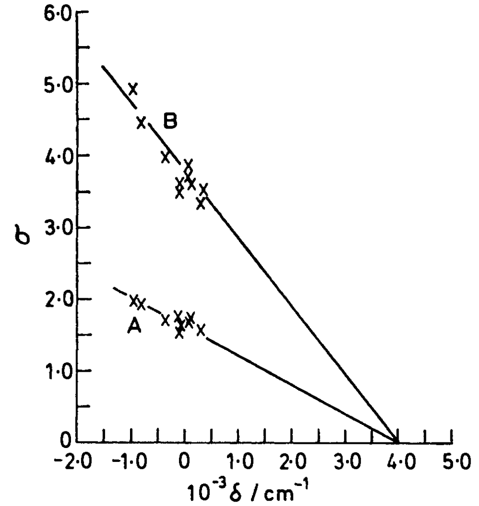

FIGURE 2 Substituent parameters δ *versus* aryl substituent constants (δp^+ for 4-substituted and δ_m for 3-substituted compounds [8,15]) for A, porphyrins (4)—(14) (see Table) and B, the corresponding dications

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[1] M. Gouterman, *J. Chem. Phys.*, 1959, **30**, 1139.

[2] M. Gouterman, G. H. Wagniere, and L. C. Snyder, *J. Mol. Spectroscopy*, 1963, **11**, 108.

[3] M. Gouterman, *J. Mol. Spectroscopy*, 1961, **6**, 138.

[4] R. S. Becker and J. B. Allison, *J. Phys. Chem.*, 1963, **67**, 2675.

[5] A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Amer. Chem. Soc.*, 1968, **90**, 6577.

[6] J. W. Buchler in ' Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Oxford, 1976.

[7] A. Antipas, J. W. Buchler, M. Gouterman, and P. D. Smith, *J. Amer. Chem. Soc.*, 1978, **100**, 3015.

[8] S. M. Pemberton, Ph.D. Thesis, University of London, 1978.

[9] M. Meot-Ner and A. D. Adler, *J. Amer. Chem. Soc.*, 1975, **97**, 5107.

[10] Ref. 6, appendices.

[11] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Amer. Chem. Soc.*, 1967, **32**, 476.

[12] A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2443.

[13] E. W. Baker, C. B. Storm, G. T. McGrew, and A. H. Corwin, *Bioinorganic Chem.*, 1973, **3**, 49.

[14] A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1968, **90**, 2735.

[15] L. P. Hine, ' Physical Organic Chemistry,' McGraw-Hill, Tokyo, 1962, 2nd edn.