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THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF PORPHYRINS—XI[1]

SELF-AGGREGATION OF ZINC(II) *MESO*-TRIFLUOROACETOXYOCTAETHYLPORPHYRIN

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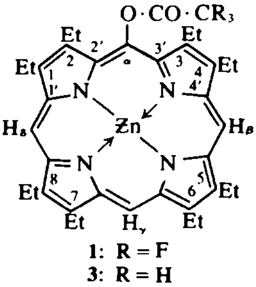
Abstract—Complex formation in zinc(II) *meso*-trifluoroacetoxyoctacthylporphyrin (1) and the corresponding acetate (3) has been studied by ^{1}H and ^{13}C NMR spectroscopy. The large concentration dependence of the ^{1}H chemical shifts of 1 has been analysed in terms of a monomer-dimer equilibrium to give $K \sim 3.0$ l mole^{-1} and monomer-dimer shifts of up to 4.2 ppm (for the γ-*meso* proton). The dimers are immediately dissociated upon addition of methanol. In complete contrast, 3 shows no concentration dependence nor any change upon addition of methanol.

The conformations of the model compounds phenyl acetate (4) and phenyl trifluoracetate (5) were studied by CNDO and solvation calculations and, for 4, by a LIS experiment. Compound 4 exists as the *endo* conformer in non-polar media, but the *exo* conformer is preferentially solvated and is also formed when 4 complexes with Eu(fod)$_3$. In compound 5, the *exo*-*endo* energy difference is smaller and is not so affected by solvation; 5 shows no LIS.

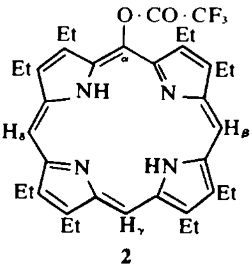
The large complex shifts found for compound 1 are best explained on the basis of a dimer structure in which the O·CO·CF$_3$ groups play no part in the association, which is presumably due to a novel metal to porphyrin interaction.

The tendency of porphyrins to aggregate and form specific complexes in solution has been known for some time, and has been widely investigated.[2] Two distinct types of complex have been proposed: one due to an interaction between the porphyrin rings in metal-free porphyrins in solution, and the second to a more specific complex between donor groups in the side-chains and the metal (e.g. Mg) in a metalloporphyrin. The two types of complex are immediately differentiated by observation of the effect of addition of small quantities of donor molecules (e.g. methanol, pyridine, tetrahydrofuran) to the solution; the former type of complex shows no appreciable change whereas the latter is immediately dissociated to monomer. However, in order to explain the remarkable concentration dependent NMR shifts observed in these aggregates, it is necessary to consider the detailed geometry of the complex in each case.

In the ^{1}HMR spectrum of zinc(II) *meso*-trifluoroacetoxy - octaethylporphyrin (1)[3] we observed (CDCl$_3$ soln) concentration dependence of the chemical shifts which was markedly greater than previously reported effects in metalloporphyrins, and moreover, totally absent in the metal-free compound 2. Furthermore, the concentration dependence was also absent in the zinc(II) *meso*-acetoxyoctaethylporphyrin (3), in which the donor capacity of the side-chain carbonyl function might be expected, *a priori*, to be greater. It was therefore decided to investigate these phenomena in detail, and herein we present a ^{1}H and ^{13}C NMR study of the porphyrins mentioned, and a theoretical and LIS study of the related compounds, phenyl acetate (4) and phenyl trifluoroacetate (5).



1: R = F
3: R = H



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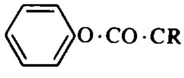

4: R = H
5: R = F

RESULTS

^{1}HMR studies. The experimental ^{1}HMR data for compound 1 are given in Table 1. Only three distinct methylene quartet patterns were resolved, but the peaks at *ca* 3.95δ are of such intensity that the remaining CH$_2$ signal lies under these. Detailed inspection of the spectrum shows that the unresolved CH$_2$ signal is not a simple 1:3:3:1 quartet but rather a more complex pattern, probably due to non-equivalent (diastereotopic) hydrogens of the methylene group, of which only some weak transitions are observed separated from the much stronger first order quartet pattern measured. This signal is presumably due to the C$_{2,3}$ methylenes. On the other hand, the C$_{2,3}$ methylenes of zinc(II) *meso*-cyano octaethylporphyrin show a clean quartet (4.34δ), one third of the intensity of the other methylenes (3.99δ); in this case, however, the fact that the cyano group is in the plane of the porphyrin ring prevents the C$_{2,3}$ CH$_2^-$ from appearing diastereotopic. In compound 1, the most notable feature of the spectrum is the large (1.2 ppm) shifts observed for the γ-*meso*-proton. These results were treated as previously[4,5] in terms of a monomer-dimer

Table 1. Proton chemical shifts (δ, ppm) of zinc(II) *meso*-trifluoroacetoxyoctaethylporphyrin (1) as a function of concentration (mole l^{-1}) in $CDCl_3$

Concentration (Molar)	meso		methylene			methyl				$CHCl_3$
	β,δ	γ			(x 2)					
0.0324	9.915	9.445	3.625	3.745	4.040	1.695	1.765	1.840	1.875	7.210
0.0634	9.740	9.070	3.390	3.550	4.020	1.590	1.690	1.835	1.910	7.190
0.0845	9.645	8.895	3.275	3.465	4.005	1.530	1.650	1.825	1.905	7.165
0.1126	9.555	8.705	3.145	3.355	3.985	1.470	1.600	1.815	1.910	7.135
0.1450	9.475	8.540	3.055	3.280	3.970	1.425	1.580	1.815	1.925	7.115
0.2028	9.340	8.290	2.870	3.100	3.950	1.345	1.510	1.795	1.935	7.050

equilibrium. In contrast to the previous studies, we found that referencing the concentration dependent chemical shifts to TMS rather that to the chloroform solvent peak gave internal shifts (e.g. a *meso*-proton vs a methyl resonance) which were accurately linear.

Employing the non-linear least squares procedure previously described[4] it was possible to fit the concentration dependence of all observed chemical shifts (referenced to TMS) with a single value for the association constant K *ca* 3.0 l $mole^{-1}$. The monomer–dimer shifts thus obtained, together with the shifts in the monomer, are shown in Table 2. Dimerisation of 1 shifts the resonances predominantly to higher field through the porphyrin ring current effect. The addition of a small quantity of methanol to a more concentrated solution of compound 1 in $CDCl_3$ displaces the signals to lower field and yields proton chemical shifts, where resolved, in close agreement with those calculated for the monomer (Table 2). This is conclusive evidence for specific coordination at the central zinc atom in the dimer, and complements the observation that the concentration dependence is absent in the metal-free porphyrin (2).

In contrast, the ^{1}HMR spectrum of 3 shows no concentration effect, nor any shift upon addition of methanol. The chemical shifts in $CDCl_3$ are also given in Table 2. The complete identity of the chemical shifts of 3 and the monomer of 1 (Table 2) is unequivocal evidence for the existence of 3 as monomer at this concentration.

^{13}*CMR studies*. With the intention of obtaining further information on the self-aggregation of compound 1, the ^{13}C spectra of 1 and 3 were obtained in $CDCl_3$ solution alone, and also after addition of methanol-d_4. Subsequently, 3 was also run in $C_2D_2Cl_4$ solution. The chemical shifts of the carbon resonances are given in Table 3, together with those of zinc(II) octaethylporphyrin [as (1), but with $O{\cdot}CO{\cdot}CF_3$ replaced with H] for comparison.

The general assignment of the signals follows from our previous studies,[6] but there are some particular points of interest. A clear distinction between overlapping C_α (adjacent to nitrogen) and C_β (peripheral) resonances can be obtained from the different intensity of the two sets of signals of the spectra in $CDCl_3$ and $C_2D_2Cl_4$. Under the standard accumulation conditions employed (Experimental) the C_α are only *ca* half of the intensity of the C_β resonances. This is probably due either to an increased line-width of the C_α signals resulting from

Table 2. Complexation shifts (ppm) for compound (1) and monomer shifts (δ, ppm) for compounds (1) and (3)

Proton	$\Delta\delta_{(monomer-dimer)}$	$\delta_{(monomer)}$ for (1)		$\delta_{(monomer)}$ for (3)[d]
		a	b	
meso (γ)	4.20	10.04	9.99	9.92
meso (β,δ)	2.09	10.21	10.08	10.06
methylene	2.73	4.01	3.9-4.1[c]	3.9-4.1[c]
methylene	2.31	4.08		
methylene	0.34	4.09		
methyl	1.28	1.88	1.88	1.87
methyl	0.92	1.90		
methyl	0.17	1.87	1.83	1.83
methyl	-0.22	1.85		

[a] Calculated from dilution experiments, see text.

[b] Measured from spectrum of (1). 0.15 M in $CDCl_3$; MeOH ca. 1.5 M.

[c] Unresolved resonances.

[d] Approx. 0.15 M in $CDCl_3$.

Table 3. ^{13}Chemical shifts (δ) for zinc(II) *meso*-trifluoroacetoxy (1) and zinc(II) *meso*-acetoxy (3) octaethylporphyrins

Compound		(1)	(1)	(3)	(3)	(3)	Zinc(II) Octaethylporphyrin
Solution[a] / Assignment		$CDCl_3$	$CDCl_3$ + CD_3OD	$CDCl_3$	$CDCl_3$ + CD_3OD	$C_2D_2Cl_4$	$CDCl_3$[d]
C=O		b	b	172.5	174.0	172.9	
C_α' ($C_{2',3'}$)		147.1	148.1	147.7	148.1	148.1	146.7
		146.6	147.4	146.7	147.0	147.1	
		145.8	146.2	145.7	145.8	145.8	
		139.2	139.4	140.9	140.5	141.1	
C_β ($C_{2,3}$)		143.9	143.8	143.3	143.1	143.9	141.1
		141.5(2)	142.1(2)	141.8	141.9	142.6	
				141.5	141.7	142.3	
		139.2	139.0	139.8	139.3	140.5	
meso	α	126.6	126.2	128.3	127.7	128.3	96.2
	β,δ	97.5	97.6	97.2	97.1	97.7	
	γ	96.2	96.7	95.8	96.0	96.6	
CH_2		22.1	22.0	22.1	22.1	22.1	19.8
		19.1(2) 19.6	19.8(3)	19.5(3)	19.8(3)	19.6(3)	
CH_3		18.3 18.5(2)	18.6(3)	18.5(3)	18.6(3)	18.5(3)	18.8
		17.1	17.2	16.9	16.9	16.9	
$CF_3(CH_3)$		115.3[c]	115.3[c]	22.1	22.1	22.1	

[a] 0.1 M in porphyrin, 1M in CD_3OD (where added).

[b] Not detected.

[c] Only centre two lines of quartet observed, $^1J_{(C-F)}$ 285 Hz.

[d] From ref. 6.

scalar relaxation of the second kind involving the nitrogen qualrupole moment (see Ref. 6 for a full treatment) or to a longer spin lattice relaxation time for these carbons. Whatever the reason, this provides a convenient method of assignment in this case, though it is not a general phenomenon in a large series of porphyrins which we have investigated.[7]

This assignment is confirmed by comparison of the spectra of compound 3 in $CDCl_3$ and $C_2D_2Cl_4$ solution (Table 3). The C_β resonances all move downfield in $C_2D_2Cl_4$ by 0.7 ± 0.1 ppm, whereas the C_α lines all move downfield by only 0.3 ± 0.1 ppm. This effect, though small is consistent and appears general in metalloporphyrins, thereby providing a simple and convenient method for assignment in complex metalloporphyrins.

Within the particular groups of signals, some assignments can be made on the basis of the well-known substituent effects.[8,9] For example, the *meso*-carbon assignment of Table 3 gives the substituent effect of the *meso*-O·CO·$CH_3(CF_3)$ groups at the *meso*-α-C, *meso*-$\beta(\delta)$-C and *meso*-α-C positions as 32.1(30.4), 1.0(1.3) and −0.4(0.0) ppm respectively. The effect at the *meso*-α-C position is particularly large [cf the corresponding effect of the O·CO·$CH_3(CF_3)$ groups in benzene (Table 5, with benzene 128.7δ^9), $\Delta\delta$ +21.9(21.7)].

Some of the resonances of the C_α and C_β carbons may also be assigned by analogy with the substituent effects of the O·CO·$CH_3(CF_3)$ groups in the benzene ring, (*ortho* −7.3(−7.5), *meta* +0.5(+1.8) ppm). With the assignment shown, the corresponding substituent effects at the carbons β and γ to the substituents are −5.8(−7.5) and +2.2(+2.7) ppm. The remaining ring resonances have shifts which are very similar to those of zinc(II) octaethylporphyrin, and no definite assignments can be made.

Likewise, the side-chain carbons show one perturbed signal for both the methyl and methylene moieties, compared with the zinc(II) octaethylporphyrin shifts; these may be assigned to the Et groups adjacent to the *meso*-substituent (i.e. the 2- and 3-Et groups). Interestingly, the perturbed methylene resonance has a downfield shift of 2.3 ppm, whereas the perturbed Me resonance has an upfield shift of 1.8 ppm. The other signals are essentially identical with those in zinc(II) octaethylporphyrin.

Unfortunately, we were unable to detect the CO resonance in 1 in either $CDCl_3$ or $C_2D_2Cl_4$ solution, presumably due to the absence of any NOE, the relatively long relaxation time for this nucleus, and the predicted multiplicity owing to the C–C–F coupling. The corresponding resonance in 3 was clearly observed, and did not, as expected, show a pronounced shift upon addition of methanol.

Comparison of the effects of addition of methanol-d_4 on the spectra of 1 and 3 is illuminating. Although addition of methanol produces downfield shifts for nearly all of the carbon signals in 1, the effects are not large (maximum 1.0 ppm), and furthermore similar, but smaller shifts are observed in 3, in which no aggregation occurs. For example, the lowest field C_α resonance of 1 moves 1.0 ppm downfield but the corresponding C_α resonance in 3 moves 0.4 ppm downfield. The most obvious change in the spectrum of compound 1 occurs with the side-chain signals, in which the number of lines is reduced from at least six to four upon addition of methanol-d_4, and as always, the high-field peaks moved down-field on addition of methanol; no such effect was observed with compound 3.

Thus, the ^{13}CMR spectra qualitatively confirm the conclusion drawn from the ^{1}H studies (*vide supra*). The dilution shifts are, however, relatively too small to be treated quantitatively. It is perhaps ironic that the factor which renders ^{13}CMR of such utility for investigations of complex molecules, namely the large spread of chemical shifts, militates against its use in such complexation studies where the actual shifts (in ppm) are, of course, of the same order in ^{1}H as in ^{13}C, but where the extraneous effects are roughly twenty times larger in ^{13}C.

Geometry of the complex. The complex formation shifts (Table 2) are of some interest. The actual magnitude of the largest shifts is more than double that of other similar complexes, even though the equilibrium constant is similar to previous values. It is important to note here that although the calculated chemical shifts on the basis of monomer–dimer equilibria agree with the observed shifts this does not exclude the possibility of trimers and higher aggregates being involved. However, it was not felt justified to further treat the observed dilution shifts in terms of monomer–dimer–trimer, etc. equilibria. Over the limited concentration range employed here, the significance of any parameters thus obtained is doubtful. Stacking of these porphyrin molecules could produce aggregates in which the shifts are much larger than in a dimer (for vertical stacking the limiting shifts are *ca* 3 times the dimer shifts), thus the significance of the dimer shifts in Table 2 is their relative values.

Nevertheless, the very large shifts obtained do suggest a closer separation of the porphyrin rings in the dimer than in previously reported porphyrin complexes, and this is further supported by the observation of both high field and low field shifts in the complex. Only for a close approach of the porphyrin rings would the ring current of one molecule produce low field shifts of any atoms in the other molecule.

We make the initial assumption that the molecules in the complex are parallel, and wish to find a geometry which will at least reproduce the main pattern of the observed complex shifts, assuming also that the complex shifts are solely due to the effect of the ring current of one molecule on the other. In order to calculate these ring current shifts we use a model based on the network approach, and parameterised so as to give good agreement with the observed shifts in other metalloporphyrins; full details of this model will be given elsewhere. (The tables of Johnson and Bovey,[10] using an effective porphyrin ring radius of 3.6 Å gave similar results but the more recent tables of Haigh and Mallion[11] gave much smaller shieldings above the ring plane).

The only certain assignment in the spectrum is of the *meso*-protons from their shifts and relative intensities (1:2), and the observation that the γ-*meso* proton is more shielded in the complex than the β,δ-*meso* protons immediately excludes the model (Fig. 1A) which might have been thought, *a priori*, to be the most reasonable. The only other complex in which both molecules are identical is Fig. 1B. A search of the calculated shifts for the various protons for varying values of the inter-ring separation (Z) and lateral displacement (Δ) was then made with the signal assignments of the CH_2 and CH_3 resonances made to be consistent with the calculated shifts. For the dimer structure Fig. 1B with $Z = 4.5$ Å and $\Delta = 1.25$ Å the calculated shifts are γ-*meso* 2.2 β,δ-*meso* 1.0, $CH_2(2,3) \sim 0.1$, $CH_2(1,4) \sim 0.2$, $CH_2(5,8)$ 0.5 and $CH_2(6,7)$ 1.0 ppm. These shifts are in the correct order but are approximately half as large as observed, indicating very likely that larger aggregates are present in solution.†

Although the agreement is reasonable, we also considered a dimer (Fig. 1C) in which the two molecules are not in identical environments. The structure also gave a reasonable correlation with the observed shifts. For $Z = 3.5$ Å and $\Delta = 1.5$ Å the calculated shifts are γ-*meso* 2.0, β,δ-*meso* 1.0, $CH_2(2,3)$ and $CH_2(6,7)$ 1.6, $CH_2(1,4)$ and $CH_2(5,8)$ 0.4 ppm. Because the aggregates are forming and separating rapidly on the NMR time-scale it is necessary to average over both molecules in Fig. 1C. In this case we obtain two pairs of equal shifts for the four methylenes.

Both structures 1B and 1C give a reasonable correlation with the observed shifts when it is remembered that aggregation will increase the absolute values of all the shifts by a factor of two or three times. In principle the complexes could be differentiated by the different assignments in the two cases; in Fig. 1B the 2,3 and 1,4 methylenes show very small shifts whereas in Fig. 1C it is the 1,4 and 5,8 methylenes. If the diastereotopic methylene signal at low field could be unambiguously assigned to the 2,3 methylenes then Fig. 1C could be eliminated. In the absence of a full analysis and assignment of the spectrum this cannot be unequivocal.

The inter-ring separation (4.5 Å) proposed for the complex is less than that estimated for non-specifically coordinating metalloporphyrin dimers (cf. 5.3–8.1 Å for the aquocoproporphyrinatothallium(III) hydroxides[5]) and closer to the "tight dimer" recently suggested[12] for the protoporphyrin-IX ferricyanides. In the example studied here there are no axial ligands on the metal atom and this would facilitate a closer approach of the two porphyrin rings.

It has been assumed[5] that the attractive interaction in dimeric species which do not involve specific coordination at the metal atom is electrostatic in origin. For this example, axial ligation at zinc by the $O{\cdot}CO{\cdot}CF_3$ group of

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†The β-methylene shifts are all slightly low compared with the *meso* proton shifts; in these estimations we assume that the position of the methylene protons is 0.36 Å from the carbon atom along the ring-carbon bond (i.e. this is the position for free rotation of the ethyl groups). The shifts thus calculated will always be too low as the shifts are proportional to $1/r^3$ and $\langle r_{Av}\rangle^{-3}$ is always less than $\langle r^{-3}\rangle_{Av}$, even for free rotation. If in addition there is any rotameric preference of the ethyl groups, the calculations would be further affected.

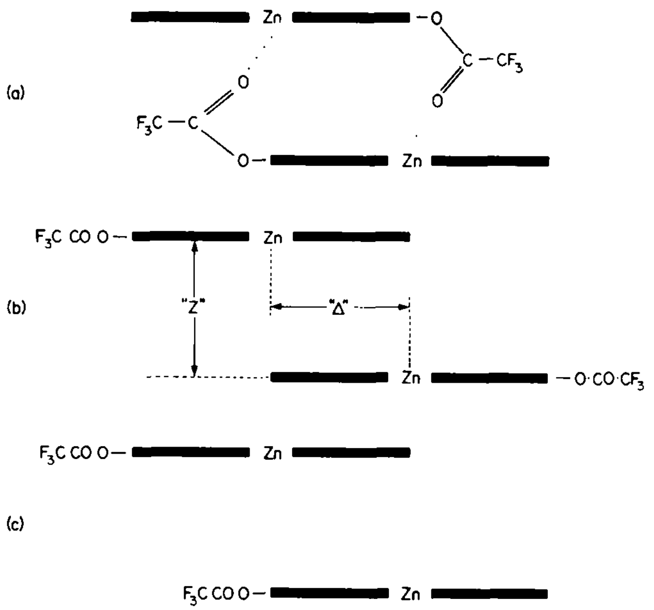

Fig. 1. Elevation views of possible dimers of 1.

the adjacent ring would enhance the tendency to dimerise. However, it is firmly established that the donor properties of the trifluoroacetate function are markedly reduced when compared with, for example, a keto function.[13] Thus, dimerisation through specific coordination here might be expected to be less favourable than in the chlorophylls.[14] The major disadvantage of the complex in Fig. 1B is that there is no possibility for zinc to side-chain interaction (*vide infra*).

Conformational studies on phenyl acetate (4) *and trifluoroacetate* (5)

Although the ^{1}H and ^{13}CMR spectra of compound 1 can be satisfactorily explained on the basis of the above model, there still remains the very intriguing question as to why the *meso*-acetoxy compound 3, in which the side-chain donor capacity is much greater than in 1, does not form similar complexes.

The experiments in which methanol was added show unequivocally that the dimerisation involves a specific metal-ligand interaction in 1. Thus, if the CO group in 1 is the ligand, there exists the possibility that its conformation in compounds 1 and 3 differs. A rationalisation of the complexation behaviour could at least be advanced if it could be shown that the preferred orientation of the CO group in 1 was as in Fig. 1A (i.e. with the CO *endo* and the CF_3 *exo*), but that the orientation in 3 was preferred with the CO *exo* and the Me *endo*. This possibility has some chemical support, in that the ester groups in compounds 1 and 3 would undoubtedly be orthogonal to the porphyrin plane due to the abutting pyrrole rings. One might then anticipate that the Me group might prefer to lie over the electron-rich porphyrin ring in 3† leaving the smaller CO group to interact with the hydrocarbon side-chains. In 1 however, the electronegative CF_3 group could well prefer the *exo* orientation.

In order to test this hypothesis we decided to combine a LIS study with molecular energy calculations; since the porphyrin molecules are much too large to be handled in our computer programmes, and also because the results from a LIS study with complex porphyrin molecules were likely to be complicated owing to the competitive presence of the strongly complexing lanthanide atom upsetting the equilibria already in operation, we determined to carry out the investigation on simpler model compounds, choosing the readily available phenyl acetate (4) and trifluoroacetate (5).

On the reasonable assumption of planar aromatic rings and ester (O·CO·C) groups, the molecular conformations are defined by two dihedral angles, ω_1 and ω_2 (Fig. 2 and Table 4). The conformer energies were calculated for the isolated molecules using the CNDO programme in the INDO approximation,[15] and the solvation energy calculations using the DIPQUADMOMS programme.[16] Standard bond lengths and angles were used and this gave from the CNDO programme both the molecular energies and the dipole moments shown in Table 4. The solvation energy calculations merely give the solvation energy for each conformer in a given solvent, and this has been added to the CHDO energies in Table 4.

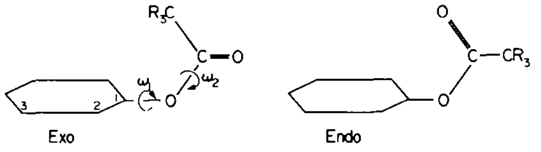

Fig. 2. *Exo* and *endo* conformations of phenyl trifluoroacetate (R = F) and phenyl acetate (R = H).

The observed dipole moment of phenyl acetate (1.50 D benzene/CCl_4; 1.54 D benzene; 1.65 D CCl_4)[17] is unequivocal evidence favouring the *cis* form ($\omega_2 = 0°$) (in the usual nomenclature[18]) in these non-polar solvents, and for which the calculated (CNDO) dipole moment (1.7 D) is in good agreement. The dipole moment determination does not provide any insight into the phenyl ring conformation (i.e. the value of ω_1) as the calculated dipole moment of 4

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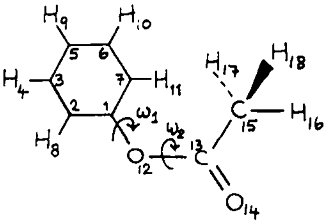
†There is no possibility of an interaction between the Zn atom and the carbonyl group of the same molecule.

Table 4. Conformer energies of phenyl acetate and phenyl trifluoroacetate in vacuo and in solution



	Conformation			Relative Energy (kcal/mole)			
	ω_1 $(C_2C_1 \rightarrow O_{12}C_{13})$	ω_2 $(C_1O_{12} \rightarrow C_{13}O_{14})$	μ(Calc.)	CNDO	Solvation Energy $\epsilon_{2.0}$	$\epsilon_{4.7}$	$\epsilon_{19.8}$
CH_3	90°	0° (endo)	1.68	0.0	-0.7	-1.2	-1.8
		180° (exo)	4.17	2.3	-2.9	-5.0	-7.2
CF_3	90°	0° (endo)	2.33	0.0	-0.4	-0.6	-0.9
		180° (exo)	3.07	1.1	-1.5	-2.5	-3.7

is independent of this angle. The CNDO energies favoured the conformation with $\omega_1 = 90°$ for both the *cis* and *trans* ($\omega_2 = 180°$) forms. We will consider therefore only these two conformers, which may be termed *exo* (ω_1 90°, ω_2 180°) and *endo* (ω_1 90°, ω_2 0°) referring to the position of the CO with respect to the benzene ring (Fig. 2).

The CNDO calculations are also consistent with the dipole moment measurements in that the *endo* conformer is predicted to be the most stable form in a non-polar medium. The solvation energy calculations show, however, that the *exo* conformer becomes increasingly more favoured in increasingly polar solvents, due of course to its larger dipole moment, and soon becomes the most stable conformer in solution.

In contrast, although the CNDO calculations give the same answer for phenyl trifluoroacetate (**5**), i.e. *endo* most stable, there is a much smaller difference between the dipole moments of the *exo* and *endo* forms in this molecule, and in consequence, the energy difference between the conformers is small in all solvents.

To further clarify these conclusions, a LIS experiment was performed on **4** and **5** using Eu(fod)$_3$ in $CDCl_3$ solution. The ^1H spectrum of **5** showed, as might have been expected, no effect whatsoever up to the highest concentrations of Eu(fod)$_3$. Indeed, the ^1H spectrum remained at all times a complex, strongly coupled multiplet *ca* δ 7.07–7.54, which was not analysed further. The ^1H spectrum of **4** on the other hand gave large shifts with Eu(fod)$_3$, producing a first order phenyl spectrum very quickly. The observed proton and ^{13}C shifts for the pure compound, and the corresponding ΔEu values[19] are given in Table 5.

Some LIS studies on esters have been performed[20] but the position of attachment of the Eu atom is still not settled.[19] Thus, we considered two possibilities, (a) attachment of the Eu atom to the CO oxygen with the magnetic axis of the complex along the Eu···O bond, and (b) attachment of the Eu atom to *both* O atoms, resulting in the magnetic axis of the complex lying along the Eu···C axis. (Note that this is identical to a time dependent model in which the magnetic axis changes from one

Table 5. ^1H and ^{13}C chemical shifts (δ) for phenyl acetate[a] (**4**) and trifluoroacetate[b] (**5**) and observed and calculated ΔEu values for phenyl acetate

	^1H				^{13}C					
	CH_3	Phenyl[c] o	m	p	CH_3 (CF_3)	C=O	Phenyl C_1	o	m	p
δ (4)	2.25	7.02	7.31	7.22	21.0	169.1	150.6	121.4	129.2	125.6
δ (5)					115.8	156.6	150.4	121.2	130.5	128.0
ΔEu(obs.)	10.48	6.96	1.50	0.76	17.00	14.90	11.32	7.45	3.58	3.28
ΔEu(Calc.)										
Model (a)	11.87	7.50	1.78	1.23	14.87	(30.14)	12.68	6.96	2.96	2.11
Model (b)	10.04	6.90	2.03	1.57	13.93	(35.79)	14.38	7.24	3.16	2.48

[a] In $CDCl_3$

[b] Pure liquid + acetone-d_6 as lock ($^1J_{CF}$ 285.0, $^2J_{CF}$ 42.8 Hz)

[c] Approx. "first-order" values.

oxygen to the other. Provided the *position* of the Eu is unchanged, the resulting shifts will be identical). A search procedure was then performed with both models to ascertain the optimum position for the Eu atom. In both cases the CO *endo* conformer gave no agreement with the observed ΔEu values. This is clearly seen merely by inspection (Fig. 3). The position of the Eu atom in this conformer in either model is essentially over the benzene ring and this will produce *high* field shifts (i.e. negative ΔEu values) for the phenyl nuclei. This is not observed.

The *exo*-conformer, however, produced reasonable agreement with the observed ΔEu values for both models. For model (a) the best fit was obtained for a Eu···O distance of *ca* 5.0 Å and a Eu···O=C angle of 110°. For model (b) the corresponding values are *ca* 3.5 Å and 103°. The calculated ΔEu values for these solutions are given with the observed values in Table 5. The rms deviation (observed minus calculated) is 1.13 and 1.61 for models (a) and (b) respectively. The only nucleus significantly in error is the CO carbon, in which a considerable contact contribution would be expected. The two models cannot be definitely distinguished, however, the main conclusion from these results is quite clear, i.e. that the phenyl acetate, *when complexed with Eu*, is in the *exo* conformation.

It is important to make the above qualification as the change in substrate conformation due to Eu complexation has been noted by several investigators recently.[21,22]

CONCLUSIONS

The CNDO and solvation energy calculations and the LIS study do form a consistent pattern in as far as the conformation of phenyl acetate (**4**) is concerned. The *exo–endo* equilibrium in phenyl acetate appears not to be very heavily biased in either direction. The *endo* conformation is clearly preferred in non-polar media, but the effect of polar solvents and Europium complexation is sufficient to reverse this equilibrium to favour the *exo* form.

The extra steric hindrance of the acetyl group by the ethyl side-chains in **3** would certainly be expected to additionally favour the *exo* conformer, in that the CO oxygen is much smaller that the Me group, and thus more easily accommodated in the *exo* position. It is therefore reasonable to infer that the acetyl in **3** markedly prefers the *exo* position, and that the gain in energy involved in forming the dimer is not sufficient to overcome the preference for the *exo* position. It is also clear that the dimer formation would not be expected to occur with the CO *exo*. For the CO in this orientation to interact with a Zn atom of a neighbouring porphyrin molecule, the planes of the interacting porphyrin molecules would be at right angles, which is highly unlikely, even without the steric requirements of the ethyl side-chains which preclude any close approach of the two molecules.

Although the absence of dimer formation in **3** is thus at least rationalised, the reason for the formation of this very stable dimer in (**1**) is still not entirely clear. The CNDO calculations indicate that the CO in phenyl trifluoroacetate (**5**) prefers the *endo* position, but only by *ca* 1 kcal/mole. This figure could easily be reversed, or increased, if a different molecular geometry had been used. Also the analogy between **1** and **5** is not as straightforward as that between **3** and **4** in that the increased steric hindrance in the porphyrin in this case favours the higher energy conformer (the *exo* form), the CF_3 group being much bulkier than the CO group. Thus, the precise conformation of the trifluoromethyl group in **1** is still uncertain.

All of these considerations lend support to the structure shown in Fig. 1B for the complex of **1**; however, Fig. 1B can have no metal to side-chain interaction and this raises the question as to what is the real attractive force in this complex. It clearly consists of a π–π interaction between the two rings in which the metal atom also plays a not unimportant role. Recent work in these Laboratories indicates that the strength of complexation in diamagnetic metalloporphyrins depends upon electron availability in the porphyrin ligand (measured, for example by the *pKa*) as well as upon the ability of the central metal ion to interact with the macrocycle (as measured by the oxidation potential or susceptibility of the metalloporphyrin towards electrophilic deuteriation, for example). This theme will be developed in future Parts of this Series.

EXPERIMENTAL

NMR spectra. The deuteriochloroform used throughout this study was passed repeatedly through a short column of alumina to remove acid and other contaminants. ^{1}HMR spectra were obtained using a Varian HA-100 instrument at about 35°, in the manner previously described.[5] The ^{13}CMR spectra were obtained using a Varian XL-100 instrument, operating in the pulse Fourier transform mode at about 35°, with complete proton noise decoupling, as previously described.[6] Due to the digitisation in the resulting 5 kHz width spectrum, the accuracy of the chemical shifts was limited to ± 0.1 ppm. TMS was employed as internal reference for both ^{1}H and ^{13}C spectra.

Materials. Porphyrins (**1**[3] and **3**[23]) were obtained following literature procedures. Phenyl acetate (**4**) and phenyl trifluoroacetate (**5**) were distilled twice before use.

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