196. *The Infrared Spectra of* N-*Heteroaromatic Systems. Part I. The Porphins.*

By S. F. Mason.

The infrared spectra of porphin, chlorin, and a number of their derivatives have been measured over the range 4000—400 cm.$^{-1}$. The spectra suggest that the porphin nucleus approximates to a symmetry D_{4h} which is reduced to V_h by the hydrogen atoms of the pyrrole N–H groups. The nitrogen atoms of the porphin nucleus are found to be extensively hydrogen-bonded, and it is shown, from a calculation of the overlap between the orbitals of a hydrogen atom and the four nitrogen atoms, that the bonding is responsible for the exceptionally low frequency of the in-plane N–H deformation vibration in porphin and chlorin. A number of bands characteristic of the porphin nucleus are listed and discussed.

The infrared spectra of a number of relatively complex natural and synthetic porphins have been reported.[1-4] A few assignments have been suggested for the vibrations of the porphin nucleus,[4] but attention has been concentrated mainly upon the characterisation

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[1] Falk and Willis, *Austral. J. Sci. Res.*, 1951, **4**, 579.
[2] Craven, Reissmann, and Chinn, *Analyt. Chem.*, 1952, **24**, 1214.
[3] Vestling and Downing, *J. Amer. Chem. Soc.*, 1939, **61**, 3511.
[4] Thomas and Martell, *ibid.*, 1956, **78**, 1338.

TABLE 1. *The infrared spectra* (cm.$^{-1}$) *of porphin and its derivatives in the solid state. Values in parentheses refer to bands which appear, and values in italics to bands which disappear, or are considerably weakened, upon the replacement of the hydrogen atoms of the* N–H *groups by deuterium.* s = *strong*; m = *moderate*; w = *weak.*

(1) Porphin

3305m	1184m
3181w	(1170w)
3102m	*1158w*
3036w	1137m
2997vw	(1098)w
2954w	1066w
2921w	1057m
2851w	1048m
2782w	1033w
2742w	995w
2669w	*970s*
2654w	951s
2597m	901m
2563vw	853s
2494vw	841s
(2463w)	809w
2422vw	792w
2115vw	*771*s
2100vw	(768s)
1745vw	749m
1589w	728s
1406m	*719*s
1352w	690s
1281w	638m
1262w	618m
1252w	(537w)
1224m	

(2) Copper porphin

3193w	1388m
3151w	1357w
3105w	1310s
3083m	1246w
3063w	1192w
3041w	1153w
3014w	1115w
2967w	1060s
2932w	1036vw
2888m	1025w
2832m	996s
2770vw	901w
2743w	857s
2681vw	852s
2690w	802w
2576w	777w
2423w	768s
2255w	744m
2120w	732w
1985w	700s
1802w	697s
1531m	618m

(3) *ætio*Porphin

3314m	115s
3100w	1060s
3052w	987m
3030w	981w
3009w	956m
2963s	918w
2930s	902m
2918s	885w
2867s	837s
1670w	796w
1459	760w
1316w	744s
1270w	730w
1262w	722w
1239w	708w
1221m	683s
1192s	648m
1143m	618m

(4) Octaethylporphin

3310m	1143w
3114w	1116s
3092w	1057s
3052w	1014s
3030w	1006m
2967s	974w
2931s	950s
2869s	893m
2795w	847w
2750w	834s
2682w	821m
1611w	795w
1469m	777w
1377w	745s
1319m	720m
1279w	699m
1264w	674m
1240m	643m
1220m	618m
1188m	

(5) Octamethylporphin

3311m	906s
2956w	837s
2912m	783m
2903m	771m
2850m	734s
2804w	714m
1400w	692s
1222m	674w
1195s	647m
1131m	618m
1111s	605w
935m	

(6) Copper octamethylporphin

3188w	1138w
3115w	1111w
3025w	1096m
2962m	940s
2902s	902w
2850s	838s
1681m	781s
1390m	725s
1230s	693w
1202w	607m
1149s	502w

(7) Magnesium octamethylporphin

3109w	1221m
3095w	1152s
3030w	1111w
2956m	1090w
910s	940m
2850s	932s
2785w	876w
1458m	834s
1342w	796w
1319w	779s
1291w	730s
1270w	695w
1262w	426w
1230m	

(8) *meso*-Tetramethylporphin

3322m	1025w
3114w	962m
3094w	954s
2916s	914s
2850s	895w
1474m	880w
1430w	776s,b
1406w	743w
1354m	709s
1240m	692
1204w	643m
1172s	624m
1122s	592w

(9) Copper *meso*-tetramethylporphin

3114m	1119w
3008w	1089s
2915s	1069s
2854s	1030w
2796w	982s
2759m	925s
2572w	892m
1526m	792w
1451m	776s
1361w	730w
1342s	700s
1305m	675m
1258s	649w
1164w	611m
1147w	

(10) *meso*-Tetraphenylporphin

3311m	1072m
3118w	1057w
3076w	1031m
3050m	1002s
3026m	*980m*
2958w	966s
2915w	920w
2851w	901w
2705w	876m
2592w	851m
(2478w)	830w
1596m	814m
1470m	795s
1440m	787s
1353m	(773w)
1287w	760m
1271w	749m
1250m	730m
1221m	*725m*
1212m	706m
1186m	699s
1170m	655s
1153m	638m
1113w	620m
(1097w)	563w
1080w	512m

(11) Copper *meso*-tetraphenylporphin

3120w	1076m
3070w	1006s
3049m	997m
3014m	990m
2916m	876w
2850w	838w
1598m	800s
1449m	763w
1349m	752m
1208w	740w
1180w	721m
1158w	700m
1113w	644m
1087w	620w

(12) Chlorin

3348m	1064w
3118m	1050m
3095m	1037s
3076w	1005w
2957m	982m
2928m	965s
2886w	958s
2732w	946s
2630w	906w
2534w	857s
1618s	840s
1594m	796m
1464m	784m
1397m	776s
1307m	770s
1254m	742w
1230w	720w
1218m	706s
1190w	696s
1166s	643m
1142s	620w

(13) Copper chlorin

2918m	1005m
2855w	993s
1612m	976m
1339w	876m
1262m	860s
1214s	839s
1180s	769w
1152m	745w
1114w	425w
1058s	

TABLE 1. (*Continued.*)

(14) *meso*-Tetramethylchlorin

3342m	1080m
3120w	1063s
3025w	1030w
3002w	1018w
2988w	968m
2918s	954s
2860s	940s
2716w	925m
2560w	916w
2494w	876m
1975w	837w
1591s	771s, b
1471s	748m
1360s	714s, b
1312m	698s
1286w	681m
1268w	636m
1249m	618w
1237s	598m
1148w	572w
1116m	

(15) Octamethylchlorin

3340m	1090m
2958m	1076w
2908s	1039m
2853m	943m
1611s	932w
1522w	917m
1450w	898s
1400w	845m
1275w	824m
1247w	779w
1230w	766s
1203s	710m
1165s	688s
1144m	650m
1127w	618w
1113m	590m

(16) Copper octa methylchlorin

3042w	1146m
3027w	1129m
3009w	1111w
2961m	1069w
2904s	981w
2850s	925s

(16) Copper octamethylch orin (*contd.*)

1648m	870w
1596m	850m
1400m	821s
1310m	779w
1278w	768w
1246m	748m
1213s	727s
1196m	690m
1152s	620m

(17) Octaethylchlorin

3338m	*1014m*
3095w	(1010m)
3049w	996s
3030w	974w
3014w	948s
2960s	905s
2930s	872w
2917s	849m
2886m	826m
2869s	*820m*
2855m	(817m)
(2491m)	*812m*
1614m	797w
1458m	773w
1400m	754w
1319w	738m
1300w	731m
1273w	*717m*
1261w	(703w)
1233m	*695m*
1208w	(682w)
1191m	645m
1169s	618m
1*145w*	(590w)
*1*110m	(512w)
1059s	

(18) Copper octaethylchlorin

3100w	1129m
3070w	1112m
2949s	1061s
2917s	1057s
2838m	1016s
1629m	988s
1573m	957s

(18) Copper octaethylchlorin (*contd.*)

1453m	916m
1390w	850s
1367w	833s
1312m	811m
1268m	746s
1225w	726s
1198s	700m
1189s	620m
1145m	

(19) Octaethyltetrahydroporphin

3351m	1129w
3100w	1111m
3072w	1062m
2950s	1057w
2917s	1007s
2856s	946m
1641w	866m
1598s	828m
1445m	788w
1385w	776s
1318w	725w
1287w	721w
1272w	682w
1239w	638m
1182s	

(20) Tetra-azaporphin

3296m	1226m
3120w	1183m
3090m	1134w
3076m	1109w
3029w	1057w
3008w	1044m
2922w	980w
2850w	963w
2130w	937s
2060vw	928s
2010vw	876w
1990vw	829s
1647m	792s
1619s	762m
1507m	740m
1480m	738m
1428w	723m
1357w	715s

(20) Tetra-azaporphin (*contd.*)

1286w	696m
1270w	638m
1261w	620w
1243m	

(21) Octamethyltetra-azaporphin

3299m	1143s
3030w	1104s
2938w	1017m
2912m	935m
2848m	887s
2745w	779ms
2666w	769s
2623w	756s
2533w	735m
2210w	709m
1985w	695s
1484s	652m
1421m	621w
1408w	600m
1262m	559w
1230w	490s
1202w	471w
1151s	

(22) Tetrahydro-octamethyltetra-azaporphin

3332m	941w
2968m	927w
2911s	915w
2868s	876s
2844s	811w
2732w	787w
1558s	773m
1492s	757w
1410w	746s
1379s	725m
1354m	716w
1296s	701m
1262w	691s
1224w	674s
1164m	653m
1140s	618w
1110s	591m
1061m	490s
1040m	467w
1007s	

of substituent groups [1,2,4] and the position of the N–H stretching frequency.[1,3,4] In the present work a study has been made of the spectra of porphin and chlorin, the parent nuclei of the porphyrin and the chlorophyll series respectively, and of a range of their simpler and more symmetrical derivatives, including the metal complexes. The frequencies and approximate intensities of the infrared absorption bands of porphin, chlorin, and their derivatives in potassium bromide discs over the range 4000—400 cm.$^{-1}$ are listed in Table 1.

The crystallographic evidence for phthalocyanine [5] suggests that the porphin nucleus approximates to D_{4h} symmetry, but belongs, more precisely, to the point group V_h (two two-fold axes in the plane through opposite *meso*-positions), owing to hydrogen bonding between the pyrrolic nitrogen atoms; [5] a conjugation distortion of the nuclear framework may also contribute to this as nickel phthalocyanine deviates slightly, though less than the parent molecule, from D_{4h} symmetry.[6] Thus the infrared spectrum of porphin should

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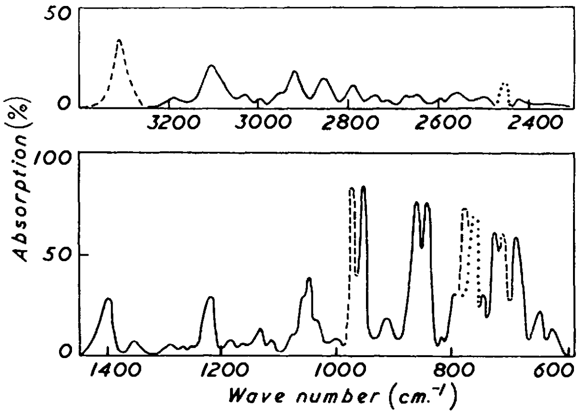
[5] Robertson, *J.*, 1936, 1195.

[6] Robertson and Woodward, *J.*, 1937, 221.

consist of a few strong bands, those allowed according to the selection rules of the D_{4h} group, and a large number of weak bands, due in part to forbidden frequencies which become allowed in combination with each other, and in part to frequencies which become allowed upon the reduction of the D_{4h} symmetry. The infrared spectrum of porphin is found to be of this character (Fig. 1, Table 1). However, the N-H vibrations should obey the selection rules of the actual point group to which the porphin molecule belongs, as the central hydrogen atoms are the main source of the reduction of the D_{4h} symmetry. If these hydrogen atoms are located on adjacent pyrrolic nitrogen atoms (cf. I), the symmetry is reduced to C_{2v} and five N-H vibrations are allowed; but if they are placed on opposite nitrogen atoms (cf. II) or symmetrically hydrogen-bond a pair of nitrogen atoms each (cf. III) the symmetry is lowered only to V_h' or V_h (two two-fold axes in the plane through the nitrogen atoms or through the *meso*-positions respectively) and only three N-H vibrations are allowed. By replacing the central hydrogen atoms with deuterium the N-H vibrations may be identified, the frequencies obtained being listed in Table 2. From the masses of the nitrogen, hydrogen, and deuterium atoms, and from the analogous case of pyrrole,[7] the frequencies of a given N-H vibration in deuterated and undeuterated porphin should have the ratio of about 1·35 for stretching vibrations and 1·1—1·3 for bending vibrations. Taking pairs of bands, one of which appears and the other disappears on deuteration, it is found (Table 2) that not more than three N-H vibrations are allowed in the porphins studied, whilst five are allowed in the case of octa-ethylchlorin, which cannot have a higher symmetry than C_{2v}. Of the five N-H vibrations of octa-ethylchlorin, only one lies in the N-H stretching-vibration region and, as only three N-H bending modes are allowed in the C_{2v} point group, the symmetry of this molecule is probably C_s.

FIG. 1. *The infrared spectrum of porphin.*



– – – *The main bands which disappear.*
. . . *The main bands which appear, upon the replacement of the hydrogen atoms of the* N-H *groups by deuterium (potassium bromide discs).*

The N-H stretching vibration of porphin and octaethylchlorin shifts only a few cm.$^{-1}$ to higher frequencies when one passes from the solid state to carbon tetrachloride solution, and the corresponding vibration of pyrrole in solution is some 150—200 cm.$^{-1}$ higher in frequency (Tables 1 and 2). Thus there is considerable hydrogen-bonding in porphins and chlorins, and it must be almost entirely intramolecular, even in the solid state. However, the bonding is of an unusual nature, as for porphin the in-plane N-H deformation vibration lies at a lower frequency than that for pyrrole by 170 or 420 cm.$^{-1}$ (Table 2), whilst in amides [8] and aromatic amines [9] hydrogen-bonding has the effect of raising the in-plane deformation frequency, as the bonding is favoured by a linear arrangement of the N-H • • • X system.

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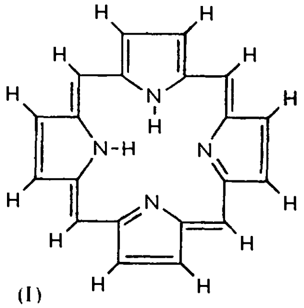
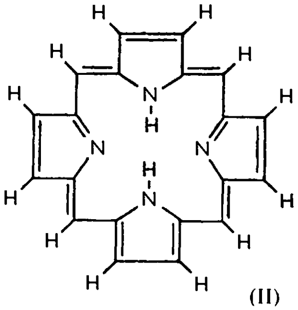
[7] Lord and Miller, *J. Chem. Phys.*, 1942, **10**, 328.

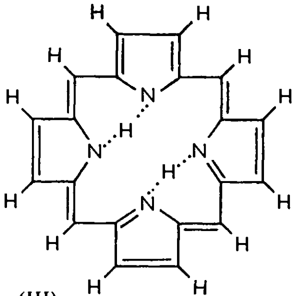
[8] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954.

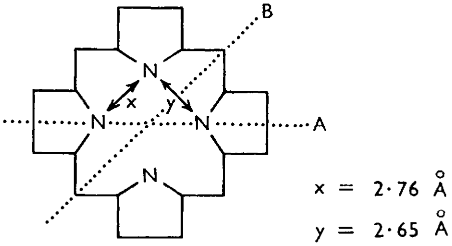
[9] Unpublished result of the author.

The unusual character of the hydrogen-bonding in porphin may be accounted for by a calculation of the overlap between the 1*s* orbital of a hydrogen atom and the hybrid 2*s*2*p* orbitals of the nitrogen atoms within the rectangular area bounded by the four pyrrolic nitrogen atoms of the porphin nucleus (Fig. 2). The crystal structure of phthalocyanine [5] shows that the C–N–C bond angles of the pyrrole rings are almost tetrahedral (108·5°) so that the bonds from nitrogen to carbon may be taken to be nearly sp^3 hybrids. The third nitrogen orbital is purely $2p\pi$, and so the fourth, directed towards the centre of the porphin molecule, is nearly digonal, *sp*. The fourth orbital is occupied by lone-pair electrons in the case of two of the four pyrrolic nitrogen atoms, and this factor also favours the assumption of a large " *s* " character in the orbitals directed towards the centre of the nucleus. Taking the dimensions of porphin (IV) to be the same as those of the azaporphin


(I)


(II)


(III)



(IV)

TABLE 2. *Infrared frequencies (cm.$^{-1}$) of the* N–H *vibrations of pyrrole and of porphin and its derivatives in the condensed state and in carbon tetrachloride solution.*

Compound	Vibration	N–H		N–D
		Solution	Condensed state	Condensed state
Pyrrole	stretch	3497 [a]	3400 [b]	2525 [b]
	i.p. deformation		1146 [b]	915 [b]
	o.p. deformation		565 [b]	450 [b]
Porphin	stretch	3309	3305	2463
	deformation		970	768
	,,		719	537
meso-Tetraphenylporphin	stretch	3315	3311	2478
	deformation		980	773
	,,		725	
Octaethylchlorin	stretch	3343	3338	2491
	deformation		1014	817
	,,		820	703
	,,		812	682
	,,		717	590

[a] Fuson, Josien, Powell, and Utterback, *J. Chem. Phys.*, 1952, **20**, 145. [b] Lord and Miller, *ibid.*, 1942, **10**, 328.

nuclear framework of phthalocyanine,[5] it is found, by using Slater orbitals,[10] that the overlap of the digonal hybrid orbitals of four nitrogen atoms and a 1*s* orbital of a hydrogen atom is considerable everywhere in the rectangle bounded by the nitrogen atoms (Fig. 2). In particular, the overlap is approximately unity round the perimeter of a circle with a radius of 0·9 Å from the centre of the molecule, and the overlap along an axis through opposite nitrogen atoms (Fig. 2*A*) up to this distance, which corresponds to a N–H bond length of 1·0 Å, is not appreciably greater than the overlap along an axis through opposite *meso*-positions (Fig. 2*B*). Overlap affords a measure of bond strength,[11] and the present calculations suggest that the V_h models of porphin (II and III) are about equally stable, whilst the C_{2v} model (I) is less stable, owing to the greater penetration of each hydrogen atom into the van der Waals sphere of the other. The overlap calculations also indicate that in-plane deformation of a N–H bond in porphin occurs more readily, and the out-of-plane deformation less readily, than in the case of pyrrole, a consequence which is supported by the frequencies of the absorptions due to these vibration modes (Table 2). On reduction to chlorin, and then to tetrahydroporphin, the porphin ring system is progressively expanded, the overlap of the nitrogen and hydrogen orbitals being reduced. Accordingly, the in-plane vibrations of the N–H group should increase in frequency in the series tetrahydroporphin > chlorin > porphin, as is found (Tables 1 and 2).

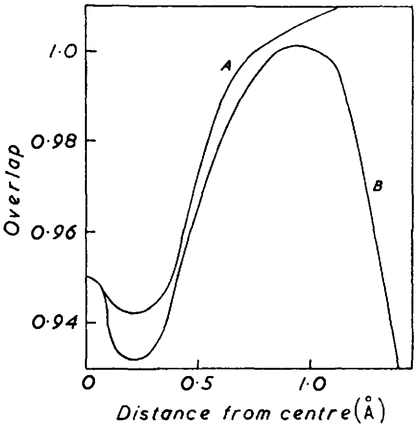


FIG. 2. *The overlap of the sp hybrid orbitals of the four nitrogen atoms directed towards the centre of the porphin molecule and the* 1s *orbital of a hydrogen atom as a function of the distance of the hydrogen atom from the centre of the molecule;* (*A*) *along an axis through opposite nitrogen atoms; and* (*B*) *along an axis through opposite* meso-*positions* [*axes* (*A*) *and* (*B*) *respectively of* (IV)].

Other absorption bands of porphin which should be indicative of the structure of the molecule are those due to the out-of-plane C–H deformation vibrations. The absorptions due to these modes in aromatic systems are quite strong,[12] and they have been well characterised.[13] Two out-of-plane C–H vibrations should absorb radiation in the D_{4h} model of porphin, three in the V_h' model (II), four in the V_h model (III), and seven in the C_{2u} model (I). In the D_{4h} point group, the C–H groups of the set of pyrrolic positions and those of the set of *meso*-positions must move in phase, but the two sets may be either in or out of phase with each other, for the allowed infrared transitions (symmetry A_{2u}). The two resultant absorption bands probably lie in the range 830—880 cm.$^{-1}$ in the porphins, since of two fairly strong bands in this range one, between 834 and 852 cm.$^{-1}$, disappears on *meso*-substitution, and the other, between 853 and 876 cm.$^{-1}$, is absent from the spectra of the compounds substituted in the pyrrolic positions (Table 1). Other bands due to out-of-plane C–H vibrations, if present, are either too weak or vary too widely in frequency from compound to compound to be identified. Six transitions due to in-plane C–H vibrations are allowed according to the D_{4h} model of porphin. The bands at 1048, 1184,

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[10] Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.
[11] Coulson, " Valence," Oxford Univ. Press, 1952.
[12] Spedding and Whiffen, *Proc. Roy. Soc.*, 1956, *A*, **238**, 245.
[13] Whiffen, *Spectrochim. Acta*, 1955, **7**, 253; *J.*, 1956, 1350.

and 1224 cm.$^{-1}$ in the spectrum of porphin may be due to the allowed in-plane deformation modes, and those at 3036, 3102, and 3181 cm.$^{-1}$ to the allowed stretching modes.

A number of bands, due to ring vibrations, appear consistently in the spectra of the majority of the compounds studied. Bands near 620, 690, 770, and 1110 cm.$^{-1}$ are particularly insensitive to substitution in the porphin nucleus and to reduction of the nucleus to the di- and the tetra-hydro-stage, suggesting that these bands are due to the vibrations of moities common to the whole series of compounds, namely, the pyrrole rings. The ring breathing vibration of pyrrole lies [7] at 1144 cm.$^{-1}$, and the 1110 cm.$^{-1}$ band of the porphins may be due to a corresponding vibration in which opposite pyrrole rings undergo the breathing motion out of phase (symmetry E_u in D_{4h}). The 620 and 690 cm.$^{-1}$ bands of the porphins may be due to similar E_u out-of-phase combinations of in-plane pyrrole ring deformation vibrations which absorb at 647 and 711 cm.$^{-1}$ respectively in pyrrole,[7] and the 770 cm.$^{-1}$ band of the porphins to an in-phase combination (symmetry A_{2u} in D_{4h}) of an out-of-plane pyrrole ring deformation vibration which absorbs [7] at 838 cm.$^{-1}$ in pyrrole itself. The fall in the frequency of these vibrations on passage from pyrrole to porphin may be ascribed to the reduction of the double-bond character of the pyrrole ring bonds in porphin, due to the exocyclic conjugation of the pyrrole nuclei, permitting readier deformation of those nuclei. The crystallographic evidence shows [5] that the αβ-bonds of the pyrrole rings in phthalocyanine are particularly long (1·49 Å), and so possess a small double-bond character. Other bands appearing regularly in the spectra of the porphins are a pair in the region 725—750 cm.$^{-1}$, and one in the range 950—1000 cm.$^{-1}$ (Table 1).

In the spectra of the substituted porphins there are a number of absorption bands due to the substituents, which are mainly either methyl or ethyl groups. For the most part these bands lie in the frequency ranges characteristic of the vibrations of such groups, but in the *meso*-tetramethyl derivatives (compounds 8, 9, and 14, Table 1) the asymmetrical C–H stretching frequency of the methyl groups is lowered by some 40 cm.$^{-1}$ and the symmetrical stretching and deformation frequencies by some 20 cm.$^{-1}$, the usual ranges for these vibrations of the methyl group [8] being 2962 ± 10, 2872 ± 10, and 1380—1370 cm.$^{-1}$ respectively. In the *meso*-tetramethylporphins there is steric hindrance between each methyl group and the β-C–H groups of the two adjacent pyrrole rings, and the resultant compression lowers the effective restoring force, and thus the frequencies, of these vibrations of the methyl group.

EXPERIMENTAL

Materials. The compounds used in the present investigation were kindly supplied by Dr. U. Eisner,[14] Professor C. Rimington kindly providing an additional specimen of porphin. The porphin derivatives listed in Table 2 were deuterated by three successive equilibrations in dioxan–deuterium oxide.

Infrared spectra. These were measured with a Perkin-Elmer model 12 C spectrometer, prisms of lithium fluoride, sodium chloride, and potassium bromide being used for the ranges 4000—2000, 2000—700, and 700—400 cm.$^{-1}$ respectively. The compounds were examined as solids included in pressed potassium bromide discs, which, contrary to previous experience,[4] gave better spectra than suspensions in mulling agents. The compounds listed in Table 2 were also examined in carbon tetrachloride solution.

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[14] Eisner, *J.*, 1957, 854, and references cited therein.