Infrared studies of symmetrically and asymmetrically substituted tetrapyrrolic macrocycles: free bases and indium derivatives

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Abstract—The infrared spectra of symmetrically and asymmetrically *para*-substituted tetraphenylporphyrins as well as their indium complexes and their aminoacid ethyl ester derivatives have been investigated and the assignment of absorption bands to characteristic vibrational modes has been proposed.

INTRODUCTION

Proteins play a very important role in performing many fundamental functions in the form of enzymes, hormones, antibodies, translocators, receptors, etc.; thus in many ways, their labelling has become an important tool in medicine both for diagnosis and for therapy. The use of a new class of bifunctional chelating agents has been developed for the labelling of such macromolecules, but these compounds seem to present an *in vivo* instability; for this reason, we turned our attention towards more stable reagents such as tetrapyrrolic macrocycles and their metallated derivatives [1, 2] and studied model coupling reactions between symmetrically and asymmetrically functionalized arylporphyrins and aminoacid esters in order to characterize clearly the coupling products.

Although porphyrins and metalloporphyrins have been extensively studied [3–12], only a few studies concern the detailed assignment of absorption bands in the infrared spectral region of *para*-substituted tetraphenylporphyrins [3, 6, 13–16]. In particular, no precise work is reported in the case of asymmetrically substituted arylporphyrins.

In the present work, a study has been made of the i.r. spectra of symmetrically or asymmetrically substituted carboxyphenylporphyrins, their aminoacid derivatives and their indium complexes.

EXPERIMENTAL

Free base porphyrins and aminoacid derivatives

The syntheses of the free base porphyrins by modification of known procedures are described in ref. [2], as well as coupling with aminoacid ethyl esters.

Indium derivatives

The indium derivatives 5, 6 and 8 were prepared by refluxing the corresponding free base with indium trichloride in glacial acetic acid and purified by chromatography on silica gel with chloroform for 6 and 8 or chloroform/methanol (60/40) for 5 [2].

TTPInCl (7) was prepared and purified following the method reported by BHATTI et al. [29].

Infrared spectra

Infrared spectra were recorded between 4000 and 300 cm^{-1} on a Perkin-Elmer 683 spectrometer coupled with a computer; samples were 0.5% dispersion in KBr pellets.

RESULTS AND DISCUSSION

The structure of the porphyrins and their indium derivatives used in this study are given in Table 1. The aminoacid esters coupled with these arylporphyrins are: leucine ethylester (LeuEt), alanine ethylester (AlaEt) and phenylalanine ethylester (PheEt).

The principal infrared absorption bands of these macrocycles which appear between 4000 and 350 cm^{-1} as well as their approximate intensities and their assignments to various modes of vibration are listed in Table 2 for the symmetrical macrocycles, in Table 3 for the asymmetrical ones and in Table 4 for the indium derivatives.

Assignments for all these spectra have been made by comparison with work done in our laboratory or published by other authors.

TCPPH₂, 1, was first prepared by BARDOS *et al.* [14] who reported its infrared spectrum in the range of $3600-700 \text{ cm}^{-1}$ as well as that of its ester derivative 2 (T(*p*-COOMe)PPH₂) and of TTPH₂ 3; one must note that for these macrocycles, i.r. assignments were relatively imprecise.

A more general vibrational analysis is given for compounds 1-3 and extensively for the aminoacid ester derivatives of 1. We have also extended this study to include the asymmetrically substituted macrocycle TTCPPH₂, 4, and its aminoacid ester derivatives as well as their indium complexes.

Free base porphyrins (Tables 2 and 3)

Infrared vibration frequencies are classified in two categories: (i) characteristic group frequencies from $3500 \text{ to } 1200 \text{ cm}^{-1}$; (ii) the "fingerprint" region of frequencies below 1200 cm^{-1} .

Vibrations in the first region are mainly stretching modes for individual bonds like N-H, C-H, C=O and have frequencies at practically constant values, irres-

	R N M	N	
n°	R, R'	М	Compound
1	$\mathbf{R} = \mathbf{R}' = \mathbf{COOH}$	2H	ТСРРН
- la	$\mathbf{R} = \mathbf{R}' = \text{CONHCHCOOEt}$	2H	T(p-COLeuEt)PPH ₂
1 b	$\mathbf{R} = \mathbf{R}' = \mathbf{CONHCHCOOEt}$	2H	T(p-COAlaEt)PPH ₂
10	$\mathbf{P} = \mathbf{P}' = \mathbf{CONHCHCOOFt}$	่วน	
10	K = K = CONTENEOOELCH2Ph	211	(p-COFIEEt)FFH2
2	$\mathbf{R} = \mathbf{R}' = \mathbf{COOMe}$	2H	$T(p-COOMe)PPH_2$
3	$\mathbf{R} = \mathbf{R}' = \mathbf{M}\mathbf{e}$	2H	TTPH ₂
4	R = MeR' = COOH	2H	TTCPPH ₂
4a	$\mathbf{R} = \mathbf{MeR'} = \mathbf{CONHCHCOOEt}$	2H	$TT(p-COLeuEt)PPH_2$
4b	$\dot{C}H_2i$ -Pr $\mathbf{R} = \mathbf{Me}\mathbf{R}' = \mathbf{CONHCHCOOEt}$	2H	$TT(p-COAlaEt)PPH_2$
4c	R = MeR' = CONHCHCOOEt	2H	TT(p-COPheEt)PPH ₂
	CH, Ph		
5	$\mathbf{R} = \mathbf{R}' = \mathbf{COOH}$	InCl	TCPPInCl
6	$\mathbf{R} = \mathbf{R}' = \mathbf{COOMe}$	InCl	T(p-COOMe)PPInCl
7	$\mathbf{R} = \mathbf{R}' = \mathbf{M}\mathbf{e}$	InCl	TTPInCi
8	$\mathbf{R} = \mathbf{M}\mathbf{e}\mathbf{R}' = \mathbf{COOH}$	InCl	TTCPPInCl

Table 1. Structures of tetraarylporphyrins and their indium derivatives

pective of the overall molecular structure. For the second category, frequencies in general arise from vibrations in which many atoms are moving simultaneously; they include in-plane (δ) and out-of-plane (γ) bendings of C-H and C-C bonds and vibrations of ring structures. Porphyrin spectra are quite complex in this region and it is not surprising to find disagreements as to their assignments.

The NH stretching vibration of pyrrole appears as a weak intensity band at 3325 ± 5 cm⁻¹ and should be indicative of intramolecular hydrogen bonding [3].

Bands of weak intensities are found in the $3150-2850 \text{ cm}^{-1}$ region and can be assigned to CH stretching modes. The bands between 3125 and 3025 cm^{-1} are associated with aromatic CH vibrations of phenyl and pyrrole rings while those in the $2980-2855 \text{ cm}^{-1}$ range involve antisymmetric and symmetric alkyl CH vibrations.

The 1740–1700 cm⁻¹ region permits clear distinction between carboxylic acid and ester, the former absorbing at a lower frequency (1700 cm⁻¹ for TCPPH₂ or TTCPPH₂). For the ester groups, by comparison with ester groups of aminoacid residues (1740 cm⁻¹ for compounds **1a**–c and 1737 \pm 3 cm⁻¹ for **4a–c**), an important shift to lower frequency is observed with T(*p*-COOMe)PPH₂ (1700 cm⁻¹) which is caused by a conjugated double bond involving both phenyl and macrocycle.

Below 1700 cm⁻¹ we found characteristic absorptions of phenyl and pyrrole groups and of *para*-phenyl substituents.

Phenyl modes. The "meso" phenyl vibrations present in all the spectra have been identified taking into account earlier studies [13, 14, 18–20], according to WILSON'S notation [18].

We have tentatively assigned those frequencies which were almost the same for each of the 10 molecules as follows (cm⁻¹): 1612 ± 3 : v_{8a} ; 1566 ± 1 : v_{8b} ; 1517 ± 3 : v_{19a} (absent in 2); 1161 ± 4 ; v_{9a} ; 1113 ± 3 : v_{18b} ; 1077 (3) and 1100 ± 4 : v_{18a} ; 817 ± 3 : v_{10a} ; 708 ± 3 : v_4 for the disubstituted phenyl groups; 702: v_4 , for the monosubstituted phenyl; 396 ± 6 : v_{16a} .

Among phenyl vibrations coupled with substituent vibrations, two of them are v_e : 1184 ± 4 and v_d : 763 ± 3 cm⁻¹ (Table 2) and v_e : 1185 ± 1, v_d : 762 ± 3 cm⁻¹ (Table 3). As phenyl substituents are different (carbo-xylic acid, carbomethoxy, methyl or aminoacid groups) it seems normal that the coupled vibration v_e and v_d , which are very sensitive to the nature of the substituent, absorb at slightly different frequencies [21].

These assignments are compatible with the results obtained by calculation for the vibrational spectra of

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	2	1a	16	1c	Assignment	Ref.
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	3320 w	3330 w	3320 w	3320 w	3330 w	$v(N-H \cdots N)$	3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3060 w	3060 w			3060 w	v(aromatic CH)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			3030 w		3030 w	v(aromatic CH)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $				2980 m	2980 w		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		2960 w	2955 s		2960 w		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		sh 2930 w	sh 2930 mw	2930 m	2930 w }	v (aliphatic CH, CH ₂ , CH ₃)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			2870 m	sh 2870			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		2855 w	1740	1.7.40)		
		1725	1740 vs	1/40 s	1/40 s	v(C=O) ester	
	1700	1725 V\$				V(C=O) ester	
	1/00 s		1680	1650	1/50	v(C=0) acid	17.10
	1610	1600	1650 vs	1650 vs	1652 s	amide I band	17,18
	1610 ms	1609 ms	1010 \$	1010 \$	1010 \$	v _{8a} (pnenyl)	13, 18, 19
	1505 mw	1307 W	sn 1505 mw	sn 1505 w	1505 W	v _{8b} (pnenyl), v(C=C)pyrrole	13-13, 18
	1616		1532 S	1538 \$	1555 S	amide II band (assoc.)	17, 18
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1313 W		\$n 1518 m	sn 1520 m	SII 1517 ms	v_{19a} (prenyl), v_{15} (pyrrole)	15, 14, 18
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1472	1471	1498 ms	1500 ms	1498 s	amide II band (free)	18
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1472 VW	14/1 W	14/2 m	14/5 m	14/6 m	v ₆ (pyrrole)	130, 18
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		1425	1450 W	1430 m	1430 mw	$o_{as}(CH_3), o(CH_2)$	4, 15
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1402 -	1455 ms	1400	1400	1447 mw	$o_{as}(CH_3)$ ester	17
135 ht1360 w1372 m1379 m1375 m $\delta_g(CH_3)$ 4, 13a1380 w1372 m1375 m $\delta_g(CH_3)$ 4, 13ash 13451350 w1345 m1346 m1348 m $v = (-N)$, pyrrole4, 13, 14, 171311 mw1310 mw1303 mw1309 mwsh 1305 v_3 (phenyl)18, 201280 vs1280 vs v_{as} (C-O) ester1717br 1271 msh 1262 s1272 m1265 mw1262 mw v_{as} (C-O) ester17sh 1224 wsh 1224 wsh 1223 wsh 123 msamide III band251180 m1180 m1187 m1188 mw1187 m v_{as} (p-subst. phenyl)19, 21sh 11651162 m1165 mw1157 w v_{as} (p-subst. phenyl)13a, 14, 18, 191110 mw1114 s1110 vw1116 mwsh 1202 m δ NH (pyrrole)101020 mw1021 ms1022 m1095 w1096 mw v_{1as} (phenyl)13a, 181020 mw1021 ms1022 m δ NH (pyrrole)13a, 18982 w982 w982 m982 w982 w924 w925 w982 w982 w982 m968 m966 m969 m v_{1a} (phenyl)13a, 18968 m966 m968 m868 m868 m δ (ring) and δ (C-O)13a, 18800 s805 s800 ms800 ms802 ms δ (ring) and δ (CH) pyrrole13a, 18968 m966 m668 m866 m δ (ring) and δ (CH) pyrrole <t< td=""><td>1405 m</td><td>1404 111</td><td>1400 mw</td><td>1400 mw</td><td>1400 mw</td><td>v_{14} (pyrrole) $v(C, O) = \delta(OH)$ acid</td><td>10</td></t<>	1405 m	1404 111	1400 mw	1400 mw	1400 mw	v_{14} (pyrrole) $v(C, O) = \delta(OH)$ acid	10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1365 mw	1290	1272	1270 -	1275	V(C=O), V(OH) acid	17
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ab 1245	1360 w	1372 m 1345 m	13/9 III 1346 m	1373 11	$v_{s}(C\Pi_{3})$	4, 134
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	sn 1343	1350 W	1345 m 1227 m	1340 m	1546 m	v(=C-N) pyrrole	4, 13, 14, 17
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1211 mm	1210	1337 III	1200	ab 1205	v (nhonvil)	19 20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1311 mw	1310 IIIW	1505 mw	1509 mw	\$111505	v_3 (piteliyi)	10, 20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	h= 1271 m	1200 VS	1272	1765	1262	$v_{as}(C-O)$ ester	17
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	or 12/1 m	sn 1202 s	1272 m	1205 mw	1202 mw	$r(CH_3)$ and $v(C=0)$	18
1192 w1212 ms1213 ms1213 ms1213 ms110 ms11, 181180 m1180 w1187 m1188 mw1187 m $v_e(phenyl)$ 19, 21sh 11651162 m1165 mw1157 w $v_{9a}(phenyl)$ 18, 191116 mw1114 s1110 vw1116 mwsh 1115 $v_{18b}(p-subst. phenyl)$ 13a, 14, 18, 191102 mw1104 s1095 vw1095 w1096 mw $v_{18a}(phenyl)$ 13a, 14, 18, 201020 mw1021 ms1022 m1021 m1022 m δ NH (pyrrole)10993 w995 w994 mw995 w $v_2(pyrrole)$ 13a, 18982 w982 w982 w982 w $v_{12}(pyrrole)$ 13a, 18968 m966 m969 m968 m969 m $v_{11}(pyrrole)$ 13a, 18sh 882 vwsh 882 vwsh 884 wsh 882 vwsh 883 vw $v_{20}(pyrrole)$ 3, 18sh 820 wsh 820 mssh 819 wsh 820 mssh 820 ms3, 18sh 739 mw734 m733 m732 m733 m $\gamma_{10}(p-subst. phenyl)$ 13a, 16702 m708 vwsh 710sh 710 v_4 (phenyl)18 v_4 (mono-subst. phenyl)18, 19670 w675 w632 vw632 vw632 vw632 vw495 vw496 vw398 vw396 vw399 vw398 vw495 vw496 vw $v_{16g}(phenyl)$ 18, 20	511 1224 W	122 4 W	511 1224 W	1212 mc	1213 m	amida III hand	17 19
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1102 w	1211 m	1212 115	ch 1200 m	annue III banu	17, 10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1180 m	1180 w	1187 m	1188 mw	1187 m	v (phenyl)	19 21
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	sh 1165	1100	1167 m	1165 mw	1157 w	v _e (phony)	18 19
1110 mw1110 mw<	1116 mw	1114 c	1110 vw	1116 mw	eb 1115	y_a (prough)	139 14 18 10
1102 mw1104 s1095 vw1095 w1096 mw1096 mw114 vs (C G) ester171020 mw1021 ms1022 m1021 m1022 m δ NH (pyrrole)10993 w995 w994 mw994 w995 w v_2 (pyrrole)13a, 18982 w982 w982 mw982 w982 w v_{12} (pyrrole)13a, 18968 m966 m969 m968 m969 m v_{11} (pyrrole)13a, 18988 w882 vwsh 882 vwsh 882 vwsh 882 vwsh 883 vw868 mw866 w869 m868 m868 m v_{20} (pyrrole)3, 18sh 820 wsh 819 wsh 819 wsh 820 mw v_{10a} (p-subst. phenyl)13a, 18800 s800 ms800 ms802 ms δ (ring) and δ (CH) pyrrole6, 13b, 16765 mw765 mw762 mw761 mw760 mw v_d (phenyl)19, 21sh 739 mw734 m733 m732 m733 m γ (NH) pyrrole7, 10725 mw δ (O=C-O)18 v_4 (mono-subst. phenyl)18, 19670 w635 vw632 vw632 vw 425 vw 493 vw485 w495 vw496 vw398 vw396 vw399 vw398 vw408 vw v_{16a} (phenyl)18, 20	1110 11.0	11143	1110 VW	i i i o mw	311115	and $v_{18b}(p-subst. phenyl)$	17
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1102 mw	1104 s	1095 vw	1095 w	1096 mw	v_{s} (phenvl)	14 18 20
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1102 1110		1070 11	1049 mw	1050 110	182(piteriji)	14, 10, 20
993 w995 w994 mw994 w995 w $v_2(pyrrole)$ 13a, 18982 w982 w982 mw982 w982 w $v_1_2(pyrrole)$ 13a, 18968 m966 m969 m968 m969 m $v_{11}(pyrrole)$ 13a, 18968 m966 m969 m968 m969 m $v_{11}(pyrrole)$ 13a, 18sh 882 vwsh 882 vwsh 884 wsh 882 vwsh 883 vw $v_{20}(pyrrole)$ 3, 18sh 820 wsh 820 mssh 819 wsh 819 wsh 820 mw $v_{10a}(p$ -subst. phenyl)13a, 18800 s805 s800 ms800 ms802 ms $\delta(ring)$ and $\delta(CH)$ pyrrole6, 13b, 16765 mw765 mw762 mw761 mw760 mw $v_d(phenyl)$ 19, 21sh 739 mw734 m733 m732 m733 m $\gamma(NH)pyrrole$ 7, 10725 mw $\delta(O=C-O)$ 18 v_4 (mono-subst. phenyl)18, 19670 w675 w632 vw632 vw632 vw485 w495 vw631 vw635 vw632 vw495 vw496 vw $v_{16a}(phenyl)$ 18, 20398 vw396 vw399 vw398 vw408 vw $v_{16a}(phenyl)$ 18, 20	1020 mw	1021 ms	1022 m	1021 m	1022 m	$\delta \mathbf{NH}$ (pyrrole)	10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	993 w	995 w	994 mw	994 w	995 w	v ₋ (pyrrole)	13a 18
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	982 w	982 w	982 mw	982 w	982 w	v. (pyrrole)	13a, 18
sh 882 vwsh 882 vwsh 884 wsh 882 vwsh 882 vwsh 883 vw868 mw866 w869 m868 m868 m868 msh 820 wsh 820 mssh 819 wsh 819 wsh 820 mw800 s805 s800 ms800 ms802 ms765 mw765 mw762 mw761 mw760 mw765 mw765 mw762 mw761 mw760 mw725 mw733 m732 m733 m733 m705708 vwsh 710sh 710725 mw702 m702 m v_4 (phenyl)18670 w675 w632 vw632 vw632 vw631 vw635 vw632 vw632 vw485 w495 vw398 vw396 vw399 vw398 vw408 vw v_{16a} (phenyl)18, 20	968 m	966 m	969 m	968 m	969 m	y ₁₁ (pyrrole)	13a. 18
868 mw866 w869 m868 m868 m v_{20} (pyrrole)3, 18sh 820 wsh820 mssh819 wsh819 wsh820 mw v_{10a} (p-subst. phenyl)13a, 18800 s805 s800 ms800 ms802 ms6, 13b, 16 v_{10a} (p-subst. phenyl)13a, 18765 mw765 mw762 mw761 mw760 mw v_{d} (phenyl)19, 21sh 739 mw734 m733 m732 m733 m v_{10m} (NH)pyrrole7, 10725 mw δ (O=C-O)18 δ (O=C-O)18sh 705708 vwsh 710sh 710 v_{4} (phenyl)18, 19670 w675 w632 vw632 vw485 w495 vw496 vw398 vw396 vw399 vw398 vw408 vw v_{16a} (phenyl)18, 20	sh 882 vw	sh 882 vw	sh 884 w	sh 882 vw	sh 883 vw		
sh 820 wsh 820 mssh 819 wsh 819 wsh 819 wsh 819 wsh 820 ms $v_{100}(p-\text{subst. phenyl})$ 13a, 18800 s805 s800 ms800 ms802 ms $\delta(\text{ring})$ and $\delta(\text{CH})$ pyrole6, 13b, 16765 mw765 mw762 mw761 mw760 mw v_{4} (phenyl)19, 21sh 739 mw734 m733 m732 m733 m $\gamma(\text{NH})$ pyrole7, 10725 mw $\delta(\text{CH})$ $\delta(\text{CH})$ 18 $\delta(\text{CH})$ 18sh 705708 vwsh 710sh 710 v_{4} (phenyl)18 $\delta(\text{O}=\text{C}-\text{O})$ 18 $\gamma(\text{phenyl})$ 18, 19670 w675 w $\delta(32 vw)$ $\delta(32 vw)$ $\delta(32 vw)$ 631 vw635 vw632 vw485 w495 vw496 vw398 vw396 vw399 vw398 vw408 vw v_{16a} (phenyl)18, 20	868 mw	866 w	869 m	868 m	868 m	v _{ac} (pyrrole)	3 18
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	sh 820 w	sh 820 ms	sh 819 w	sh 819 w	sh 820 mw	v ₁₀ (<i>p</i> -subst. phenvl)	13a 18
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	800 s	805 s	800 ms	800 ms	802 ms	$\delta(ring)$ and $\delta(CH)$ pyrrole	6. 13b. 16
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	765 mw	765 mw	762 mw	761 mw	760 mw	v ₁ (phenyl)	19. 21
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	sh 739 mw	734 m	733 m	732 m	733 m	v(NH)pyrrole	7. 10
sh 705708 vwsh 710sh 710 v_4 (phenyl)18702 m v_4 (mono-subst. phenyl)18, 19670 w675 w631 vw635 vw632 vw632 vw493 vw485 w495 vw496 vw398 vw396 vw399 vw398 vw408 vw v_{16a} (phenyl)18, 20	725 mw					$\delta(\mathbf{O}=\mathbf{C}-\mathbf{O})$	18
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	sh 705	708 vw	sh 710	sh 710		v_{\star} (phenvl)	18
670 w 675 w 631 vw 635 vw 632 vw 632 vw 632 vw 493 vw 485 w 495 vw 496 vw 398 vw 396 vw 399 vw 398 vw 408 vw v ₁₆₀ (phenyl) 18, 20					702 m	v ₄ (mono-subst. phenvl)	18, 19
631 vw 635 vw 632 vw 632 vw 632 vw 493 vw 485 w 495 vw 496 vw 398 vw 396 vw 399 vw 398 vw 408 vw v ₁₆₄ (phenyl) 18, 20	670 w	675 w					
493 vw 485 w 495 vw 496 vw 398 vw 396 vw 399 vw 398 vw 408 vw v ₁₆₆ (phenyl) 18, 20	631 vw	635 vw	632 vw	632 vw	632 vw		
398 vw 396 vw 399 vw 398 vw 408 vw v ₁₆₆ (phenyl) 18, 20		493 vw	485 w	495 vw	496 vw		
	398 vw	396 vw	399 vw	398 vw	408 vw	v _{16a} (phenyl)	18, 20

Table 2. Infrared spectra of symmetrically para-substituted tetraphenylporphyrins and their aminoacid derivatives

vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; sh, shoulder; br, broad; ν , stretch; δ and γ , deformations; r, rocking; frequency values are in cm⁻¹.

styrene and its seven deuterated vinylic isotopomers [19].

Pyrrole and skeletal modes. Important bands involving a large number of CH deformations, C-C stretchings and bendings, concern pyrrole ring and skeleton modes, most of these vibrations being highly coupled.

Among the pyrrole vibrations, it has been possible to make the following assignments by comparison with earlier work [13, 18], according to LORD's notation [22] (cm⁻¹): v_{15} : 1517 ± 3 (except 2), v_6 : 1473 ± 3, v_{14} : 1403 ± 3, v_2 : 994 ± 2, v_{12} : 983 ± 1, v_{11} : 968 ± 2, v_{20} : 867 ± 3 (except 3), v_{15} , v_6 and v_{14} concern ring vibrations; v_2 , v_{12} and v_{11} involve in-plane bending of CH.

Bands at 1565 cm^{-1} (Table 1) and $1566 \pm 1 \text{ cm}^{-1}$ (Table 2) have been assigned to pyrrole C=C vibrations [13a, 14, 15]. THOMAS *et al.* [13a] assigned the 1350 cm⁻¹ frequency to pyrrolic =C-N, on the basis of its partial single bond character.

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ref.
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	
1565 m1565 w1565 w1565 w1565 w1565 w v_{8b} (phenyl), $v(C=C)$ pyrrole13-15, 181558 w1558 w1558 w1558 w1558 w1558 wsh 1533 mwsh 1532 mwsh 1532 mamide II band (assoc.)17, 181515 ms1517 mw1518 mw1517 m v_{19a} (phenyl), v_{15} (pyrrole)13, 14, 181475 s1475 ms1472 ms1472 ms1473 s v_6 (pyrrole)13b, 18	. 19
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	18
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	
1515 ms1517 mw1518 mw1517 m v_{19a} (phenyl), v_{15} (pyrrole)13, 14, 181497 mw1498 m1498 samide II band (free)181475 s1475 ms1472 ms1472 ms1473 s v_6 (pyrrole)13b, 18	
1497 mw 1498 m 1498 s amide II band (free) 18 1475 s 1475 ms 1472 ms 1472 ms 1473 s ν_6 (pyrrole) 13b, 18	, 18
1475 s 1475 ms 1472 ms 1472 ms 1473 s v_6 (pyrrole) 13b, 18	
	8
sh 1455 m 1455 w sh 1455 m 1452 m 1456 m $\delta_{ss}(CH_3), \delta(CH_2)$ 4, 13	
1406 m 1406 m 1402 mw 1402 mw 1402 m v ₁₄ (pyrrole) 18	
1386 w v (C–O), δ (OH) acid 17	
1380 mw 1380 w 1373 mw 1379 mw 1374 ms δ_s (CH ₃) 4, 13a	
1355 s 1353 m 1350 m 1349 ms 1350 s v(=C-N) pyrrole 4, 13, 14, 17	14, 17
1311 vw 1314 vw 1309 w v ₃ (phenyl) 18, 20	
br 1280 m v _{as} (C–O)acid 17	
1258 mw 1265 s 1262 m 1263 s 1262 s r(CH ₃) and v(C-O) 18	
1227 s 1225 m 1224 m 1224 m 1224 ms porphyrin core vibration 25	
sh 1220 ms sh 1220 mw sh 1218 m sh 1218 m sh 1218 ms $r(CH_3)$	
sh 1207 w sh 1210 mw sh 1205 m amide III band 17, 18	
$\frac{1186 \text{ s}}{1186 \text{ m}} = \frac{1185 \text{ m}}{1185 \text{ m}} = \frac{1185 \text{ s}}{1185 \text{ s}} = \frac{v_e(\text{phenyl})}{v_e(\text{phenyl})} = \frac{19, 21}{19, 21}$	
1158 mw 1158 vw 1158 mw 1162 mw 1157 mw v_{9a} (phenyl) 18, 19	
1112 m sh 1110 ms 1110 ms 1110 ms 1110 ms $v_{18b}(p-\text{subst. phenyl})$ 13a, 14, 18,	4, 18,
1077 mw 1100 ms 1099 m 1096 ms 1098 ms $v_{1g_0}(\text{phenyl})$ 14, 18, 20	20
1026 m 1024 s 1024 m 1024 s 1024 ms $\delta(\text{NH})$ pyrrole 10	•
990 ms 990 mw 995 mw 995 mw 995 mw v_2 (pyrrole) 15a, 18	5
982 ms 984 mw 984 mw 984 mw 983 mw v_{12} (pyrrole) 13a, 18	5
970 vs 909 s 909 vs 909 vs 909 vs 909 s v_{11} (pyrrole) 13a, 18	5
902 mw 901 w 901 w 901 w 901 w 901 w 201 w 91 w 920 w	
839 mw 840 w 838 w 830 w 920 w $7_{20}(\text{pyrrote})$ $3, 18$	
635 m 630 630 635 635 635 8	٥
802 vs $802 vs$ 802	3 16
502 13 13 13 13 13 13 13 13	, 10
5h750 vw 765 w 761 w 762 w 760 w v (nhenvi) 10.21	
$739 \times 737 \text{ ms}$ 736 ms 736 ms 736 ms 737 m $\gamma(\text{NH})$ $\gamma(\text{NH})$	
711 w 711 w 710 w 710 w 510 w 510 w 100 w 100 w	
700 m $(100 m)$ $100 m$ 10	
647 w 646 vw 647 vw 646 vw 645 vw	
637 w 635 vw 637 vw 635 vw 635 vw	
563 w 565 w 563 w 562 w 563 w	
527 m 528 mw 526 w 528 w 528 w	
475 w 482 w 482 w 482 w	
413 mw 405 m 400 mw 400 vw 403 m v_{16a} (phenyl) 18, 20	

Table 3. Infrared spectra of TTPH2, TTCPPH2 and its aminoacid derivatives

Abbreviations as Table 1.

The band which appears at 1023 ± 3 cm⁻¹ can reasonably be assigned to the in-plane NH bending vibration, the out-of-plane NH bending vibration could be the absorption at 735 ± 4 cm⁻¹. The values, while a little higher than normal, are still in agreement with those in the literature [10].

The very intense band present in all the spectra at 802 ± 3 cm⁻¹ and common to all ligands, free bases or metalloderivatives, has been suggested to be a pyrrole unit vibration [6, 13b]; in a more recent study to locate structure-sensitive bands, NAKAMOTO *et al.* [16] have

shown that this band could be ascribed to a vibration involving deformation of the pyrrole ring with a contribution from the in-plane bending of pyrrolic CH.

Substituent modes. Para-methyl groups absorb near 1453 cm⁻¹ (antisymmetric in-plane bending) while the band at 1376 ± 4 cm⁻¹ is assigned to their symmetric in-plane bending vibrations.

In the case of ester 2, the antisymmetric in-plane bending of the methyl group could be the absorption at 1435 cm^{-1} .

Several C–O stretching frequencies are present in these macrocycles; aminoacid ester chains contribute to an absorption near 1262 cm^{-1} while the intense absorption at 1280 cm^{-1} characterizes the ester 2 (antisymmetric stretching); its symmetric stretch is found at 1114 cm^{-1} .

In the case of free acids 1 and 4, a broad absorption near 1271 and 1280 cm⁻¹ respectively is observed. The weak band present near 1386 cm⁻¹ could arise from a C–O vibration coupled with an OH in-plane deformation vibration [17].

Absorptions associated with amide functions in compounds 1a-c and 4a-c may be used diagnostically to prove their presence. These absorptions have been determined by comparison with the spectra of starting materials 1 and 4 and of ethyl ester aminoacid hydrochlorides.

The coupling of aminoacid ethyl esters with porphyrins 1 and 4, give rise to amide I, II and III absorptions at respectively: 1651 ± 1 , 1535 ± 3 , $1212 \pm 1 \text{ cm}^{-1}$ for compounds 1a-c and 1648 ± 2 , 1532 ± 1 , $1207 \pm 3 \text{ cm}^{-1}$ for 4a-c. These values are consistent with those observed in the case of secondary amides [17]. One must note that the band at $1498 \pm 2 \text{ cm}^{-1}$, present in the aminoacid derivatives, could be attributed to the free amide II band, the amide II band around 1530 cm^{-1} being the associated form [18].

Indium derivatives

The i.r. spectra of indium chelates **5–8** (Table 1) have been recorded; Table 4 lists their vibrational frequencies and their principal assignments.

After complexion with a metal, the changes in the i.r. spectra depend little on the nature of the metal when it is divalent; in the case of indium III, a trivalent species, the i.r. spectra are altered because of the different structure and symmetry of the complex. This is due to the displacement of indium out of the macrocyclic plane and the consequent distortion of the porphyrin skeleton to give a square pyramidal structure [23].

By comparison with the corresponding free bases, the reduction of the symmetry in the indium derivatives results in an increase in the number of absorption bands, many of which have low intensities. Nevertheless, many bands remain relatively unchanged.

The most fundamental modification concerns NH stretching bands and absorptions around 990 cm^{-1} .

As expected, the absorption bands due to NH stretching are absent from the spectra of the indium derivatives [3], as well as the in-plane and out-of-plane NH bendings around 1023 and 735 cm⁻¹, respectively.

The other characteristic difference between the infrared spectra of their corresponding free bases (in Tables 2 and 3) and the indium complexes is that the three bands appearing between 966 and 996 cm⁻¹ for the free bases collapse to one strong band at 1010 cm^{-1} in the chelates; this intense band has been attributed to a strong porphyrin ring vibration [6, 13b] coupled with CH vibration of the pyrrole units [15, 24].

Some other minor changes are observed after metallation with indium: in particular, the two bands at 1232 ± 2 and 1210 ± 1 cm⁻¹ could be assigned to porphyrin core vibrations, originating in the splitting of the 1224 cm⁻¹ band in the corresponding free bases [25]; this splitting could be due to the lowering of the symmetry when indium is introduced.

All the other absorption bands characteristic of peripheral substituents are relatively insensitive to the introduction of indium.

In the indium chelates 5 and 8, the C-O acid stretching vibration appears at slightly higher frequency than in their corresponding free ligands, whereas in the case of the ester derivative 6, no change is observed.

The band at 1385–1386 cm⁻¹ of the carboxylic acid derivatives 5 and 8 is assigned to a C–O stretching vibration coupled with an OH in-plane deformation [17]; the 1270 cm^{-1} absorption for 5 should have same origin.

For the ester derivative 6, just as in its corresponding free base, the two strong intensity bands at 1284 and 1115 cm^{-1} could be associated with C–O–C stretching vibrations.

Taking into account the complexity of porphyrin ligand absorptions and the strong interaction between metal and ligand, it is rather difficult to detect any characteristic absorptions for indium-ligand vibrations; such absorptions are expected to lie in the far infrared region, but in this range absorption bands possess very weak intensity and probably represent coupled mode vibrations [4]. We have compared the indium derivatives with their corresponding free bases after accumulation of their i.r. spectra between 500 and 250 cm^{-1} . With these conditions, the medium band observed around 410 cm⁻¹ in the free bases gives rise to two medium bands near 430 and 398 cm⁻¹ for the indium derivatives. By comparison with its corresponding free base, we previously observed in the Raman spectrum of chloro indium tetraphenylporphyrin the presence of a peak at 398 cm⁻¹ which could be assigned to the In-Cl stretching (27). Taking into account this result, the band appearing in the i.r. spectra of compounds 5-8 at 398 cm^{-1} , could also be attributed to In-Cl stretching according to a literature report [28].

CONCLUSION

The results reported here support our hypothesis that vibrational spectroscopy and especially infrared spectroscopy can be diagnostic for the *para*-phenylsubstituted porphyrins and their indium derivatives. In particular, absorption bands relative to the substituents may be used to assert their presence. For indium derivatives, the most characteristic feature is the very strong band at 1010 cm^{-1} which can be checked for indium insertion. Since these complex molecules possess a great number of vibrations, the fact that the macrocycle is symmetrically or asym-

5	6	7	8	Assignment	Ref.
		3045 w		v (aromatic CH)	3
	3000 w	3020 mw 2960 mw	3020 w	v (aromatic CH)	3
	2950 w)	v(aliphatic CH, CH ₂ , CH ₃)	
		2919 mw	2920 w		
	1726	2865 w	2868 w)		16
1704	1725 VS		1706	v(C=O)ester	15
1704 VS	1600 -	ab 1612 m	1/00 mw		15 18 10
1000 vs	1569	1568 m	1569 mm	v_{8a} (phenyl) v_{8a} (chenyl) v_{8a}	13, 10, 19
1538 w	1308 W	1300 W	1545 m	v ₈₆ (pnenyi),v(C=C)pyrrole	150, 15, 16
ch 1516 vw	eh 1517 vuv	1518 m	1518 mw	y (nhenyl) y (nyrrole)	13 14 18
1505 w	1504 vw	eh 1505 w	sh 1506 w	v_{19a} (preny), v_{15} (pyrrole) v(C-C) phenyl, $v(C-N)$ pyrrole	15, 14, 16
1475 w	1477 mw	1478 s	1475 m	v (pyrrole)	135 18
1475 4	1453 w	1470 3 1450 mw	1473 m	δ (CH ₂)	150, 10
	1435 ms	1450 114	1455 ₩	δ (CH ₂) ester	17
1403 ms	1402 m	1404 w	sh 1402 m	v. (pyrrole)	13h 18
1385 m	1.02 m		1385 s	$v(C-O), \delta(OH)$ acid	17
1336 mw	sh 1335 mw	1338 ms	1339 m	v (= C - N)	15 24
1312 m	1310 m	1300 w	1300 w	v _s (phenvl)	18, 20
	br 1284 vs		1000 0	$v_{-}(C-O)$ ester	17
br 1270 ms	01 120 1 10			$v_{as}(C-O)$ acid	17
01 12/0 110		1261 ms		r(CH ₂)	18
sh 1234 m	sh 1230 vw	1231 w	1234 vw	porphyrin core vibration	25
1209 ms	1209 ms	1210 ms	1211 ms	porphyrin core vibration	25
	1192 m			FF,	
1178 m	1180 m	1182 ms	1183 m	v. (phenyl)	19. 21
1221 m				e (p) - /	,
	1115 s			$v_{\bullet}(C-O)$ ester	17
1103 m	sh 1105 s	1108 ms	1110 m	v _{18b} (p-subst. phenyl)	13b, 15, 18
1075 mw	1075 mw	1070 ms	1072 m	v _{isc} (phenyl)	17, 18, 24
1010 vs	1010 vs	1010 vs	1010 vs	δ (CH) pyrrole and	6, 13b, 15, 24
				porphyrin ring vibration	
965 vw	964 mw			ring deformation	10
890 vw	890 w		890 vw	0	
869 mw	867 mw	sh 868 w	sh 864 w	v ₂₀ (pyrrole)	3, 18
		847 mw	848 w		
825 w	824 m	sh 819 w	828 w	$v_{10a}(p-subst. phenyl)$	13a, 18
798 s	800 ms	800 s	800 s	δ (ring) and δ (CH) pyrrole	6, 13b, 16, 24
sh 789 s			sh 782 mw		
sh 767 ms	765 s			pyrrole ring	15
	sh 747 mw	755.mw		pyrrole ring	15
732 vw	732 vw	735 vw	735 vw		
721 m	721 ms	723 m	725 ms	porphyrin ring deformation	26
sh 707 w	709 m			v ₄ (phenyl)	18
	695 w				
663 w	665 w	665 vw	664 vw		
637 vw	637 w	641 vw	635 vw		
575 w	575 w	572 w	571 w		
520 w		526 m	525 w		
483 w	494 mw		485 w		
		432 w	429 w		
420 vw	418 vw	419 vw	sh 418 vw		

Table 4. Infrared spectra of indium porphyrins: TCPPInCl (5), T(p-COOMe)PPInCl (6), TTPPInCl (7) and TTCPPInCl (8)

Abbreviations as in Table 1.

metrically substituted does not cause any appreciable modification of the i.r. spectra.

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