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AN NMR INVESTIGATION OF THE ATROPISOMERS OF *MESO*-O-TOLYLPORPHINATONICKEL (II)

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As part of our interest in the NMR spectra of transition metal porphyrins we have studied several diamagnetic metal complexes of *meso*- *o*, *m*, and *p*-tolylporphyrins. The nickel (II) complex of *meso*-*o*-tolylporphyrin, Ni(*o*-CH_3)TPP, is of particular interest. The NMR spectra of Ni (*o*-CH_3)TPP in CS_2, $CDCl_3$ and C_6D_6 are shown in Figure I. These spectra show several interesting features. First, the effect of the ring current of the porphyrin ring is clearly seen: The ortho-tolyl ring proton of Ni(*o*-CH_3)TPP appears at lower field (∼ 7.8 ppm, depending on solvent) than the meta and para protons (∼ 7.5 ppm, depending on solvent),(1) and the methyl protons of Ni(*o*-CH_3)TPP are shifted upfield 0.58 ppm from those of Ni(*m*- or *p*-CH_3)TPP.** These shifts are consistent with the predictions of ring current theory(1,3) and the positions of the ortho-aryl and ortho-methyl protons: It is well established(4) that the phenyl rings of *meso*-tetraphenylporphyrins are considerably out of the plane of the porphine ring; molecular models show that the *ortho*-phenyl ring protons lie *outside* the porphine ring *pi* system, and are thus expected to be de-shielded by the magnetic field of the ring current, while the protons of a methyl group in the *ortho* position of the phenyl ring lie *inside* the perimeter of the pi system of the porphine ring, and are thus expected to be shielded by the magnetic field of the ring current.

The second obvious feature of the NMR spectra of Ni(*o*-CH_3)TPP is the multiple methyl resonances. This phenomenon is observed for all metal complexes of *meso*-*o*-tolylporphyrin,(2) whether they are diamagnetic or paramagnetic, although the peaks of the latter type are quite broad and overlap extensively.(2) The pattern of peaks observed for Ni(*o*-CH_3)TPP, their

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** The methyl resonance in Ni(m- or p-CH_3)TPP in CS_2 appears as a sharp singlet 2.58 ppm downfield from TMS.(2)

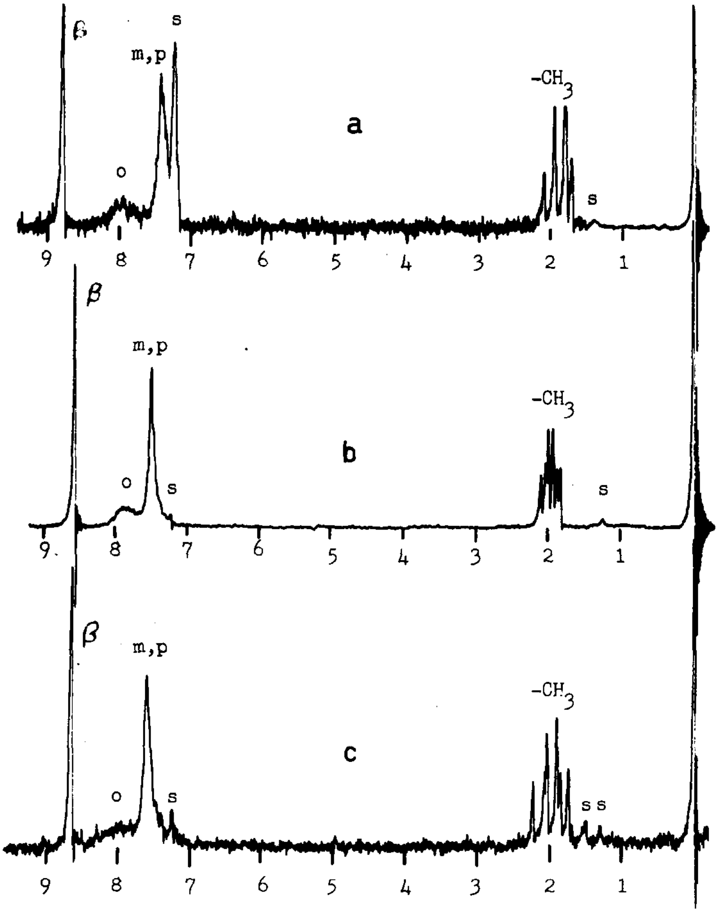

Figure I. NMR spectra of Ni(o-CH_3)TPP at 30° in (a) C_6D_6, (b) CS_2, and (c) $CDCl_3$. Chemical Shifts are given as δ, ppm, relative to TMS. Solvent, impurity, or spinning sideband peaks are marked "s". Methyl proton peaks are labelled -CH_3, ring protons = o and m,p, and pyrrole protons = β.

average chemical shift, and the separations between peaks differ in each solvent investigated: $CHCl_3$, CH_2Cl_2, and CS_2 all show patterns of 6 peaks, whereas C_6H_6, C_6H_5Cl, C_6H_5Br, C_6H_5I, and $C_6H_5CH_3$ show patterns of four peaks, and C_6H_5CHO and $C_6H_5NO_2$ show only one broad peak at 60MHz. No concentration dependences in peak positions were observed over the accessible concentration range (approximately 0.01 M to 0.001 M). The field dependence of these spectra* and the unequal spacing of the methyl peaks rule out the possibility of spin-spin coupling as the source of these patterns. It therefore appears that each peak is due to a unique type of methyl group.

The largest number of methyl peaks observed for **Ni(o-CH_3)TPP** in any solvent is six, of approximate intensity ratios 1:1:2:2:1:1, and no additional peaks are suggested from inspection of spectra recorded at 220MHz.

This multiplicity of methyl resonances is believed to be due to atropisomerism(5) of this porphyrin which arises from restricted rotation about the aryl-porphine bond. Another case of such isomerism has recently been reported.(6) The four isomers possible in this system may be described in terms of the positions of the methyl groups with respect to the plane of the porphine ring: "4 up", "3 up, 1 down", "2 up, 2 down-cis", and "2 up, 2 down-trans". The statistical ratio of these isomers is 1:4:2:1, respectively, if the porphyrin is formed by completely random linking of pyrrole and o-tolualdehyde units.(7) The "3 up, 1 down" isomer contains three types of methyl groups, abundance 1:2:1, while the other three isomers contain sets of 4 equivalent methyl groups. This analysis predicts a maximum of six types of methyl groups of idealized intensity ratios 1:1:2:2:1:1, which is very close to the apparent ratios of peaks in Figure Ib and c. Other patterns observed may result from accidental superposition of two or more peaks.

This is the first report of atropisomerism of porphyrins to be observed by NMR, although meso-o-hydroxyphenylporphyrin has been separated by thin layer chromatography into four components, whose visible spectra were identical, of relative abundance 1:4:2:1.(6) Attempts to separate the isomers of the less polar Ni(o-CH_3)TPP are in progress.

For any solvent, the methyl peaks move closer together as the temperature is raised, but they do not broaden. At a temperature of 180^o in bromobenzene the methyl peaks still appear to be individual peaks, separated by only 0.035 ppm, and thus overlapping extensively at 60 MHz. Because broadening is not observed as the peaks move, it would appear that chemical exchange is

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* NMR spectra were recorded at 60, 100, and 220 MHz.

not the cause for the movement. At the high-temperature extreme where the peaks overlap, however, the possibility of line broadening due to chemical exchange cannot be ruled out. The separation of 0.035 ppm (2.1 cps at 60 MHz) at 180° places an upper limit of 4.7 sec^{-1} on the rate constant for rotation of an o-tolyl group about the tolyl-porphine bond,(8) and predicts $\Delta G^{\ddagger} > 26$ kcal/mole.*

The variety of splitting patterns observed and the temperature dependence of the separations between peaks (as well as the variations in chemical shifts of other protons in Ni(o-CH_3)TPP as a function of solvent (see Figure I)) suggest that solvation effects may be quite important in this system. The nature of these solvation effects and other aspects of this system are under further investigation.

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* Gottwald and Ullman(6) report $\Delta G^{\ddagger} = 24.0$ kcal/mole for rotation of a hydroxyphenyl group in H_2(o-OH)TPP, $\Delta G^{\ddagger} = 25.4$ kcal/mole for the same process in its copper (II) complex, and rate constants of 1.5×10^{-5} sec^{-1} and 1.2×10^{-6} sec^{-1}, respectively, at 23°C.