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A model of porphyrin ring current effect

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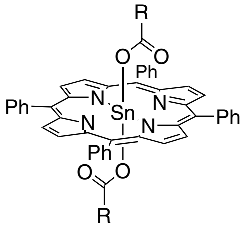
Abstract—A new simple model of porphyrin ring current effect was proposed based on a line current approximation. It can reproduce the porphyrin-induced shifts for some Sn(IV)(tpp) dicarboxylate complexes quite satisfactorily.

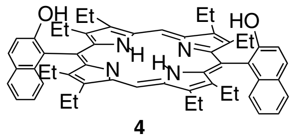
It is well known that NMR chemical shifts reflect molecular structure. Hence, variation in the local environment affects chemical shieldings, and the change in chemical shifts of nuclei caused by adjacent substituents provides valuable information about the relative arrangement of the nuclei under study with respect to these nearby substituents.[1] The chemical shift changes caused by the nearby substituents can thus be applicable for conformational analysis. 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] The chemical shift changes caused by secondary induced magnetic fields due to aromatic ring current have proven effective for this purpose.[3]

However, the quantification of such shielding effects has been rather limited, and this situation has restricted broad application of the technique. In order to extend the applicability of the method of chemical shift simulation to compounds carrying porphyrin ring[4] we have developed a new simple model of porphyrin ring current effect that is applicable to dynamic structure analysis utilizing molecular dynamic simulation.[5]

Many models of porphyrin ring current effect have been reported since the first calculation of ring current shifts described by Becker and Bradley.[6] They are based on mainly three approaches, classical dipolar,[7] semi-classical Johnson–Bovey type double current loops,[3a–c] and quantum mechanical one.[8] Our new model is based on a classical line current approximation as discussed originally by Longuet-Higgins and Salem.[9] In this simple model, the secondary magnetic field at a given proton is calculated on the assumption that the line current follows exactly C–C and C–N bonds of porphyrin ring. Since our new model is so simple it can be easily applicable to a dynamic structure analysis utilizing molecular dynamic simulation. In order to have induced shifts caused by the porphyrin ring current effect, estimation of magnitude of the line current have to be given correctly. For this purpose, established geometry of



1 : R = 1-naphthyl
2 : R = 1-adamantyl
3 : R = Ph



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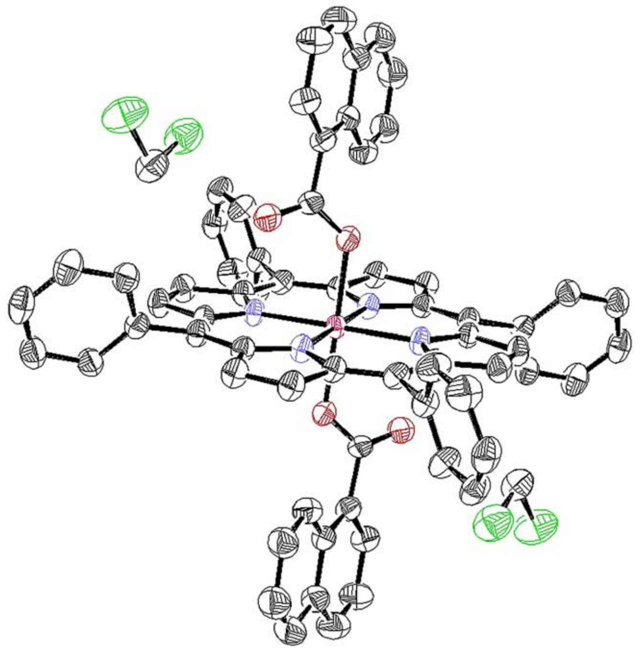

Figure 1. X-ray crystal structure of **1**·2CH_2Cl_2. Hydrogen atoms are omitted for clarity.

compounds having the known induced shift values caused from the porphyrin ring current effect is necessary. We utilized several dicarboxylate complexes of Sn^{IV} (tetraphenylporphyrin) reported by Sanders and co-workers.[10] The structure of dibenzoate complex in the crystalline state has been reported;[11] however, that of naphthalene-1-carboxylate is not known, therefore, an X-ray crystallographic analysis of dinaphthalene-1-carboxylate complex of Sn^{IV} (tpp) **1** was carried out (Fig. 1).[11]

As can be clearly seen the naphthalene ring of **1** is perpendicular to the porphyrin ring. The carboxylate plane (O–C═O) of **1** has roughly staggered arrangement[7l] where the plane is perpendicular to the porphyrin through two *meso* carbon atoms. However, the naphthalene plane has roughly eclipsed[7l] with respect to the porphyrin nitrogen atoms. The atomic coordinates of all the protons of this compound are obtained, however, since it is known that the structure obtained by an X-ray crystallographic analysis has lesser positional accuracy of protons than that of heavier elements, Density functional theory (DFT) calculation (at the B3LYP/LANL2DZ level of theory) was, hence, carried out to have precise geometry of the compound.[12] The structure thus obtained is slightly different from that in the crystalline state. Although, the orientations of the carboxylate planes of the two structures are quite similar with each other, those of the naphthalenes with respect to the carboxylate plane are different. The DFT structure has smaller dihedral angle of the two planes (15.6) than that in the crystalline state (35.7). The similar DFT calculation was also carried out on two compounds, adamantane-1-carboxylate complex of Sn^{IV} (tpp), **2** and dibenzoate complex of Sn^{IV} (tpp), **3** at the B3LYP/LANL2DZ level of theory.

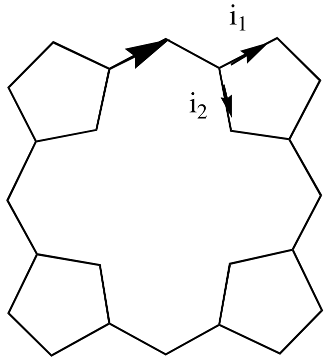

Figure 2. Current loop model for porphyrin ring.

Now we can estimate the magnitude of the line current of the porphyrin ring since the precise structures of several dicarboxylate complexes of Sn^{IV} (tpp) and the complexation induced shifts of the dicarboxylates are known. Our current loop model is similar to that of Abraham's one (Fig. 2).[7a] In this model a current running along the two C–C bonds passing through a *meso* position separates into two (i_1, i_2) at α-position of a pyrrole ring. We employed the Abraham's ratio ($i_1/i_2 = 2.146$) of the two currents. We can estimate the magnitude of the line current of outer and inner arcs of the pyrrole ring ($i_1 = 0.87i_B$, $i_2 = 0.41i_B$, where i_B is the line current of benzene ring[2a]) to reproduce the complexation induced shift values of **2** and **3**. Table 1 gives the observed[10] and calculated ring current shifts[13] in **2** and **3**. The root mean square (rms) error is satisfactorily small (0.055 ppm). Excellent correlation of these data is obtained in a linear regression analysis [7 data (range of the observed shift, 0.81–3.19 ppm) $\Delta\delta_{obs} = a\cdot\Delta\delta_{calc}$; $a = 1.0085$, $R^2 = 0.997$].

In the case of **1**, the situation is not so simple and the calculated induced shift of naphthalene protons cannot reproduce the observed one at all. The calculated induced shift[13] of H_8 (6.46 ppm), the closest proton to the porphyrin ring is far larger than the observed (0 °C, 4.79 ppm[14]). Since the naphthalene ring of **1** is not symmetrical with respect to the naphthalene and carbonyl pinched C–C bond, two orientation of the naphthalene ring is possible. One is the orientation found in the calculated structure and the other is that obtained by 180° rotation around the C–C bond. The DFT calculation showed that both of them are energy minima on the potential energy surface. Since the energy

Table 1. Observed[10] and calculated ring current shifts[13] in **2** and **3** (ppm)

Nucleus	Shifts	
	Obsd	Calcd
H_2(**2**)	2.96	2.90_6
H_3(**2**)	1.10	1.15_6
H_{4eq}(**2**)	1.17	1.22_2
H_{4ax}(**2**)	0.81	0.88_6
H_o(**3**)	3.19	3.12_7
H_m(**3**)	1.15	1.15_2
H_p(**3**)	0.95	0.89_6

Table 2. Observed (0 °C)[14] and calculated ring current shifts[13] in **1** (ppm)

Nucleus	Shifts	
	Obsd	Calcd
H_2	3.02	2.95_9
H_3	1.12	1.10_5
H_4	0.98	0.86_9
H_5	0.71	0.71_8
H_6	0.61	0.56_6
H_7	1.07	0.92_9
H_8	4.79	4.74_5

difference of the two structures is small, it should be not unusual to assume that both of them are present in solution.

Excellent agreement of the calculated induced shifts with those of the observed was given when both of the conformers are present in the solution in a 67:33 ratio at 0 °C. Table 2 gives the observed and calculated ring current shifts in **1**. The root mean square (rms) error is again satisfactorily small (0.075 ppm). Excellent correlation of these data is obtained in a linear regression analysis [7 data (range of the observed shift, 0.60–4.79 ppm) $\Delta\delta_{\mathrm{obs}} = a\cdot\Delta\delta_{\mathrm{calc}}$; $a = 1.0186$, $R^2 = 0.998$].

In order to examine the applicability of this ring current model, we calculated the complexation induced shifts of quinones for the supramolecular complexes of *cis*-bis(2-hydroxy-1-naphthyl) porphyrin **4** reported by Ogoshi and co-workers.[15] Since the structures of these complexes were not known, molecular mechanics calculations (Macromodel V6.5, Amber* force field) were carried out. The calculated complexation shifts of four protons of benzoquinone (BQ) in BQ·**4** complex are in between 4.55 and 5.02 ppm, the average value is 4.64 ppm that is very close to the observed (4.86 ppm). The same procedure was repeated for the complexation shift of methyl signal in duroquinone·**4** complex to give a good reproduction ($\Delta\delta$calc 2.33 ppm) of the observed (2.22 ppm). The successful reproduction of the complexation shifts of these quinone protons supports the wide applicability of this simple model for porphyrin ring current effect.

Acknowledgements

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11. The crystal data for **1**·$2CH_2Cl_2$ are as follows; **1**·$2CH_2Cl_2 \cdot C_{66}H_{42}N_4O_4Sn \cdot 2CH_2Cl_2$, FW = 1240.62, triclinic, space group *P*-1 with $a = 8.6600(5)$, $b = 12.1150(8)$, $c = 15.0710(7)$ Å, $\alpha = 104.541(4)$, $\beta = 104.088(4)$, $\gamma = 104.171(2)°$, $V = 1403.48(14)$ Å^3 and $Z = 1$. Data were collected at 298 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by autoindexing several images in each data set separately with the program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK. (The programs DENZO and SCALEPACK are available from Mac Science Co., Z. Otwinowski, University of Texas, Southwestern Medical Center.) Of 5813 total unique reflections, 5010 were considered observed at the level of $|Fo| > 4.0\sigma|Fo|$. On WinGX (Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837–838), the structures were solved by the direct method (SIR-97, Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G. Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115–119) and refined by full-matrix least squares refinements on F^2 (SHELXL-97, Sheldrick, G. M. Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions. The structure converged with $R = 0.1029$, $wR = 0.2311$. Crystallographic results have been deposited with the Cambridge Crystallographic Data Centre, UK as supplementary publication number CCDC No. 256448. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033 or e-mail: data_request@ccdc.cam.ac.uk.
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