673. *The Proton Magnetic Resonance Spectra of Porphyrins. Part I. The Effect of β-Substitution* on the Proton Chemical Shifts of Porphyrins.*

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Proton magnetic resonance spectra of dications (I) of some porphyrins are summarised in the Table. The chemical shifts are greatly affected by the ring current of the aromatic system, and hence assignments are straightforward. Further, the effect of β-substituents on the chemical shifts of *meso*- and N–H protons can be accounted for by simple addition; in certain cases the arrangement of the β-substituents in isomeric porphyrins ("type isomers") can be assigned from these considerations.

Proton magnetic resonance spectra have been described briefly for solutions of porphyrins in deuterochloroform [1] and -trifluoroacetic acid.[2] The present research is an extension of the latter measurements into a systematic survey, including more complex porphyrins derived from natural products.

Porphyrins are very suitable for a detailed proton magnetic resonance study for several reasons. The positions of protons and other substituents around the porphin skeleton are well separated, and therefore, apart from coupling inside a complex substituent, the protons do not interact magnetically. Consequently the spectrum consists merely of single peaks, except for the part due to complex side-chains, and small variations in chemical shifts can be measured directly without any analysis. Also, the large ring current [3] in the porphin nucleus spreads the spectrum out, *e.g.*, the chemical shifts of the *meso*-protons are about 5 p.p.m. to low field of the normal value for olefinic protons and the chemical shifts of the N–H protons are about 12 p.p.m. to high field of the normal value.[1,2] In fact, the spectrum of a porphyrin extends over practically the whole range yet observed in proton magnetic resonance spectroscopy. Assignments of the main groups in the spectrum to varieties of substituent is straightforward.

Elsewhere [4] it will be shown that the chemical shifts observed in porphyrins can be accounted for by a semi-classical calculation of ring currents. In this paper, our theoretical interest is in the connection between small changes in the chemical shifts of *meso*- and N–H protons and alterations of the neighbouring β-substituents; the effects of β-substituents are apparently additive, and, in certain cases, it is possible to predict different spectra for isomers differing only in the "type," [5] *i.e.*, the distribution of the β-substituents. Part III will deal with the effects of substitution in the *meso*-positions.

Experimental

Measurements.—The porphyrins were dissolved (20—70 mg./c.c., 0·03—0·10M, depending on availability) in trifluoroacetic acid (TFA) or deuterotrifluoroacetic acid (DTFA). The spectra were measured at about 25° on a Varian 60 Mc./sec. dual-purpose spectrometer at a usual sweep rate of about 8 c. per sec. per sec. Tetramethylsilane was used as the internal reference, and chemical shifts (see Table) are given on the τ scale. Side-bands were generated from a convenient, large peak, usually that of trifluoroacetic acid or, in the deutero-acid, tetramethylsilane. The position of the trifluoroacetic acid peak (variable from $-1{\cdot}5$ to $+0{\cdot}5$, cf.

* While the positions occupied in (I) by H_α, H_β, H_γ, and H_δ have been universally described as *meso*, those occupied by R^{1-8} have been described as β and nuclear. We shall use β and also, in conformity with the practice of H. Fischer and others, propionate (Pe) and acetate (A) for the systematically named 2-methoxycarbonylethyl and methoxycarbonylmethyl substituents. Other abbreviations are Pr for n-propyl, Vi for vinyl, TFA for trifluoroacetic acid, and DTFA for deuterotrifluoroacetic acid.

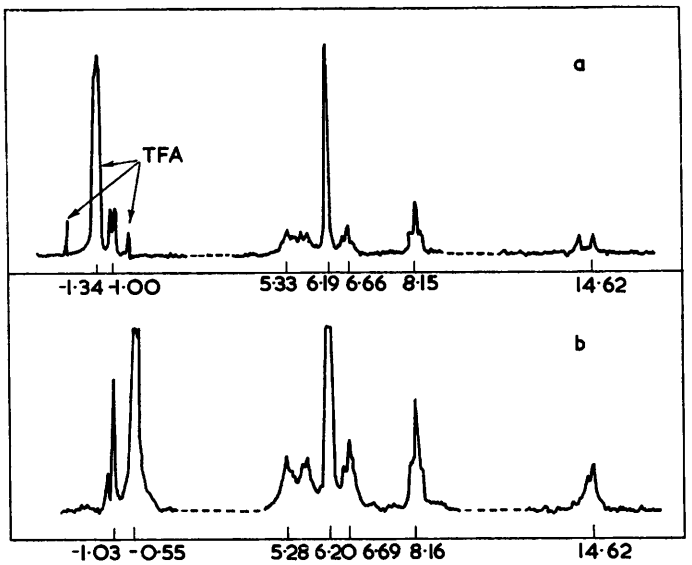
[1] Becker and Bradley, *J. Chem. Phys.*, 1959, **31**, 1413.
[2] Ellis, Jackson, Kenner, and Lee, *Tetrahedron Letters*, 1960, No. 2, 23.
[3] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 180.
[4] Part II, Abraham, *Mol. Phys.*, in the press.
[5] Fischer and Stangler, *Annalen*, 1927, **459**, 62.

Figure) was very sensitive to concentration of the solute, being shifted 0·05 p.p.m. to high field by addition of 1% of tetramethylsilane. Side-bands of trifluoroacetic acid were therefore only used in presence of tetramethylsilane. Each spectrum was measured three times, the mean deviations for the resolved peaks being ±1 c./sec., *i.e.*, ±0·01 p.p.m. The N–H peaks were exceptional in being broader and somewhat dependent on concentration, and the reproducibility of these τ values was about ±0·05 p.p.m. The other values were completely independent of concentration or small changes in the medium.

Materials.—Commercial trifluoroacetic acid was purified by distillation through a short column. Deuterotrifluoroacetic acid was prepared, by vacuum-line techniques, from redistilled trifluoroacetic anhydride and 99·8% deuterium oxide, and the product was purified by fractional distillation under reduced pressure.

The samples of porphin [6] and uroporphyrin II octamethyl ester [7] were kindly supplied by Professor C. Rimington and Dr. S. F. MacDonald, to whom we are grateful. The remaining

Proton magnetic resonance spectra of (a) *mesoporphyrin II dimethyl ester, and* (b) *mesoporphyrin IX dimethyl ester, in trifluoroacetic acid* (TFA) *at* 60 Mc./sec.



compounds were prepared in Liverpool, and we thank P. A. Burbidge, J. Ellis, and P. Johnston, for their assistance with this work, some of which will be included in later publications. The dimethyl esters of mesoporphyrin IX and protoporphyrin IX were prepared from commerical samples of the acids by means of methanolic hydrogen chloride, and they were purified by chromatography in benzene on alumina, followed by crystallisation from chloroform–methanol. Octamethylporphin, ætioporphyrins I and II, and mesoporphyrin II dimethyl ester were prepared from pyrromethenes by essentially classical methods,[8] but the synthesis of coproporphyrin II tetramethyl ester was analogous to that of uroporphyrin II by Arsenault, Bullock, and MacDonald.[7]

Ætioporphyrin III, tetramethyltetrapropylporphyrin III, and coproporphyrin III tetramethyl ester were all prepared by variants [9] of Siedel and Winkler's method.[10] The " type " purity of porphyrins produced by such " non-rational " [11] syntheses from single pyrrole units is still in doubt.[12] However, even the completely random mixture will contain 75% of type

[6] Krol, *J. Org. Chem.*, 1959, **24**, 2065.
[7] Arsenault, Bullock, and MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 4384.
[8] Fischer and Orth, " Die Chemie des Pyrrols," Akademische Verlag, Leipzig, 1937, Vol. II, Part I.
[9] Cf. Bullock, Johnson, Markham, and Shaw, *J.*, 1958, 1430.
[10] Siedel and Winkler, *Annalen*, 1943, **554**, 162.
[11] MacDonald and Michl, *Canad. J. Chem.*, 1956, **34**, 1768.
[12] Mauzerall, *J. Amer. Chem. Soc.*, 1960, **82**, 2601, 2605; Morsingh and MacDonald, *ibid.*, p. 4383.

III and IV isomers,[13] and it should have the same proton magnetic resonance spectrum as either of these isomers according to the theory developed in this paper.

Results and Discussion

Assignments of Spectral Regions.—As porphyrins are diacidic bases,[14] they should exist as dications (I) when dissolved in trifluoroacetic acid. This is confirmed by the area, corresponding to four protons, of the N–H peaks around 14·5. The assignment of these peaks is based on their absence from spectra of solutions in deuterotrifluoroacetic acid. This

Chemical shifts in proton magnetic resonance spectra of porphyrins.

Solutions in trifluoroacetic acid or, where marked *, deuterofluoroacetic acid.

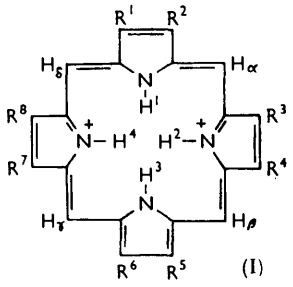
Compound (Substituents of (I))	τ Values of protons: N–H	*meso*	β-Substituents: CH_3	CH_2–CH_3		CH_2–CH_2–CO_2CH_3			Others
Porphin	14·40								H
R^{1-8} = H	—*	−1·22							0·08
Octamethyl Porphin	14·82	−0·98	6·22						
R^{1-8} = Me	—*	−0·98	6·24						
Ætioporphyrin I	14·80	−1·00	6·22	5·70	8·16				
$R^{1,3,5,7}$ = Me	—*	−1·00	6·20	5·70	8·15				
$R^{2,4,6,8}$ = Et									
Ætioporphyrin II	14·81	−1·02	6·19	5·69	8·16				
$R^{1,4,5,8}$ = Me									
$R^{2,3,6,7}$ = Et									
Ætioporphyrin III	14·86	−1·00	6·22	5·71	8·18				
$R^{1,3,5,8}$ = Me									
$R^{2,4,6,7}$ = Et									
Tetramethyltetrapropylporphin III	14·76	−0·98	6·23						CH_2–CH_2–CH_3 5·75 7·73 8·75
$R^{1,3,5,8}$ = Me									
$R^{2,4,6,7}$ = Pr									
Coproporphyrin II tetramethyl ester	14·29	−1·22 (α, γ)	6·17			5·27	6·70	6·22	
$R^{1,4,5,8}$ = Me		−1·06 (β, δ)							
$R^{2,3,6,7}$ = Pe									
Coproporphyrin III tetramethyl ester	14·26	−1·12 †	6·17			5·33	6·68	6·22	
$R^{1,3,5,8}$ = Me	—*	−1·21 (γ)	6·16			5·32	6·65	6·21	
$R^{2,4,6,7}$ = Pe		−1·11 (α, β)							
		−1·02 (δ)							
Uroporphyrin II octamethyl ester	—*	−1·27 (β, δ)				5·29	6·70	6·21	CH_2–CO_2CH_3 4·54 6·12
$R^{1,4,5,8}$ = A		−1·17 (α, γ)							
$R^{2,3,6,7}$ = Pe									
Mesoporphyrin II dimethyl ester	14·36 (1, 3)	−1·07 (α, γ)	6·19	5·71	8·15	5·33	6·66	6·19	
$R^{1,3,5,7}$ = Me	14·62 (2, 4)	−1·00 (β, δ)							
$R^{2,6}$ = Et									
$R^{4,8}$ = Pe									
Mesoporphyrin IX dimethyl ester	14·48 (3, 4)	−1·18 (γ)	6·19	5·69	8·16	5·28	6·69	6·24	
$R^{1,3,5,8}$ = Me	14·62 (1, 2)	−1·03 (α, β, δ)							
$R^{2,4}$ = Et									
$R^{6,7}$ = Pe									
Protoporphyrin IX dimethyl ester	14·37	−1·21 (γ)	6·21			5·32	6·72	6·25	$CH=CH_2$ 1·71 3·43 3·61
$R^{1,3,5,8}$ = Me		−1·03 (α, β, δ)							
$R^{2,4}$ = Vi									
$R^{6,7}$ = Pe									

* In deuterotrifluoroacetic acid. † Partially obscured by solvent.

[13] Cookson and Rimington, *Biochem. J.*, 1954, **57**, 476.
[14] Neuberger and Scott, *Proc. Roy. Soc.*, 1952, *A*, **213**, 307.

exchange between the hydrogen atoms attached to nitrogen and those of the solvent is usually too slow to affect the proton magnetic resonance spectra observed in trifluoroacetic acid. In such cases, the solvent peak is very sharp and the N–H peaks are broad owing to quadrupole relaxation of the nitrogen nuclei.[15] Occasionally, for example, with porphin itself, both the solvent and N–H peaks are very broad, presumably as a result of more rapid exchange, approaching the separation between the peaks[16] (*i.e.*, a proton is attached to a nitrogen atom for about 10^{-4} sec.). This broadening, which became more pronounced in concentrated solutions, made the location of the N–H peak in porphin uncertain to $\pm 0{\cdot}1$ p.p.m. and the N–H peaks of uroporphyrin II octamethyl ester were not detected at all.

The remaining peaks, which are caused by protons attached to carbon atoms, are quite sharp, although still appreciably broader than those from smaller molecules, *e.g.*, impurities,* owing to the relatively slow rotation of the large porphyrin molecules.[17] The Table records spectra of a variety of compounds sufficient to secure the group assignments, and these agree generally with the conclusions of previous workers.[1,2] A new general observation, which we have confirmed with other compounds, is that a proton in a β-position is more shielded than one in a *meso*-position to the extent of 1·3 p.p.m. Calculations[4] of the ring current account for this result and for the displacement of the chemical shifts of all protons on the periphery of the aromatic porphyrin nucleus. As an instance of this displacement, the chemical shift of β-methyl groups is virtually identical with that of the methyl group attached to an oxygen atom in the methyl ester of a carboxylic acid. In compounds containing groups of both kinds, such as the methyl esters of protoporphyrin and mesoporphyrin, the values of the relevant chemical shifts are rendered less certain by this coincidence, but those given are consistent with the other tabulated values. Another complication of the spectra of methyl esters is the gradual appearance at 5·93 of a signal from methyl trifluoroacetate, arising from transesterification of the solvent, but this is only noticeable after the solution has been kept for several weeks at room temperature.



(I)

It is interesting to compare the results from coproporphyrin III tetramethyl ester with those reported by Becker and Bradley[1] for a solution of the same compound in deuterochloroform. The slightly smaller spread in the spectrum of the neutral molecule can be satisfactorily accounted for by the variation in the ring current,[4] in comparison with the more symmetrical dication, but there is a puzzling difference between the peaks corresponding to the *meso*-protons. A singlet is tabulated for the neutral molecule,[1] but a 1 : 2 : 1 triplet is observed in deuterotrifluoroacetic acid solution (only the major peak could be measured in trifluoroacetic acid, as the solvent peak partially obscured the group of *meso*-peaks). Probably the neutral molecules, unlike the dications, are mixtures of tautomers and hence this region of the spectrum may not be so readily resolved. On the other hand, multiplets of unspecified complexity are tabulated for the dimethyl esters of mesoporphyrin IX, protoporphyrin IX, and hæmatoporphyrin IX.

Effects of β-*Substituents on the Chemical Shifts of* meso-*Protons.*—Spectra of five octaalkylporphyrins are recorded in the Table, and the chemical shifts for all the *meso*-protons are −1·00 (±0·02). On the other hand, the value in porphin itself is −1·22, and hence the effect of alkyl substitution at all the β-positions is to increase the shielding constants for the *meso*-protons by 0·22 p.p.m. Presumably the two β-substituents which are

* The unexplained, sharp peak at 7·7 reported earlier [2] has not been encountered in the present work, and an impurity must have been responsible.

[15] Pople, *Mol. Phys.*, 1958, **1**, 168.
[16] Gutowsky, McCall, and Slichter, *J. Chem. Phys.*, 1953, **21**, 279.
[17] Bloembergen, Purcell, and Pound, *Phys. Rev.*, 1948, **73**, 679; and ref. 3, chapter 9.

immediate neighbours of a particular *meso*-proton will have the greatest effect on its chemical shift. If this " neighbouring " effect were entirely responsible for the increase in shielding constant noted above, then any *meso*-proton situated between two alkyl groups should have the same chemical shift, irrespective of the rest of the molecule. Although this is unlikely to be true in extreme cases, it is confirmed by the results listed in the Table; in coproporphyrin III tetramethyl ester there is one *meso*-proton (δ) situated between two β-methyl groups and a peak of intensity 1 at −1·02; in both mesoporphyrin II dimethyl ester and coproporphyrin II tetramethyl ester there are two *meso*-protons (β, δ) between β-alkyl substituents and correspondingly peaks of intensity two at −1·02 and −1·06 respectively; and in mesoporphyrin IX dimethyl ester there are three such *meso*-protons (α, β, δ) and a peak of intensity three at −1·03. There is thus good reason to assign these peaks to the corresponding *meso*-protons, and to accept the mean of the ten tabulated values, −1·01 (mean deviation ±0·02), as the expected chemical shift of a *meso*-proton between two β-alkyl substituents. There is some indication that the shielding is reduced by carboxylated side-chains at more remote β-positions, but, if it exists, this effect is apparently of the same order as the experimental error.

In the Table there are five compounds with *meso*-protons situated between two propionate substituents, and in each case there is a peak of the expected intensity in the same region. These peaks are from the γ-protons of coproporphyrin III tetramethyl ester (−1·22), mesoporphyrin IX dimethyl ester (−1·18), and protoporphyrin IX dimethyl ester (−1·21) and the α,γ-protons of coproporphyrin II tetramethyl ester (−1·22) and uroporphyrin II octamethyl ester (−1·17); their mean value is −1·19.

Moreover, there are two examples of *meso*-protons between methyl and propionate substituents, namely the α,β-protons of coproporphyrin III tetramethyl ester and the α,γ-protons of mesoporphyrin II dimethyl ester, and peaks of intensity two are observed at −1·11 and −1·07 respectively. The mean value of −1·09 is consistent with the hypothesis that the effects of the alkyl and propionate substituents are additive. Accepting this hypothesis, we define the contribution of a β-substituent R on the chemical shift of the neighbouring *meso*-proton as R_M and we take porphin itself as the reference compound ($H_M = 0$). Then $Alkyl_M = 0{\cdot}11$ and $Pe_M = 0{\cdot}02$.

Further values can be obtained in the same way. The β,δ-protons of uroporphyrin II octamethyl ester, flanked by acetate groups, are responsible for a peak at −1·27, and hence $A_M = -0{\cdot}03$. The α,β-protons of protoporphyrin IX dimethyl ester lie between methyl and vinyl substituents, and their signal (−1·03) coincides with that of the δ-proton, which is between methyl groups; hence $Vi_M = Me_M = 0{\cdot}11$.

The main importance of these parameters lies in prediction of the relative positions of peaks from *meso*-protons in complex porphyrins. (In so far as β-substitution affects all the *meso*-protons, there may be some discrepancies, but these should concern absolute rather than relative values and the correlation of the tabulated data is very satisfactory.) Some general predictions can be made concerning porphyrins which differ only in the distribution of their β-substituents (" type isomers " [5]). First, in the familiar series where identical pairs of β-substituents, A and B, are distributed on the four pyrrolic rings, the *meso*-protons of type I isomer will give rise to a single peak, those of the type II isomer to two lines of equal intensity, and those of the type III and IV isomers to a triplet of intensity 1 : 2 : 1. The separation of the peaks in the doublet and of the outermost lines in the triplet will be $2(A_M - B_M)$. Provided that A_M and B_M differ sufficiently, proton magnetic resonance provides a simple method of distinguishing isomers, and the spectra of the tetramethyl esters of coproporphyrin II and III illustrate this well.

The analysis can be extended to more complex porphyrins, but a corresponding amount of information cannot always be obtained. For instance, the fifteen mesoporphyrins [5] should give rise to only two patterns; types III, IX, and XIII, which are related to coproporphyrins II, III, and IV, respectively, should have a pair of peaks with intensities three and one in the *meso*-region, while the remaining twelve isomers should have a symmetrical

doublet. The spectra (see Figure) of the dimethyl esters of mesoporphyrin II and IX show this effect. On the other hand, there should be six different patterns from the fifteen isomeric deuteroporphyrins, although it is unlikely that they could all be distinguished experimentally. In combination with the classical methods, proton magnetic resonance spectroscopy should be very useful in distinguishing between particular possibilities.

Effects of β-Substituents on the Chemical Shifts of N–H *Protons.*—The chemical shifts of the N–H protons will be considered in much the same way as the shifts of the *meso*-protons, but the analysis cannot be so definite. On any simple theory, all the octa-alkylporphyrins should show a single N–H peak at the same position. In fact, while single peaks are observed, the five tabulated values spread between 14·76 and 14·86, but this variation is probably due to experimental uncertainties, *e.g.*, the effect of concentration. If the shift of any given N–H proton is affected only by the two β-substituents attached to the same pyrrole ring, the coproporphyrins should also show a single peak because each ring has a methyl and a propionate substituent; indeed single peaks have been observed at 14·29 and 14·26. Further, in the mesoporphyrins there should be two equal peaks arising from the rings with methyl-ethyl and methyl-propionate substituents, respectively. Doublets are observed (see Figure) but at approximately 14·6 and 14·4 instead of 14·8 and 14·3, the positions expected by comparison with the octa-alkylporphins and coproporphyrins. Apparently the assumption of a simple " neighbouring " effect is insufficient, although it does account for the main phenomena. As the basicity of porphyrins, *i.e.*, the acidity of their conjugate acids, is affected considerably by β-substitution [14] and the chemical shift of N–H protons is expected to be connected with their acidity, it is probable that β-substituents have a general effect on the shifts of all four protons in addition to the particular effect in the same pyrrolic ring.

It should also be remarked that protoporphyrin IX, like the mesoporphyrins, should show a doublet, but actually the N–H peak was very broad and fine structure could not be detected.

If fine structure of the N–H peak is observed, the " neighbouring " assumption is likely to be useful despite its limitations, and the following parameters, analogous to those calculated for the *meso*-protons, may serve as an approximate guide to the chemical shifts: $Alkyl_N = 0{\cdot}21$, $Pe_N = 0{\cdot}01$.

Conclusion.—We hope to examine the proton magnetic resonance spectra of a wider variety of porphyrins, including chlorins and degradation products of chlorophyll, and it may be that the correlations deduced from the present data will be modified. Nevertheless, the parameters should serve as a guide to future work, and certain instructive comparisons can be made.

The introduction of a β-methyl substituent increases the chemical shift of the neighbouring *meso*-proton by 0·1 p.p.m. and that of the closest N–H proton by 0·2 p.p.m. In both cases the methyl group is four bonds away from the proton concerned. Figures are not available for the corresponding effect on N–H protons in simple pyrroles, but the introduction of a methyl group at position 2 increases the chemical shift of the 4-proton, which is again four bonds away, by about 0·2 p.p.m.[18] Thus the mechanism of the shifts may be the same in the pyrrole and the porphyrin series and it could be based on either the inductive effect or the dipole field [19] of the methyl group. The latter mechanism would explain why the effect on a *meso*-proton is smaller. It is in the plane perpendicular to the dipole axis and passing through the dipole, while the N–H proton is close to the dipole axis and therefore experiences a much larger dipole field. It should be noted that substitution of a methyl group at a *meso*-position has a much larger effect, which will be described in Part III, and that there a different mechanism must be involved.

The large decrease in shielding of *meso*- (0·1 p.p.m.) and N–H (0·2 p.p.m.) protons, when

[18] Abraham and Bernstein, *Canad. J. Chem.*, 1961, **39**, 905.
[19] Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

a β-alkyl substituent is replaced by a propionate group, is at first rather surprising as the carbonyl group is so distant if the side-chain is extended. However, a coiled conformation, in which the side-chain is first bent upwards (the plane of the ring system being taken as horizontal) and then inwards, brings the carbonyl group close to the *meso*-proton and particularly close to the N–H protons. To some extent this conformation can be regarded as the form of lowest energy, because the two polar groups are brought as near to each other as possible. The effect of the carbonyl group may be due to either its dipole field or its magnetic anistropy. Alternatively, the carbonyl group may neutralise the effect of the ethyl substituent, so that it becomes equivalent to a hydrogen atom.

The effect of a β-acetate substituent on the neighbouring *meso*-proton is even larger than that of a propionate substituent, in agreement with the foregoing suggestions. Unfortunately, the value of A_N, which might help to distinguish between them, is not available because the N–H peaks of uroporphyrin II octamethyl ester could not be observed.

It is evident, when the spectra of the dimethyl esters of protoporphyrin IX and mesoporphyrin IX are compared, that the " neighbouring effect " of a vinyl substituent is similar to that of other alkyl groups. Presumably the similarity is due to the non-polar nature of the vinyl group, and it may be that polar conjugative substituents, for instance, aldehyde and ketone groups, will be found to have a more noticeable effect, possibly too great to be accommodated in simple " neighbouring " parameters.

Although the main concern of this paper is with the effects of β-substitution in other parts of the porphyrin molecule, the potential value of proton magnetic resonance in identifying the β-substituents themselves of new porphyrins should not be overlooked. For example, an unsubstituted β-position, like that in cytodeuteroporphyrin,[20] would be apparent from a peak at about 0·1 (τ scale). Again, the signals from a propyl group, a component of chlorobium chlorophyll,[21] are spread out by the ring current so that its detection becomes straightforward. The signals from vinyl groups are very characteristic and displaced from the usual position. A drawback of the proton magnetic resonance method at present is the need for a comparatively large sample (10—30 mg.). The spectra of methyl esters, rather than the corresponding carboxylic acids, are tabulated because the esters were more readily purified, but the acids generally dissolve sufficiently in trifluoroacetic acid and they give similar spectra. In the porphyrin series combustion analysis is frequently not very informative, and we have found our spectra very helpful in counting β-substituents.[22]

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Basic Physics Division, National Physical Laboratory.
Organic Chemistry Department, University of Liverpool. [*Received, February 14th*, 1961.]

[20] Marks, Dougall, Bullock, and MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 3183.
[21] Holt and Morley, *J. Amer. Chem. Soc.*, 1960, **82**, 500.
[22] Ellis, Jackson, Jain, and Kenner, unpublished work.