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CONFORMATIONAL ANALYSIS OF DINAPHTHALENE-1-CARBOXYLATE COMPLEX OF SN^{IV}(TETRAPHENYLPORPHYRIN)

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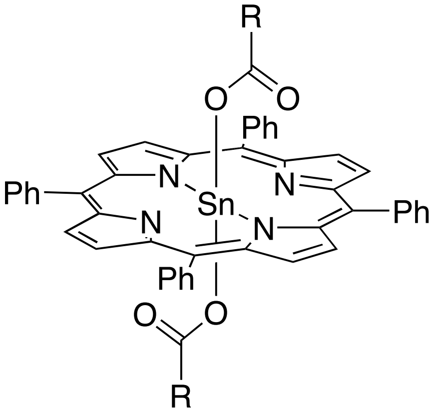
Abstract – Conformational analysis of dinaphthalene-1-carboxylate complex of Sn^{IV}(tpp) (**1**) in solution was carried out using temperature dependent ^{1}H NMR spectra and chemical shift simulation method. It was found that two vertical conformers are in equilibrium in solution for **1**.

It is well known that NMR chemical shifts reflect molecular structure. Hence, variation in the local environment affects chemical shieldings, and the change in chemical shifts of nuclei caused by adjacent substituents provides valuable information about the relative arrangement of the nuclei under study with respect to these nearby substituents.[1] From this point of view, we have developed an efficient method for conformational analysis of flexible organic compounds by using chemical shift simulation technique.[2] In the course of expanding the applicability of the method of chemical shift simulation to compounds carrying porphyrin ring,[3] we have found that NMR chemical shifts of dinaphthalene-1-carboxylate complex of Sn^{IV}(tpp: tetraphenylporphyrin) (**1**) (Figure 1) are temperature dependent. This suggests that at least two conformers are present for **1** in solution. In this paper we report the conformational analysis of **1**.



1 : R = 1-naphthyl
2 : R = ph
3 : R = 9-anthracenyl

Figure 1

Two conformations, 'vertical' and 'horizontal', were proposed for the structure of aromatic carboxylate complex of Sn^{IV}(tpp).[4] The former based on the structure of dibenzoate complex (**2**)[5] in which benzoates bound with their aromatic rings perpendicular to the porphyrin plane, with the dihedral angle Sn-O-C-C of *ca.* 180 °. An attractive π-π or donor-acceptor interaction between the anthracene and the porphyrin rings was claimed as the main cause for the horizontal conformation of anthracene-9-carboxylate complex of Sn^{IV}(tpp) (**3**) in which the anthracene ring is roughly coplanar to the porphyrin ring.[4]

In order to elucidate which of the two structures is predominant in **1**, the conformational analysis of **1** in solution was carried out. Although the naphthalene ring of **1** was known to have perpendicular arrangement to the porphyrin ring in the crystalline state,[6] it is known that the structure obtained by an X-Ray crystallographic analysis is not always identical with that found in solution.[7] In order to elucidate the structure in solution, a dichloromethane solution of **1** was subjected to NMR measurement at various temperatures (Figure 2). At room temperature two prominent signals were found at 5.10 and 4.63 ppm. These are assigned to H2 and H8, respectively and are both significantly up-field shifted from the corresponding proton of the uncomplexed naphthalenecarboxylic acid. When lower the temperature the former shifted to the lower and the latter to the higher magnetic fields. This suggested that at least two conformers are in equilibrium in solution, however, it is difficult to identify how many conformers are contributing to the equilibrium because neither signal separation nor extensive signal broadening was detected down to –90 °C.

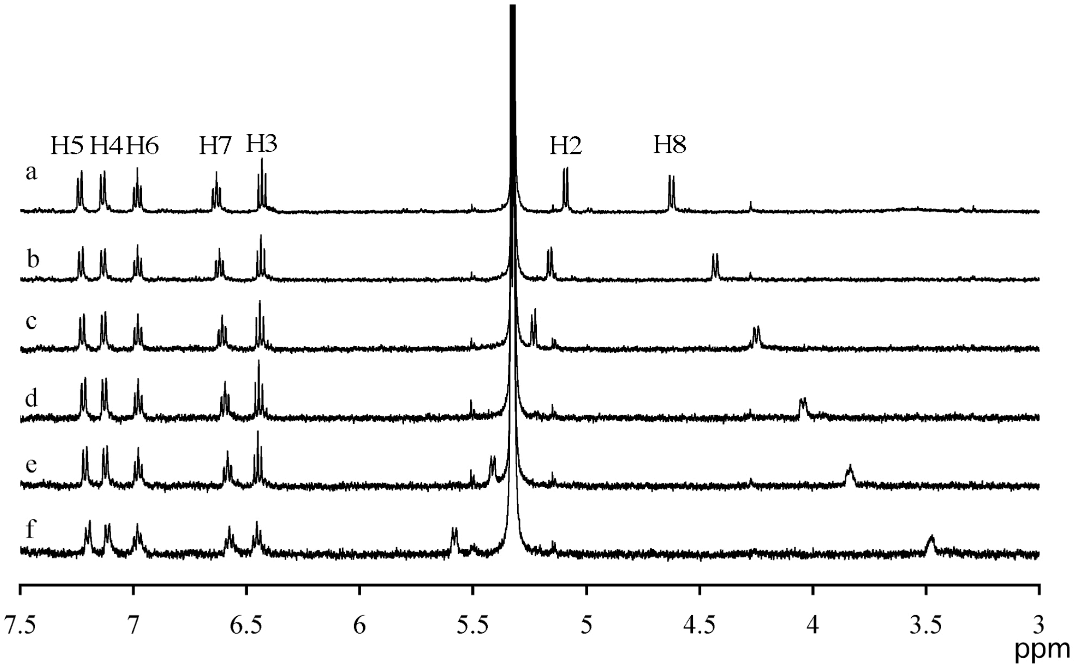


Figure 2. A part of proton NMR spectra of 1 at various temperatures, (a) 25 °C, (b) 0 °C, (c) -20 °C, (d) -40 °C, (e) -60 °C and (f) -90 °C.

To obtain the possible structure in solution, the X-Ray structure was subjected to the calculation of density functional theory (DFT, at the B3LYP/LANL2DZ level of theory).[8] The perpendicular structure was further supported by the calculation. Since the naphthalene ring of **1** is not symmetrical with respect to the arene carbonyl C-C bond, two orientation of the naphthalene ring is possible. One is the orientation found in the calculated structure (*exo*) and the other is that obtained by 180 ° rotation around the C-C bond (*endo*). The DFT calculation showed that both of them are energy minima on the potential energy surface and both structures have the vertical conformation of the aromatic ring with respect to the porphyrin plane (Figure 3). Next step of the conformational analysis is to determine how they are populated at a given temperature in solution.

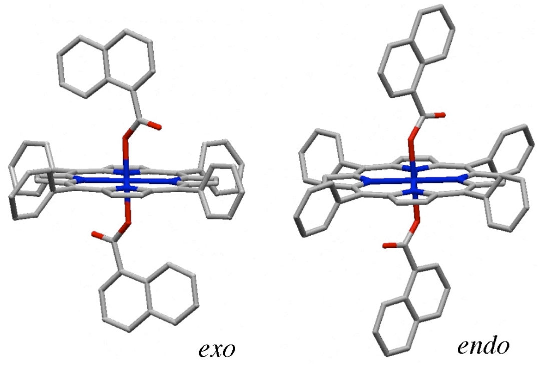


Figure 3. DFT structures of 1 (a) *exo*, (b) *endo*.

In order to determine the relative ratio of the two conformers in solution, the chemical shift changes caused by secondary induced magnetic fields due to porphyrin ring current was found to be very informative. Before determining the relative ratio of the two, the theoretical induced shifts of the naphthalene protons of the two DFT structures were estimated by the calculation of the porphyrin ring current effect, which was newly developed by our group,[6] and they are shown in Table 1.

Table 1. Calculated Ring-Current Shifts for 1 (ppm)

Nucleus	Shifts	
	exo	*endo*
H2	2.084	4.774
H3	0.983	1.359
H4	0.852	0.903
H5	0.739	0.675
H6	0.588	0.519
H7	1.069	0.638
H8	6.105	1.926

Excellent agreement of the calculated and observed induced shifts was given when we assume that both of the conformers are present in the solution in a 58:42 ratio at 25 °C. Table 2 shows the observed and calculated ring current shifts in **1**, which is obtained by mixing the calculated induced shifts of the *exo* structure with those of the *endo* at the given ratio. The relative ratio of the two conformers is temperature dependent and the temperature variation of the relative ratio estimated by the same procedure is shown in Table 3.

From this analysis, the free energy difference between the two structures at a given temperature was obtained. Thermodynamic parameters of the equilibrium of the two conformers ($\Delta H_{endo\text{–}exo}$ = 4.19 kJ/mol, $\Delta S_{endo\text{–}exo}$ = 11.2 J/mol•deg) were obtained by van't Hoff plot analysis.

Table 2. Observed and Calculated Ring-Current Shifts for 1 (ppm) at 25 °C

Nucleus	Shifts	
	Obsd	Calcd
H2	3.24	3.20_2
H3	1.12	1.13_9
H4	0.98	0.87_3
H5	0.71	0.71_2
H6	0.59	0.55_9
H7	1.02	0.89_0
H8	4.38	4.36_8

Table 3. Relative ratio (%) of two conformers of 1 in CD_2Cl_2

Temperature (°C)	*exo*	*endo*
25	58.4	41.6
0	62.0	38.0
-20	65.6	34.4
-40	69.3	30.7
-60	73.3	26.7
-90	80.2	19.8

In summary, we found that there are two conformers for **1**, both of them have vertical structures in which the aromatic ring have perpendicular arrangement with respect to the porphyrin plane. The two conformers are in equilibrium in solution and the relative ratio of the two conformers is dependent on the temperature, and the thermodynamic data of the conformational equilibrium were obtained.

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