A Spectroscopic Study of the Protonation of Porphins and Corroles

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The protonation behaviour of four porphyrins, two corroles, and aza-aetioporphyrin I in toluene–acetic acid mixtures has been studied by visible spectrophotometry. The macrocycles exist in the monoprotonated form in glacial acetic acid. The acidities of the seven monocations are compared. *N*-methyl substituted porphyrins are more basic than their unsubstituted analogues. The protonation in acetic acid–sulphuric acid mixtures of the monocations derived from five of the macrocycles have also been studied. Dications are formed at low sulphuric acid concentrations. The addition of a third proton at high sulphuric acid concentrations occurred for a corrole and aza-aetioporphyrin I.

THE porphyrin nucleus contains four nitrogen atoms all of which are theoretically capable of accepting a proton in acidic solutions.[1] However only the monoprotonated (monocation) and diprotonated (dication) forms have been observed. The two forms may be characterized by their visible spectra.[1,2] There is some controversy concerning the existence of monocations and dications in acidic solutions. Evidence that the monocations are less favourable thermodynamically than the dications has been presented and is thought to show that the protonation of a neutral porphyrin leads directly to the formation of the dication.[3-5] However Aronoff[6]

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[1] J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier Amsterdam, 1964.

[2] A. Neuberger and J. J. Scott, *Proc. Roy. Soc.*, 1952, *A*, **213**, 307.

[3] S. Aronoff and C. A. Weast, *J. Org. Chem.*, 1941, **6**, 550.

[4] R. I. Walter, *J. Amer. Chem. Soc.*, 1953, **75**, 3860.

[5] T. I. Strelkova and G. P. Gurinovich, *Biophysics*, 1968, **13**, 1164.

[6] S. Aronoff, *J. Phys. Chem.*, 1958, **62**, 428.

and Scott[2,7] have shown that several porphyrins give clearly distinguishable spectra due to monocations in solutions for which the acidity was insufficient to cause diprotonation. Monocations of porphyrins have also been observed to exist in aqueous solutions of detergents.[1] The present work was undertaken in an attempt to characterize the protonation behaviour of some porphyrins and corroles in solutions of varying acidity. It was also hoped that the results would give an indication of the relative basicity of the macrocycles.

EXPERIMENTAL

Octaethylporphyrin and aetioporphyrin were prepared by standard methods[8] and their identity was confirmed by u.v. and n.m.r. spectroscopy. The synthesis and details of the physical criteria used to establish the identity and purity of the *N*-methylporphyrins,[9] the aza-porphyrin,[10] and the corroles[11] have been described elsewhere. Their protonation in solutions of acetic acid in toluene was studied for the complete range of solvent composition. Stock solutions of the macrocycles in toluene were prepared by weight and were diluted by volume with toluene and acetic acid to give a series of solutions of a fixed concentration of macrocycle in solvent containing increasing concentrations of acetic acid. Spectra of the solutions were determined using a Unicam SP 800 spectrophotometer with a thermostatted (25 ± 0·2 °C) cell compartment. Preliminary investigations showed that the spectral changes which occur on the protonation of the macrocycles are most suitable for quantitative study in the range 14,500—22,500 cm^{-1}. Only this region of the spectrum was therefore measured.

The protonation equilibria of three porphyrins and one corrole in solutions of sulphuric acid in acetic acid were also studied. The acid solutions were prepared by volume from 100% H_2SO_4, acetic acid, and solutions (prepared by weight) of the macrocycles in acetic acid. Solutions of 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-20-azaporphyrin and 2,3,7,8,12,13,17,18-octaethyl-21-(3-bromo-n-propyl)-porphyrin in acetic acid were unstable and showed signs of decomposition after 20 and 48 h respectively. Fresh solutions of these compounds in acetic acid were prepared immediately before use.

TABLE 1

The macrocycles for which the protonation behaviour has been studied

Macrocycle	Code letter
2,3,7,8,12,13,17,18-Octaethylporphyrin	A
Aetioporphyrin I	B
8,12-Diethyl-2,3,7,13,17,18,21-heptamethylcorrole	C
2,3,7,8,12,13,17,18-Octaethyl-21-methylporphyrin	D
8,12-Diethyl-2,3,7,13,17,18,22-heptamethylcorrole	E
2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-20-aza-porphyrin	F
2,3,7,8,12,13,17,18-Octaethyl-21-(3-bromo-n-propyl)-porphyrin	G

RESULTS

The seven macrocycles for which measurements of the protonation equilibria have been made are listed in Table 1 together with code letters which will be used throughout this paper to refer to the compounds.

The spectrum of the neutral unprotonated form of compound A in toluene is compared in Figure 1 with the spectrum of compound A in acetic acid. Spectra of A in toluene–acetic acid mixtures of low acetic acid content were identical to the spectrum of A in toluene. Similarly at high (up to 100%) acetic acid concentrations the spectrum of A was independent of acid concentration showing that the equilibrium protonation of A, which occurs at intermediate acetic acid concentrations, lies completely on the protonated side in glacial acetic acid. The spectra of A in solutions containing intermediate concentrations of acetic acid were consistent with the presence of equilibrium mixtures of the neutral compound and the protonated form which exists in acetic acid. There was no detectable evidence for the presence in the solutions of other species derived from the parent porphyrin. Similar results were observed for compounds B and C for which the spectra are shown in Figure 1. The positions of the absorption maxima and the corresponding extinction coefficients for the three macrocycles are given in Table 2.

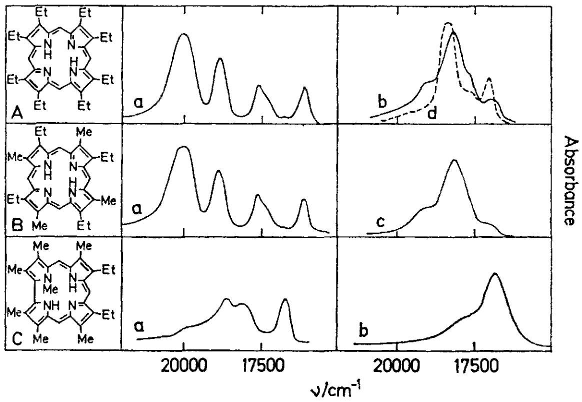

FIGURE 1 Visible spectra of compounds A and C in (a) toluene and (b) acetic acid, and of compound B in (a) toluene and (c) toluene (10% v/v)–acetic acid (90% v/v). Spectrum (d) is of A in a solution of sulphuric acid (*ca.* 0·3 mol l^{-1}) in acetic acid

The ratio of the concentrations c_P and c_N of the protonated and neutral forms of a macrocycle in a mixed toluene–acetic acid solvent is given by equation (1) where D, D_N,

$$(c_P/c_N) = (D - D_N)/(D_P - D) \qquad (1)$$

and D_P are the optical densities at a particular wavelength and for the same path length optical cells of a fixed concentration of the macrocycle in the mixed solvent, in toluene, and in acetic acid respectively. The variation of (c_P/c_N) with solvent composition for compounds A—C is given in Table 3. The results are the average values deduced from optical density measurements at two wavelengths, one corresponding to an absorption maximum of the neutral species and the other corresponding to an absorption of the protonated species. The ratios (c_P/c_N) deduced from the two sets of data were in reasonable agreement for ratios in the approximate range $0{\cdot}1 < (c_P/c_N) < 10$.

The behaviour of compounds D and G in toluene–acetic acid mixtures was similar to that for A—C except that D

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[7] J. J. Scott, *J. Amer. Chem. Soc.*, 1955, **77**, 325.

[8] R. L. N. Harris, A. W. Johnson, and I. T. Kay, *Quart. Rev.*, 1966, **20**, 211.

[9] R. Grigg, G. Shelton, A. Sweeney, and A. W. Johnson, *J.C.S. Perkin I*, 1972, 1789.

[10] R. Grigg, A. W. Johnson, and G. Shelton, *J. Chem. Soc.* (*C*), 1971, 2287.

[11] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.

TABLE 2

Spectral data for compounds A—C in toluene (neutral form) and in acetic acid (monocations)

	Neutral compounds		Monocations	
Porphyrin	$\tilde{\nu}_{max.}$/cm^{-1}	($\varepsilon_{max.}/\varepsilon_I^N$)†	$\tilde{\nu}_{max.}$/cm^{-1}	($\varepsilon_{max.}/\varepsilon_I^N$)†
A *	16,000	1·00	16,800	0·70
	17,550	1·10	18,000	2·60
	18,800	1·93	19,000	1·10
	20,000	2·65		
B	16,050	1·00	16,900	0·65
	17,550	1·09	18,100	2·35
	18,900	1·74	19,050	0·95
	20,050	2·54		
C	16,650	1·00	16,800	0·91
	18,000	0·88	18,000	0·27
	18,600	1·00		
	19,800	0·45		

* The spectrum (Figure 1d) of the dication of A had maxima at 16,950 and 18,300 cm^{-1}. † Because of the error incurred in preparing solutions of the macrocycles by weighing very small quantities of solid absolute extinction coefficients are not given. All extinction coefficients are quoted relative to the value (ε_I^N) for band I [1] in the visible spectrum of the neutral macrocycle.

TABLE 3

The extent of protonation of compounds A—C in toluene–acetic acid mixtures at 25 °C

A		B		C	
v/v Acetic acid (%)	2 + $\log_{10}\left(\frac{c_P}{c_N}\right)$	v/v Acetic acid (%)	2 + $\log_{10}\left(\frac{c_P}{c_N}\right)$	v/v Acetic acid (%)	2 + $\log_{10}\left(\frac{c_P}{c_N}\right)$
20	0·777	30	1·137	10	0·450
37	1·356	40	1·673	20	1·177
44	1·548	50	1·884	40	1·893
52	1·834	60	2·200	50	2·165
60	2·237	70	2·636	60	2·398
68	2·649	80	3·308	70	2·887
76	3·064			80	3·199

and G existed virtually completely in their protonated forms at much lower (<5% v/v) acetic acid concentrations. The spectra of the two compounds in 5—90% v/v acetic acid were independent of solvent composition showing that medium effects on the spectra of the protonated compounds were negligible. The absorption maxima and extinction coefficients of D (Figure 2) and G (Figure 3) in their neutral and protonated forms are listed in Table 4. Both compounds underwent further protonation in solutions of sulphuric acid in acetic acid. The spectra of the species which resulted from the protonation equilibrium in sulphuric acid–acetic acid mixtures are shown in Figures 2 and 3 and the positions and extinction coefficients of their absorption maxima are given in Table 4. Spectra were measured for a series of concentrations of sulphuric acid in acetic acid and, by use of an equation analogous to equation (1), enabled the calcuation of the protonation ratios (c_S/c_P) where c_P and c_S are the concentrations of the species formed by protonation of the compounds in toluene–acetic acid mixtures and in sulphuric acid–acetic acid mixtures respectively. The results are given in Table 5, together with the ratios (c_P/c_N) for the protonation equilibrium which occurs in solutions of acetic acid in toluene.

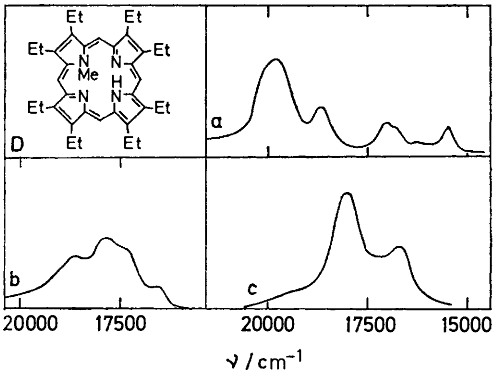

FIGURE 2 Visible spectra of compound D in (a) toluene, (b) toluene (10% v/v)–acetic acid (90% v/v), and (c) 2·98 × 10^{-4}M-H_2SO_4 in acetic acid

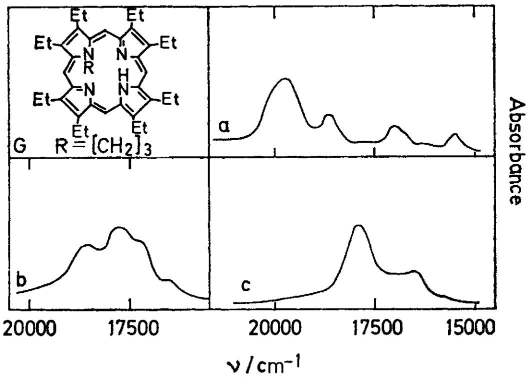

FIGURE 3 Visible spectra of compound G in (a) toluene, (b) toluene (20% v/v)–acetic acid (80% v/v), and (c) 0·037M-H_2SO_4 in acetic acid

TABLE 4

Spectral data for compounds D and G ($\tilde{\nu}_{max.}$/cm^{-1})

Compd.	Solvent					
D	Toluene	$\tilde{\nu}_{max.}$	15,450	17,000	18,650	19,750
		($\varepsilon_{max.}/\varepsilon_I^N$)†	1·00	1·35	2·15	4·30
D	10% Toluene 90% acetic acid	$\tilde{\nu}_{max.}$	16,550	17,300	17,850	18,600
		($\varepsilon_{max.}/\varepsilon_I^N$)†	0·95	2·55	3·25	2·20
D	2·98 × 10^{-4}M-H_2SO_4 in acetic acid	$\tilde{\nu}_{max.}$	16,700	18,000		
		($\varepsilon_{max.}/\varepsilon_I^N$)†	1·95	3·95		
G	Toluene	$\tilde{\nu}_{max.}$	15,450	17,000	18,650	19,750
		($\varepsilon_{max.}/\varepsilon_I^N$)†	1·00	1·52	2·37	4·42
G	20% Toluene 80% acetic acid	$\tilde{\nu}_{max.}$	16,500	17,250	17,800	18,550
		($\varepsilon_{max.}/\varepsilon_I^N$)†	0·90	2·53	3·32	2·21
G	0·037M *-H_2SO_4 in acetic acid	$\tilde{\nu}_{max.}$	16,500	17,900		
		($\varepsilon_{max.}/\varepsilon_I^N$)†	1·74	3·89		

* Spectrum unchanged for G in 7·5M-H_2SO_4 in acetic acid. † See footnote to Table 2.

The spectrum of compound F (Figure 4a) was independent of solvent composition for toluene–acetic acid mixtures in the range 0—80% v/v acetic acid. However in acetic acid (Figure 4b) the spectrum was distinctly different from that in toluene showing that protonation of the neutral compound occurs in the 80—100% v/v range of acetic acid concentration. In solutions of sulphuric acid in acetic acid two further distinct protonation equilibria were apparent. At low sulphuric acid concentrations a protonation occurred which was complete (Figure 4c) for $c_{H_2SO_4}$ = *ca.* 10^{-4} mol l^{-1}. No further change in the spectrum was observed for sulphuric acid concentrations up to *ca.* 0·5 mol l^{-1}. At higher concentrations further protonation occurred and was complete (Figure 4d) for $c_{H_2SO_4}$ = *ca.* 7 mol l^{-1}. The protonation ratios for both the equilibria which occurred in solutions of sulphuric acid were measured as a function of acid concentration (Table 6). The absorption maxima and corresponding extinction coefficients for compound F and the products of the three consecutive protonation equilibria are given in Table 7.

The spectra of compound E in toluene and in acetic acid are given in Figure 5. The protonation equilibrium was studied in detail and protonation ratios for 5—35% v/v acetic acid in toluene were evaluated (Table 8). The spectrum of compound E in acetic acid was unaffected by the addition of sulphuric acid up to a concentration of *ca.* 0·1 mol l^{-1}. At higher concentrations of sulphuric acid two further protonation equilibria were apparent but occurred in overlapping ranges of acid concentration. The overlap precluded the measurement of protonation ratios for the equilibria. Inspection of the spectra showed that the two

TABLE 5

The extent of protonation of compounds D and G in toluene–acetic acid mixtures, and the protonation ratios for the further protonation which occurs in solutions of sulphuric acid in acetic acid

(*a*)

Compound D v/v Acetic acid (%)	Compound D $2 + \log_{10}\left(\frac{c_P}{c_N}\right)$	Compound G v/v Acetic acid (%)	Compound G $2 + \log_{10}\left(\frac{c_P}{c_N}\right)$
0·4	1·601	1·0	1·952
0·8	1·840	2·0	2·510
1·2	2·304	3·0	2·782
1·6	2·775	4·0	3·167
2·0	3·269		

(*b*)

$10^5c_{H_2SO_4}$	$2 + \log_{10}\left(\frac{c_S}{c_P}\right)^a$	$10^5c_{H_2SO_4}$	$2 + \log_{10}\left(\frac{c_S}{c_P}\right)$
2·98	0·372	5·97	1·172
4·47	0·942	6·72	1·645
5·97	1·385	7·45	2·405
7·45	1·653	7·45	2·405
8·20	2·279	8·20	2·669
8·96	2·681	8·96	2·705
11·18	3·215	9·70	2·927

[a] Stoicheiometric concentration of D *ca.* 1·24 × 10^{-5} mol l^{-1}.
[b] Stoicheiometric concentration of G *ca.* 1·04 × 10^{-5} mol l^{-1}.

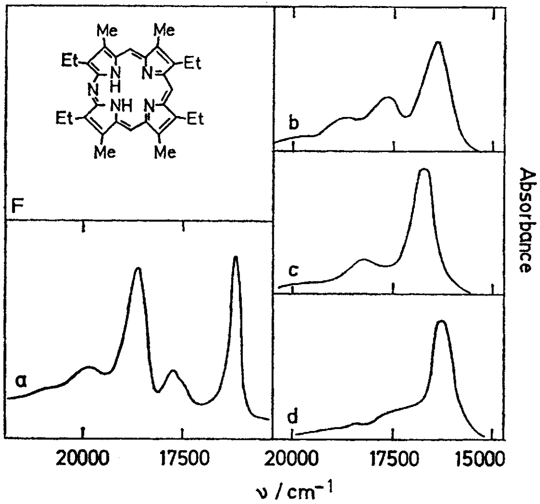

FIGURE 4 Visible spectra of compound F in (a) toluene, (b) acetic acid, (c) 3·73 × 10^{-4}M-H_2SO_4 in acetic acid, and (d) 11·2M-H_2SO_4 in acetic acid

TABLE 6

Protonation ratios for compound F in solutions of sulphuric acid in acetic acid at 25 °C. The ratios (c_S/c_P) and (c_R/c_S) refer to the protonation equilibria which occur with sulphuric acid at low and high concentrations respectively

$10^5c_{H_2SO_4}$ (mol l^{-1})	$2 + \log_{10}\left(\frac{c_S}{c_P}\right)^*$	$c_{H_2SO_4}$ (mol l^{-1})	$2 + \log_{10}\left(\frac{c_R}{c_S}\right)$
1·49	0·620	0·746	0·237
2·98	1·134	1·49	1·127
3·73	1·398	2·24	1·924
4·47	1·750	2·98	2·104
5·22	2·250	3·35	2·549
5·97	2·501	3·73	2·805
6·34	2·866	4·47	3·033
		5·22	3·455

* Stoicheiometric concentration of F = 4·8 × 10^{-5} mol l^{-1}.

TABLE 7

Spectral data for compound F($\bar{\nu}_{max.}$/cm^{-1})

Solvent					
Toluene	$\bar{\nu}_{max.}$	16,250	17,800	18,650	19,800
	$(\varepsilon_{max.}/\varepsilon_I^N)^*$	1·00	0·31	0·93	0·32
Acetic acid	$\bar{\nu}_{max.}$	16,400	17,700	18,850	
	$(\varepsilon_{max.}/\varepsilon_I^N)^*$	0·72	0·47	0·41	
7·5 × 10^{-3}M-H_2SO_4 in acetic acid	$\bar{\nu}_{max.}$	16,700	18,100		
	$(\varepsilon_{max.}/\varepsilon_I^N)^*$	0·73	0·18		
8·2M-H_2SO_4 in acetic acid	$\bar{\nu}_{max.}$	16,250	17,600		
	$(\varepsilon_{max.}/\varepsilon_I^N)^*$	1·10	0·22		

* See footnote to Table 2.

TABLE 8

The extent of protonation of compound E in toluene–acetic acid mixtures at 25 °C

v/v Acetic acid (%)	$2 + \log_{10}\left(\frac{c_P}{c_N}\right)$	v/v Acetic acid (%)	$2 + \log_{10}\left(\frac{c_P}{c_N}\right)$
5	0·972	25	2·245
10	1·374	30	2·522
15	1·626	35	2·673
20	2·077		

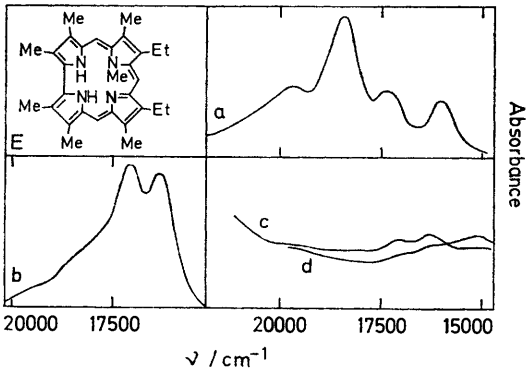

FIGURE 5 Visible spectra of compound E in (a) toluene, (b) acetic acid, (c) 2·24M-H_2SO_4 in acetic acid, and (d) 2·98M-H_2SO_4 in acetic acid

successive protonation steps were 50% complete at sulphuric acid concentrations of *ca.* 1 and 7·5 mol l⁻¹. The spectrum of the species formed at the lower sulphuric acid conconcentrations could not be measured because compound E does not exist entirely as that species in any solution of sulphuric acid in acetic acid. Spectra of solutions in which E exists predominantly as the species were comparatively featureless in the 15,000—20,000 cm⁻¹ spectral range (Figures 5c and d). The protonation which occurred at high sulphuric acid concentrations led to the complete disappearance of the intense Soret band in the spectrum at 23,800 cm⁻¹ and is thus associated with interruption of the aromatic chromophore. This results from protonation at the C-5 *meso*-position.[12] An intense band with a maximum in the range 23,500—26,500 cm⁻¹ appeared in all the spectra, for all the neutral compounds and their protonated forms, recorded in the present work except for the product of the final protonation of compound E for which the spectra are shown in Figure 6. The Soret band (Figure 6a) is replaced by a much weaker band (Figure 6c) at 27,300 cm⁻¹ ($\varepsilon_{max.} \approx$ 33,000 l mol⁻¹ cm⁻¹). The absorption maxima in the range 15,000—20,000 cm⁻¹ and the corresponding extinction coefficients for compound E in toluene–acetic acid, and concentrated sulphuric acid in acetic acid are given in Table 9.

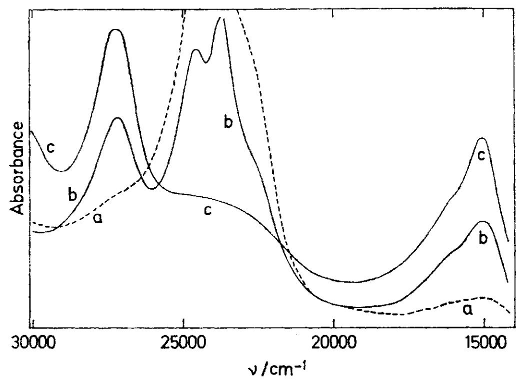

FIGURE 6 Spectra of compound E in (a) 2·98M-H_2SO_4 in acetic acid, (b) 7·45M-H_2SO_4 in acetic acid, and (c) 14·90M-H_2SO_4 in acetic acid

TABLE 9

Spectral data for compound E ($\bar{\nu}_{max.}$/cm⁻¹)

Solvent					
Toluene	$\bar{\nu}_{max.}$	16,000	17,400	18,400	19,700
	$(\varepsilon_{max.}/\varepsilon_I^N)$*	1·00	1·18	2·60	1·27
Acetic acid	$\bar{\nu}_{max.}$	16,300	17,050		
	$(\varepsilon_{max.}/\varepsilon_I^N)$*	2·84	3·02		
11·2M-H_2SO_4 in acetic acid	$\bar{\nu}_{max.}$	15,100			
	$(\varepsilon_{max.}/\varepsilon_I^N)$*	4·47			

* See footnote to Table 2.

DISCUSSION

The visible spectra of compounds D and G in acetic acid are characteristic of monocations formed by single protonation of the neutral compounds. Similarly the spectra of compounds A and B in acetic acid are more similar to typical spectra of monocations than of dications.[1,2] The spectra of the two corroles C and E in acetic acid may also be assigned to monocations after consideration of the protonation behaviour of the corroles in toluene–acetic acid mixtures. The variation of $\log_{10}(c_P/c_N)$ with solvent composition for the six macrocycles A—G is shown in Figure 7. The curves for A—C and E are approximately parallel where protonation occurs in overlapping ranges of acetic acid concentration.

The acid dissociation of a macrocycle monocation SH^+ in toluene–acetic acid mixtures may be represented by equilibrium (2) in which S is the neutral unprotonated

$$SH^+ + CH_3CO_2H \rightleftharpoons S + CH_3CO_2H_2^+ \qquad (2)$$

macrocycle. The variation of the protonation ratio (c_{SH^+}/c_S) with solvent composition is therefore given by equation (3) in which *a* represents an activity and *y* an activity coefficient such that $a_i = c_i y_i$ for species i, and

$$\log_{10}\left(\frac{c_P}{c_N}\right) = \log_{10}\left(\frac{c_{SH^+}}{c_S}\right)$$
$$= pK_1^S + \log_{10}\left(\frac{y_S a_{CH_3CO_2H_2^+}}{y_{SH_+} a_{CH_3CO_2H}}\right) \qquad (3)$$

K_1^S is the equilibrium constant for equation (2). The activities and activity coefficients may be referred to standard states in acetic acid solvent. The identities given in equation (4) are therefore valid for 100%

$$y_S = y_{SH^+} = y_{CH_3CO_2H^+} = a_{CH_3CO_2H^+} = 1 \qquad (4)$$

acetic acid and concentrations of S and SH^+ approaching infinite dilution. This treatment ascribes the variation of activity coefficients with solvent composition entirely to medium effects involving transfer of species from acetic acid to toluene–acetic acid mixtures. Variations in activity coefficients due to the finite concentrations of S and SH^+ in the solutions are ignored. This is acceptable since the concentrations of S required for the present spectroscopic study never exceeded 5 × 10⁻⁵ mol l⁻¹. The equilibrium constant K_1^S is the acid dissociation constant of SH^+ in acetic acid.

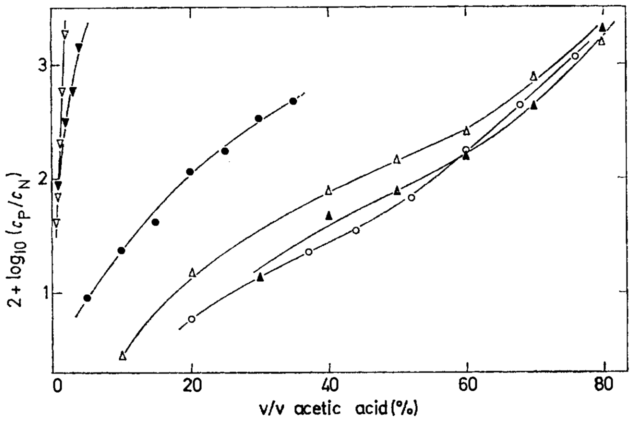

FIGURE 7 The variation of $\log_{10}(c_P/c_N)$ with the concentration of acetic acid in toluene–acetic acid mixtures for compounds A (○), B (▲), C (△), D (▽), E (●), and G (▼)

The protonation ratio of another macrocycle R is

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[12] M. J. Broadhurst, R. Grigg, G. Shelton, and A. W. Johnson, *J.C.S. Perkin I*, 1972, 143.

given by a similar equation to (3) and is related to the protonation ratio of S by equation (5). It follows

$$\log_{10}\left(\frac{c_{\mathrm{SH}^+}}{c_{\mathrm{S}}}\right) - \log_{10}\left(\frac{c_{\mathrm{RH}^+}}{c_{\mathrm{R}}}\right) = \mathrm{p}K_1{}^{\mathrm{S}} - \mathrm{p}K_1{}^{\mathrm{R}} + \log_{10}\left(\frac{y_{\mathrm{S}}y_{\mathrm{RH}^+}}{y_{\mathrm{R}}y_{\mathrm{SH}^+}}\right) \quad (5)$$

that $\log_{10}(c_{\mathrm{P}}/c_{\mathrm{N}})$ for two macrocycles will be parallel functions of acetic acid concentration providing that the same number of protons are added in the two protonation equilibria and that the activity coefficient term in equation (5) is insensitive to solvent composition. The latter condition is probably valid providing the two molecules R and S are of similar chemical structure.[13] The results shown in Figure 7 therefore confirm that the protonations of the two porphyrins A and B and the two corroles C and E in toluene–acetic acid mixtures involve the addition of the same number of protons in each case. The spectroscopic evidence is consistent with the addition of a single proton and the existence of porphyrins and corroles as monocations in acetic acid. A quantitative comparison of the basicities of the porphyrins supports this conclusion.

Equation (5) allows a quantitative comparison of the acid dissociation constants of molecules *via* the vertical distances parallel to the ordinate axis between parallel curves in Figure 7. Although exact parallelism is not maintained, and would be fortuitous,[13] comparison of the curves has enabled the deduction of the series of relative $\mathrm{p}K_1$ values listed in Table 10. As an added indication of the relative basicities the acetic acid, concentrations at which 50% protonation of the macrocycles occurs are also given. The deduction of the $\mathrm{p}K_1$ values involved neglect of the influence on the protonation equilibria of ion pairing between the monocations and the acetate counterions formed by proton transfer from acetic acid to the macrocycles [equation (6)].

TABLE 10

Relative values of the acid dissociation constants of the monocations of seven macrocycles in toluene–acetic acid mixtures at 25 °C

Macrocycle	$(\mathrm{p}K_1 - \mathrm{p}K_1{}^{\mathrm{A}})$	v/v Acetic acid (%) (50% protonation)
A	0	56
B	0·10	54
C	0·35	44
D	4·09	0·9
E	1·28	20
F	<0	*ca.* 80—90
G	3·64	1·1

$$\mathrm{S} + \mathrm{CH_3CO_2H} \rightleftharpoons \mathrm{SH^+} + \mathrm{CH_3CO_2^-} \rightleftharpoons \mathrm{SH^+{\cdot}CH_3CO_2^-} \quad (6)$$

The influence of ion pairing is impossible to assess and may in part be responsible for the lack of parallelism between the plots of $\log_{10}(c_{\mathrm{P}}/c_{\mathrm{N}})$ against acetic acid concentration. The errors in $\mathrm{p}K_1$ incurred by neglect of ion pairing cannot be estimated. However the values will give a reliable indication of the relative basicities of the macrocycles. The absolute $\mathrm{p}K_1$ values for the macrocycles in acetic acid cannot be deduced from the present measurements and therefore the values in Table 10 are quoted with respect to $K_1{}^{\mathrm{A}}$, the acid dissociation constant of compound A.

The similarity between the basicities of compounds A and B is expected since the replacement of the methyl groups in aetioporphyrin I by ethyl groups should have little effect. However *N*-methyl substitution causes an appreciable increase in basicity. The magnitude of the difference (4·09 units) between the $\mathrm{p}K_1$ values for compound A and its 21-methyl analogue (D) is too great to arise solely from the electronic effect of the methyl group. The increased basicity is probably caused by steric strain which results from the presence of the 21-methyl substituent. The effect of *N*-methyl substitution on the basicity of a porphyrin has also been reported by Neuberger and Scott[2] who measured the apparent acid dissociation constants K' of the monoprotonated forms of coproporphyrin I and *N*-methylcoproporphyrin I in aqueous solutions of ionic strength 0·1 mol l^{-1}. The values were $\mathrm{p}K' = 7{\cdot}1$ for the monocation of coproporphyrin I and $\mathrm{p}K' = 11{\cdot}3$ for its *N*-methyl analogue. These values are consistent with the present results for octaethylporphyrin despite the added complication for the coproporphyrins of the ionization of carboxylic acid groups.

The conclusion that compound A exists as its monocation in acetic acid solution is confirmed by the further protonation to the dication which occurs in solutions of sulphuric acid in acetic acid (Figure 1d). The clear distinction between the first and second protonation steps of A is consistent with Neuberger and Scott's[2] estimate that the first and second dissociation constants of the dications of porphyrins such as aetioporphyrin in water differ by *ca.* 3 units on the p*K* scale. The present results are in accord with a difference of at least 3 p*K* units in acetic acid solvent. The monocations of D and G were also protonated to give the dications (Figures 2c and 3c) in dilute solutions of sulphuric acid in acetic acid. The variation of the protonation ratios with sulphuric acid concentration agrees closely for the two porphyrins (Figure 8). The dissociation constants for the first dissociation of the dications derived from D and G must be equal to within ±0·1 p*K* units. The acid dissociation constant $K_2{}^{\mathrm{S}}$ of a porphyrin dication $\mathrm{SH_2}^{2+}$ in acetic acid is given by equation (7) which combined with equation (3) leads to equation (8).

$$K_2{}^{\mathrm{S}} = (a_{\mathrm{CH_3CO_2H_2^+}}a_{\mathrm{SH^+}}/a_{\mathrm{CH_3CO_2H}}a_{\mathrm{SH_2^{2+}}}) \quad (7)$$

$$\log_{10}\left(\frac{c_{\mathrm{SH}^+}}{c_{\mathrm{S}}}\right) - \log_{10}\left(\frac{c_{\mathrm{SH}^{2+}}}{c_{\mathrm{SH}^+}}\right) = \mathrm{p}K_1{}^{\mathrm{S}} - \mathrm{p}K_2{}^{\mathrm{S}} + \log_{10}\left(\frac{y_{\mathrm{S}}}{y_{\mathrm{SH_2^{2+}}}}\right) \quad (8)$$

Extrapolation of the protonation ratios of the monocations of D and G to $c_{\mathrm{H_2SO_4}} = 0$ (Figure 8) suggests that $\log_{10}(c_{\mathrm{SH_2^{2+}}}/c_{\mathrm{SH^+}}) < -3$ for these compounds in acetic acid. Similar extrapolation of the protonation ratios of the neutral porphyrin A (Figure 7) to 100%

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[13] C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.

acetic acid, and combination with the data in Table 10, shows that $\log_{10}(c_{SH^+}/c_S) \approx 6{\cdot}3$ for compounds D and G in acetic acid. Hence, taking $y_S \approx y_{SH_2^{2+}} \approx 1$, the difference between pK_1 and pK_2 for the two dissociations of the dications derived from compounds D and G is >*ca.* 9·3 units. This figure compares with those of 10·6 and *ca.* 7·3—8·3 reported for *N*-methylcoproporphyrin I and its tetramethyl ester respectively in water.[2] Equation (7) leads to equation (9) in which pH* is a pH scale referred to 100% acetic acid as standard state. Half protonation ($c_{SH^+} = c_{SH_2^{2+}}$) of D and G occurred at $c_{H_2SO_4} = 7{\cdot}5 \times 10^{-5}$ mol l^{-1}.

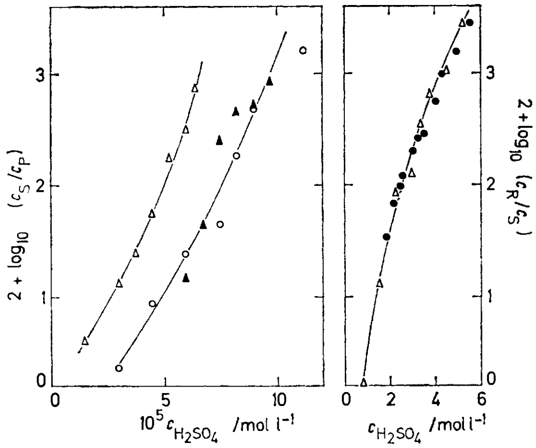

FIGURE 8 The variation of the protonation ratios with concentration of sulphuric acid in acetic acid for compounds D (○), G (▲), and F (△). Points ● are Hall and Spengeman's data[16] for the protonation of 2,4-dichloro-6-nitroaniline (at *ca.* 23 °C)

$$\begin{aligned} pH^* &= -\log_{10} a_{CH_3CO_2H_2^+} \\ &= pK_2^S + \log_{10}\left(\frac{c_{SH^+}}{c_{SH_2^{2+}}}\right) + \log_{10}\left(\frac{y_{SH^+}}{y_{SH_2^{2+}}}\right) \quad (9) \end{aligned}$$

It follows, even if sulphuric acid were a strong acid in acetic acid, that $pK_2^S >$ *ca.* 4 for the dications of D and G in acetic acid.

The aza-porphyrin F exists as the monocation (Figure 4b) in acetic acid. The protonation of the monocation in dilute solutions of sulphuric acid in acetic acid gives rise to the dication for which the spectrum (Figure 4c) is similar to that of the dianion formed by the loss of two protons from F.[14] The concentrations of sulphuric acid which caused protonation of the monocation of F were less than the stoicheiometric concentrations of F which were added to the solutions (Table 6). The variation of protonation ratio with sulphuric acid concentration is therefore a spectroscopic titration curve in which the progressive protonation of the monocation is to some extent buffering the pH* of the solution. The results indicate that the monocation of F is a stronger base (probably by *ca.* 1 p*K* unit) than the monocations of D or G in acetic acid.

Potentiometric data for the titration of some porphyrins (including compound B) with perchloric acid in acetic acid solution have shown that two moles of perchloric acid were required to titrate the basic species generated in acetic acid by one mole of porphyrin.[15] The suggestion [2] that the titration involves neutralization of one pair of acetate anions per porphyrin molecule is based on the assumption that the porphyrins exist as their dications in acetic acid. This suggestion is not compatible, at least for compound B, with the conclusion reported here that B exists as its monocation in acetic acid. The stoicheiometry of the reaction which occurs during titration is probably more correctly represented by equation (10) and involves the neutralization of one acetate ion and the protonation of one cation per porphyrin molecule.

$$SH^+ + CH_3CO_2^- + 2HClO_4 \longrightarrow SH_2^{2+} + CH_3CO_2H + 2ClO_4^- \quad (10)$$

The further protonation of the dication of F which occurs at high sulphuric acid concentrations involves the addition of one proton to each dication. Thus the protonation ratios give a nearly identical variation with sulphuric acid concentration to the ratios observed by Hall and Spengemen [16] for the protonation of 2,4-dichloro-6-nitroaniline ($pK_{SH^+} = -3{\cdot}29$ in water at 25 °C) [13] in the same solutions (Figure 8). The protonation of the dication derived from F therefore gives an acid species for which the first dissociation constant K_3 in water is probably given by $pK_3 \approx -3{\cdot}3$. This conclusion is based on the assumption that the acidity function behaviour [13] (with all activity coefficients referred to water as standard state) is identical for the protonation of 2,4-dichloro-6-nitroaniline and of the dication derived from compound F in solutions of sulphuric acid in acetic acid. The identity of the curves in Figure 8 and the parallelism between the H_0 acidity functions for solutions of sulphuric acid in water and in acetic acid [16] suggest that the estimate of pK_3 in water is reliable to within ±0·2 units. The addition of a third proton to compound F presumably involves protonation of the *meso*-nitrogen atom.

The *N*-methyl substituted corrole E exists as its monocation in acetic acid. The formation of the dication in sulphuric acid–acetic acid solutions requires a higher concentration of sulphuric acid (*ca.* 1 mol l^{-1} for 50% protonation) than is necessary for the corresponding formation of the dication of the *N*-methyl substituted porphyrin D. The neutral corrole E is similarly a weaker base than D (Table 10). Present knowledge concerning the protonation of corroles is insufficient to enable the site at which the second proton is added to be decided, but the presence of the Soret band rules out protonation on sites which would interrupt the aromatic chromophore. The addition of a third proton causes the disappearance of the Soret band from the spectrum which suggests that the protonation site is the C-5 *meso*-position.[12]

[2/1069 *Received*, 11*th May*, 1972]

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[16] N. F. Hall and W. F. Spengemen, *J. Amer. Chem. Soc.*, 1940, **62**, 2487.