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PORPHYRIN ACIDS

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Abstract—The structural change from the porphyrin free base to monoacid and diacid by successive protonation has been studied by the IR, visible and NMR spectroscopy. The results have indicated that the cation and anion of the porphyrin diacid are strongly associated through H-bonding. The far IR spectra show especially marked differences in the free base, monoacid, and diacid due to the changes of the inner core of the porphyrin ring.

INTRODUCTION

The chemical behavior of porphyrin monoacid and diacid has been a subject of much interest since recent investigations have provided reliable evidence to support the porphyrin acid as the most probable reaction intermediate in metal incorporation processes.[1,2] The X-ray crystallographic study of $\alpha,\beta,\gamma,\delta$-tetraphenylporphin acid has concluded that the original porphyrin ring deforms to lose planarity by the crowding of four inner protons.[3] Recently it has been suggested that the deformation of porphyrin ring plays an important role in metal incorporation and protonation.[4,5] However, the spectroscopic studies on the structure of porphyrin acid have been limited to the visible and NMR measurements in acid solution such as HCl aq, $HClO_4$ aq and CF_3COOH.[6-9] Furthermore, no investigation on the structure of chemically isolated monoacid has been reported for the sake of troublesome handling in separation.

The main purpose of this work is to report the spectroscopic studies on the chemically isolated porphyrin monoacid and diacid in solution and solid state to elucidate structural change of porphyrin ring due to successive protonation.

EXPERIMENTAL

Materials. Octaethylporphyrin ($OEPH_2$) was prepared according to the procedure of Inhoffen *et al.*[10] and purified by chromatography on alumina (Brockmann, Grade III) with chloroform.

General preparative method for diacids **1–4**. To 100 mg of $OEPH_2$ in 20 ml of conc acid [HCl (**1**), HI (**2**), $HClO_4$ (**3**) and HBF_4 (**4**)] MeOH was added until the free base dissolved completely. The soln was concentrated to a small volume. Deep purple crystals were obtained on standing at room temp, washed with ether, and dried over P_2O_5 *in vacuo*. The presence of anion was confirmed by the characteristic IR absorptions; 1140, 1150, 645 and 632 cm^{-1} for ClO_4^-, 1150, 1030, 535 and 524 cm^{-1} for BF_4^- and 132 cm^{-1} for I_3^-.[11,12]

Monoacid **5**.[†] A solution of **2** (100 mg) in 50 ml MeOH was refluxed until reddish orange crystals precipitated. The crystals were collected, washed with MeOH and dried over P_2O_5 *in vacuo*. Analytical values, NMR data with the N—H ··· stretching vibration and visible spectra are listed in Tables 1, 2 and 3 respectively.

Deuteration of the inner N—H hydrogen atoms of diacids **2** and **4** was completed by dissolving 10 mg of the diacid into 1 ml of CH_3OD purchased from Merck Co., and stirring for 3 hr at room temp. The N-deuterated monoacid was obtained by refluxing of **2** in CH_3OD.

Spectral measurements. IR spectra were obtained using a Beckman IR-12 and a Hitachi G-3 spectrophotometers. The IR spectra were measured in $CDCl_3$ soln (4000–1500 cm^{-1}), KBr disk (4000–400 cm^{-1}) and Nujol mull (4000–400 cm^{-1}). Far-IR spectra were obtained using a Perkin-Elmer-Hitachi FIS-3 far-IR spectrophotometer. Calibration of frequency reading was made with polystyrene film and water vapor. The NMR spectra were determined in $CDCl_3$ with a Varian HA 100 instrument. The visible spectra were measured on a Hitachi EPS-3T spectrophotometer.

RESULTS AND DISCUSSION

Table 2 lists the NMR chemical shifts of the —CH= and N—H protons, and the IR frequency of the N—H stretching vibration of the diacids and free base in $CDCl_3$. These two proton chemical shifts show no appreciable concentration dependency in the region of $8 \sim 27 \times 10^{-3}$ M. The —CH= and N—H chemical shifts of the porphyrin free base in CF_3COOH appear at lower magnetic field and higher magnetic field, respectively, in comparison with the corresponding chemical shifts in $CDCl_3$.[14]

The visible spectrum measurement shows that the free base in large amount of CF_3COOH is exclusively converted into the porphyrin dication. The

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[†] Samuels *et al.* have obtained the compounds formulated as $C_{36}H_{48}N_4I_4$ and $C_{36}H_{47}N_4I_3$ by treatment of $OEPH_2$ with iodine in AcOH.[13] Although they have never mentioned about their chemical structures, these compounds are concluded as monoacid and diacid in comparison with the visible spectra of **2** and **5**.

Table 1. Elemental analysis

Compound	Molecular Formula	Calcd (%) C	H	N	I	Found (%) C	H	N	I
1	$C_{36}H_{48}N_4Cl_2$	71·15	7·96	9·22		70·89	7·81	8·89	
2	$C_{36}H_{48}N_4I_4$	41·40	4·63	5·37	48·61	41·40	4·66	5·31	47·88
3	$C_{36}H_{48}N_4O_8Cl_2$	58·77	6·58	7·62		58·33	6·41	7·49	
4	$C_{36}H_{48}N_4F_8B_2$	60·86	6·81	7·89		60·01	6·91	8·01	
5	$C_{36}H_{47}N_4I_3$	47·17	5·17	6·11	41·54	47·43	5·20	5·87	41·42

Table 2. NMR and prominent IR data of $OEPH_2$ and OEP-diacids*

	Chemical shift (τ) and multiplicity (Hz)				ν(N—H)[c] (cm^{-1})
Compound	=CH—	—CH$_2$—	—CH$_3$—	—NH—	
1	−0·49 (s)	5·96 (q) (J = 7·4)	7·96 (t) (J = 7·5)	12·07 (s)	2950
3	−0·58 (s)	5·90 (q) (J = 7·4)	8·20 (t) (J = 7·5)	14·58 (s)	3210
4	−0·61 (s)	5·87 (q) (J = 7·4)	8·17 (t) (J = 7·5)	14·92 (s)	3290
$OEPH_2$	−0·18[a]			13·74[a]	3315
$OEPH_2$	−0·98[b]			14·65[b]	

*The NMR measurement of 5 was not successful because of its low solubility in $CDCl_3$.

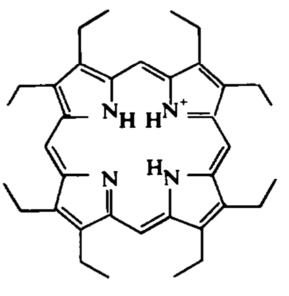
[a] Ref. 10.

[b] Values measured in CF_3COOH.[13]

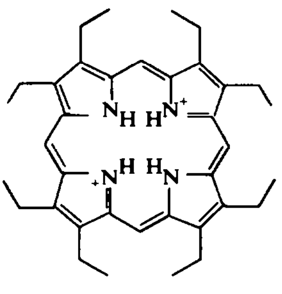
[c] Measured in $CDCl_3$. The diacid (2) shows strong and broad band at 3025 cm^{-1} in KBr disk.

Table 3. Electronic spectra of OEP-acids

Compound	$\lambda_{max}^{CHCl_3}$ nm (log ε)
1	419 (5·25); 554 (4·18); 559 (4·17); 577 (3·78); 599 (3·98)
2	404 (5·37); 563 (3·98); 587 (3·70); 605 (3·56)
3	408 (5·55); 551 (4·17); 554 (4·16); 576 (3·74); 597 (3·92)
4	405 (5·50); 550 (4·17); 554 (4·16); 575 (3·75); 595 (3·89)
5	397 (5·24); 534 (3·95); 560 (4·08); 572 (3·98); 604 (3·58)

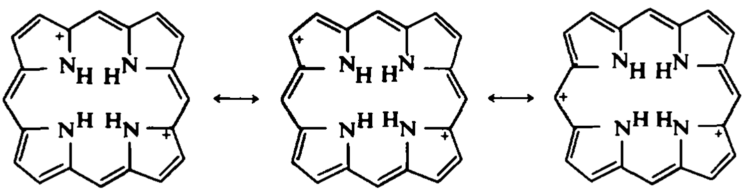


$OEPH_3^+$



$OEPH_4^{2+}$

changes of chemical shifts in CF_3COOH have been interpreted by the increase of ring current field strength due to the additional cannonical structures expanding 18π electron system to the outer 20-membered ring as is shown below.[15] The NMR spectra of the porphyrin diacids in $CDCl_3$ show marked shifts for the —CH= and —NH protons in comparison with those of the free base. Especially the latter value is considerably dependent on the anion as is seen in Table 2. The large down-field shift of —NH protons of 1 indicates that chloride ion interacts strongly with the inner protons. Pres-



ent results cannot be merely explained by the change in the ring current. The IR spectra of the porphyrin diacids in $CDCl_3$ exhibit a strong absorption in the region from 2950 to 3290 cm^{-1} assigned to the N—H stretching vibration (ν(N—H)). The ν(N—H) of the porphyrin diacids are lower than that of the free base and are markedly dependent on the paired anion in the aprotic solvent.

The present results are most probably explained in terms of the strength of H-bond between the N—H proton and the anion. Consequently, the stronger association results in the more deshielding of the N—H protons and the higher electron density of the methine C atom due to the migration of negative charge from anion to the positively charged porphyrin core. The porphyrin diacid in the aprotic solvent is very akin to the ion-paired structure as has been proposed in the metal incorporation process.[2] The visible spectrum of the diacid shows slight shift with change of the anion as is shown in Table 3.

The visible spectrum of **2** in methanol is entirely different from the spectrum measured in chloroform and shows similar spectrum of the monoacid as is shown in Fig 1. This fact indicates that the diacid **2** dissociates into the monoacid and hydrogen iodide in the protic solvent as is shown below. Moderate heating of **2** in methanol gave the reddish orange crystals of **5** in quantitative yield.

$$\mathrm{OEPH_4^{++}(I^-)(I_3^-)} \xrightarrow[\mathrm{CH_3OH}]{} \mathrm{OEPH_3^{+}(I_3^-) + HI}$$

Conversion to the monoacid was monitored by the visible spectrum. The monoacid shows two sharp IR absorptions at 3330 cm^{-1}, which are rather higher frequency bands than those of the diacids and comparable to those of the free base. This experimental result suggests that the association between the monocation and I_3^- anion through hydrogen bonding is smaller than the interaction between the dication and the anions. Appreciable stability of the monoacid in the solid state might be attributed to relatively large size of the I_3^- in crystalline space.

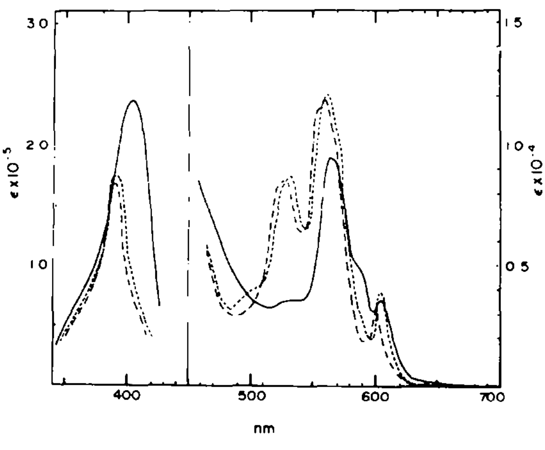


Fig 1. Visible spectra of7 **2** (———, in $CHCl_3$, –·–·–, in CH_3OH) and **5** (--- in $CHCl_3$).

Fig 2 demonstrates the IR spectra of the free base, the monoacid (**5**) and the diacid (**2**) from 4000 to 400 cm^{-1} in the KBr pellet. The diacids **1**–**4** show almost the same spectra except for the absorptions due to the anion group. Stone and Fleischer have reported that the region of greatest difference in the IR spectra of the free base and diacid of tetraphenylporphin (TPP) is 1500 ~ 1100 cm^{-1}.[3] The band at 1350 cm^{-1} in the free base due to the C—N stretching vibration almost disappear in the diacid. The diacid shows a strong absorption at 1225 cm^{-1}, of which assignment has never been established. However, the IR spectra of the free base, monoacid and diacids of $OEPH_2$ are different from the cases of TPP.

Marked differences among the IR spectra of the free base, monoacid and diacid have been found in the KBr region and even in the far-IR region. Firstly, the two bands at 1675 and 1607 cm^{-1} of the free base are almost free in the diacid. The corresponding bands still remain as weak bands in the monoacid. The diacid shows a strong absorption at 1520 cm^{-1} and the monoacid shows two band of medium strength at 1526 and 1506 cm^{-1}, whereas a very weak band is observed at 1498 cm^{-1} for the free base. The two bands of the free base are mainly due to the C—N and C—C stretching vibrations of the neutral pyrrolic rings. Characteristic band at around 1500 cm^{-1} of the acids is probably attributed to the C—N stretching vibration of the protonated pyrrolic ring. This explanation can be rationalized by the increase of the C—N bond length of the protonated pyrrolic ring. If the positive charges delocalize at the outer 20-membered ring, the C—N bond order is reduced. Secondly, the monoacid and diacid show two strong absorptions and one broad strong absorption at around 560 cm^{-1}, respectively. The corresponding band is entirely free in the free base. Since those bands disappear upon deuteration of the inner NH protons, they are reasonably assigned to the N—H out-of-

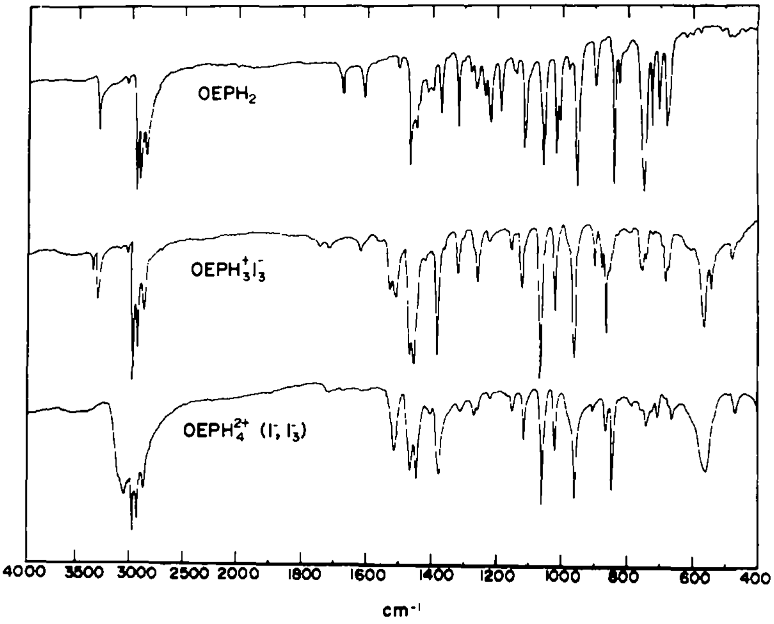


Fig 2. I.R. spectra of the free base, **5** and **2**.

plane deformations. It is noted that the N—H out-of-plane deformations appear at considerably higher frequency region (745 cm^{-1}) than those of the acids. Thirdly, the far-IR spectra of the free base and the acids exhibit remarkable difference. Fig 3 demonstrates the far-IR spectra of the free base and acids from 400 to 100 cm^{-1}. The band assignments in this region are not so easy without normal coordinate analysis. The band at 359 cm^{-1} of metalloporphin complex has been assigned to the CCN in-plane bending on the basis of normal coordinate analysis.[16] Therefore, the band at 320 cm^{-1} of the free base is probably due to the CCN in-plane bending vibration.[17] This band is free in the spectra of the diacids and still remains in the monoacid. The diacids show two new bands at around 246 and 201 cm^{-1}. The spectrum of **5** shows four bands at 266, 250, 224, and 185 cm^{-1}. The band at 320 cm^{-1} of the free base and monoacid can be interpreted as the CCN bending mode due to the neutral pyrrolic ring. The bands at 250 and 200 cm^{-1} appeared in the diacids are presumably due to the CCN bending mode of the protonated pyrrolic ring. The complicated far-IR spectrum of **2** indicates lower symmetry of the porphyrin inner core of the monoacid. Intense band at 140 cm^{-1} of **2** and **5** is assigned to the asymmetric stretching mode of the I_3^- ion[11,12] since the perchlorate salt (**3**) does not show the corresponding absorption.

In conclusion, the porphyrin diacid in aprotic solvent is associated with the anion through hydrogen bonding. The strength of association depends upon the nucleophilicity of the anion. Porphyrin monoacid is obtainable when the specific anion such as I_3^- is present. Finally the present result verifies the concept of the porphyrin-ion pair at the ground state in aprotic solvent.

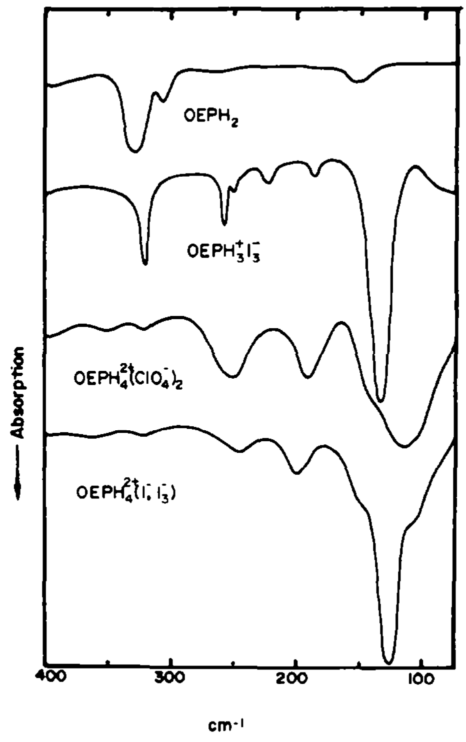


Fig 3. Far-I.R. spectra of the free base, **5**, **3** and **2**.

REFERENCES

[1] D. A. Brisbin and R. J. Balahura, *Canad. J. Chem.* **46**, 3431 (1968)

[2] B. F. Burnham and J. J. Zuckerman, *J. Am. Chem. Soc.* **92**, 1547 (1969)

[3] A. Stone and E. B. Fleischer, *Ibid.* **90**, 2735 (1968)

[4] B. Shah, B. Shears and P. Hambright, *Inorg. Chem.* **10**, 1828 (1971)

[5] R. Khosropour and P. Hambright, *Chem. Comm.* 13 (1972)

[6] S. Arnoff and M. Calvin, *J. Org. Chem.* **8**, 205 (1943)

[7] S. Arnoff, *J. Phys. Chem.* **62**, 428 (1958)

[8] R. I. Walter, *J. Am. Chem. Soc.* **75**, 3860 (1953)

[9] R. Grigg, R. J. Hamilton, M. L. Jozefowicz, C. H. Rochester, R. J. Terrell and H. Wickwar, *J. Chem. Soc.* Perkin II, 407 (1973)

[10] H. H. Inhoffen, J.-H. Fuhrhop, H. Voigt and H. Brockman, Jr., *Liebigs Ann.* **695**, 133 (1966)

[11] S. G. W. Gim and J. L. Wood, *Trans. Faraday Soc.* **62**, 777 (1966)

[12] G. C. Hayward and P. J. Hevelsa, *Spectrochim. Acta* **23**, A, 2309 (1972)

[13] E. Samuels, R. Shuffleworth and T. S. Stevens, *J. Chem. Soc.* (C), 145 (1968)

[14] R. Bonnet, I. A. D. Gale and G. F. Stephenson, *Ibid.* Perkin I, 1168 (1967)

[15] W. S. Caughey, J. O. Alben, W. Y. Fujimoto and J. L. York, *J. Org. Chem.* **31**, 2631 (1966)

[16] H. Ogoshi, Y. Saito and K. Nakamoto, *J. Chem. Phys.* **57**, 4149 (1972)

[17] H. Bürger, K. Burczyk and J. H. Fuhrhop, *Tetrahedron* **27**, 3257 (1971)