

## Shielding Effects in $^1\text{H}$ NMR Spectra of Halogen-Substituted *meso*-Tetraphenylporphyrin Derivatives

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*Chemical shift increments in  $^1\text{H}$  NMR spectra for halogen atoms occupying the phenyl rings in meso-tetraphenylporphyrin derivatives were determined. They should receive attention in the interpretation of the spectra of a wide range of porphyrins.*

**Keywords:** Porphyrins,  $^1\text{H}$  NMR, chemical shifts, increments, halogens.

## Эффекты экранирования в $^1\text{H}$ ЯМР спектрах галогензамещенных производных мезо-тетрафенилпорфирина

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*В работе определены инкременты атомов галогенов в фенильных кольцах производных мезо-тетрафенилпорфирина для химического сдвига в  $^1\text{H}$  ЯМР спектрах. Полученные данные могут быть полезны при интерпретации спектров обширного ряда порфиринов.*

**Ключевые слова:** Порфирины,  $^1\text{H}$  ЯМР спектры, химические сдвиги, инкременты заместителей, галогены.

### Introduction

Porphyrins are important group of heterocyclic compounds, present in well-known biological materials (e.g., chlorophyll, heme, vitamin B<sub>12</sub>). They are intensively studied in recent years. A selective functionalization of natural as well as readily available synthetic porphyrins should be mentioned herein due to their potential use as sensitizers in photodynamic cancer therapy (PDT),<sup>[1]</sup> molecular-based multi-bit memory storage,<sup>[2]</sup> electron-donor parts in artificial photosynthetic models,<sup>[3]</sup> etc. On the other hand, since the beginning of these investigations an extensive spectroscopic research is conducted. Among others, in the synthetic projects the correct signals assignment in NMR is of significant importance. The above problem is also discussed in this paper.

While collecting material to this work we found in the literature a large number of mistakes done in the interpretation of the spectra or very rough assignments of the signals, e.g. presentation of signals as the multiplets that is not a proof of the structure.

Some years ago, we started working on phenyl substituted porphyrins and we observed regularity in appearance of the chemical shifts of the protons in phenyl rings in which additional substituents were present. We have undertaken studies to determine NMR increments for these substituents in the porphyrin system, similarly to work of Jackman and Sternhell concerning benzene ring.<sup>[4]</sup> We could not use benzene increments herein because the local magnetic field affecting chemical shifts is generated by ring currents not only in benzene ring (red arrows) but also in large [18 $\pi$ ]-electron aromatic porphyrin

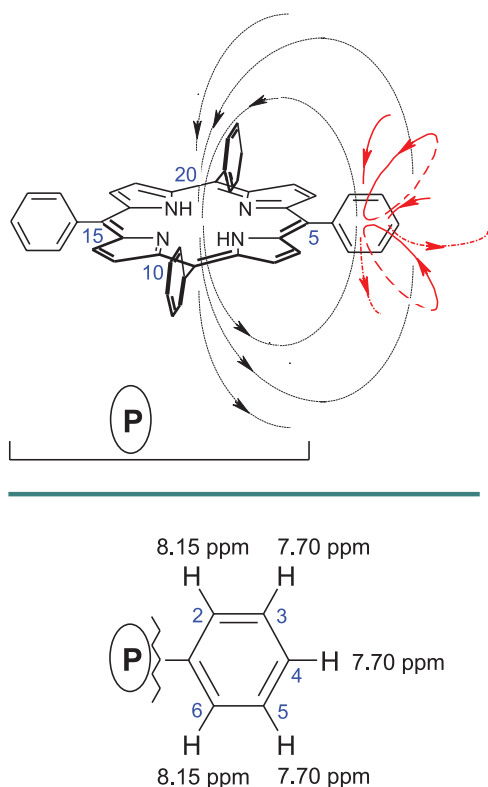


Figure 1.

system (black arrows, Figure 1). Very good model for these investigations was *meso*-tetraphenylporphyrin, *m*-TPP (and derivatives).

## Results and Discussion

In this paper, to determine NMR increments we would like to perform calculations for a series of similar substituents. These calculations have preliminary nature. As exemplary substituents the halogens were selected. On the other hand, as it was mentioned above, *m*-TPP skeleton was chosen as a parent porphyrin structure.

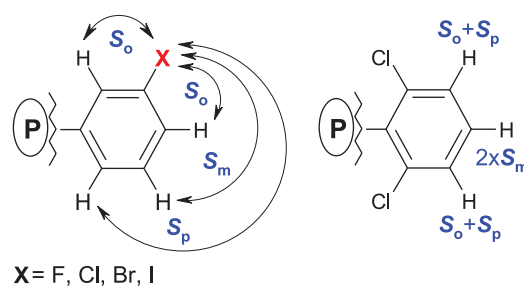


Figure 2.

In *meso*-tetraphenylporphyrin system the chemical shifts for protons in phenyl rings  $\delta_{\text{parent[TPP]}}$  are as follows:  $\delta_{\text{H-2/H-6}}=8.15$ ,  $\delta_{\text{H-3/H-5}}=7.70$ ,  $\delta_{\text{H-4}}=7.70$  (Figure 1).<sup>[5]</sup> To calculate increments for all halogens:  $S_o$  (*ortho*),  $S_m$  (*meta*), and  $S_p$  (*para*), we were looking for data (proton chemical shifts) in a number of publications. A further literature search showed that only a minority of the published papers offers the desired informations. Thus, a series of porphyrins was also prepared in our laboratory – most of them substituted in *meso*-phenyl rings with halogen in position 3-. They were reported in our previous papers.<sup>[6,7]</sup> Such substitution pattern allows calculations of *ortho*-, *meta*-, and *para*- values (according to equation  $S_{o/m/p} = \delta_{\text{obs}} - \delta_{\text{parent[TPP]}}$ ) as the each ring contains protons situated in *ortho*-, *meta*-, and *para*-positions in relation to the halogen atom (see Figure 2).

Using data calculated for 3-halosubstituted derivatives a list of increments was collected for fluorine, chlorine, bromine, and iodine (Table 1, only entries with 3-mono-substituted rings). We added some other data previously described in the literature and data of 2,6-dichlorophenyl derivative.<sup>[7]</sup> In the latter case, the chemical shifts of H-3/5 protons are equal  $\delta=7.79$ . Theoretically, it can be presented with the equation:  $\delta=7.70_{\text{parent[TPP]}} + S_o + S_p$  (Figure 2). Thus, the  $S_o$  and  $S_p$  cannot be estimated separately (only a sum is possible to calculate), while the  $S_m$  can be determined,  $\delta_{\text{H-4}}=7.70$  ( $7.70_{\text{parent[TPP]}} + 2 \times S_m = 7.70 \Rightarrow S_m = 0.00$ ). On the basis of the above data, the increments  $S_o$ ,  $S_m$ ,  $S_p$  were calculated for all halogens (Table 1).

**Table 1.** Calculated values of  $^1\text{H}$  NMR increments  $S_i(\delta)$  for halogens in *meso*-phenyl substituted porphyrin systems.

Ph in porphyrin <sup>a,b</sup>	SM <sup>c</sup>	H-2	H-3	H-4	H-5	H-6	Lit.	$S_o$	$S_m$	$S_p$
<b>P</b> ( <i>m</i> -TPP)		8.15	7.70	7.70	7.70	8.15	[5]			
3-F-C <sub>6</sub> H <sub>4</sub> -P	4	7.95	–	7.52	7.73	8.02	[7]			
	3	7.93	–	7.54	7.74	8.00	[7]			
	2	7.93	–	7.55	overlpd <sup>d</sup>	7.99	[7]			
<b>average<sup>c</sup></b>		[7.94]	–	[7.54]	[7.74]	[8.00]		–0.21; –0.16	0.04	–0.15
4-F-C <sub>6</sub> H <sub>4</sub> -P	4	8.17	7.47	–	7.47	8.17	[12]	–0.23	0.02	–
3-F-4-NO <sub>2</sub> - -C <sub>6</sub> H <sub>3</sub> -P <sup>f</sup>	1	8.17	–	–	8.48	8.17	[7]			
	2	8.17	–	–	8.49	8.17	[7]			
	3	8.17	–	–	8.51	8.16	[7]			
	4	overlpd	–	–	ca 8.50	overlpd	[7]			
<b>average</b>		[8.17]	–	–	[8.50]	[8.17]		–0.25	–0.15	–0.25
<b><math>S_{\text{H(av)}}[\text{F}]</math></b>								–0.21	–0.03	–0.20

Continuation of Table 1.

3-Cl-C <sub>6</sub> H <sub>4</sub> -P	4	8.22	–	7.65–7.84	7.65–7.84	8.10	[6]			
	3	8.23	–	7.66–7.86	7.66–7.86	8.11	[6]			
	1	overlpd	–	overlpd	overlpd	8.10	[8a]			
<b>average</b>		<b>[8.23]</b>	–	<b>N/a<sup>g</sup></b>	<b>N/a</b>	<b>[8.10]</b>		<b>0.08</b>	<b>N/a</b>	<b>–0.05</b>
4-Cl-C <sub>6</sub> H <sub>4</sub> -P	4	8.14	7.75	–	7.75	8.14	[13]			
	4	8.13	7.74	–	7.74	8.13	[14]			
<b>average</b>		<b>[8.14]</b>	<b>[7.75]</b>	–	<b>[7.75]</b>	<b>[8.14]</b>		<b>0.05</b>	<b>–0.01</b>	<b>–</b>
2,6-Cl <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -P	4	–	7.79	7.70	7.79	–	[7]	$\Sigma_{So+Sp}=0.09$	<b>0.00</b>	$\Sigma_{So+Sp}=0.09$
3-Cl-4-NO <sub>2</sub> - -C <sub>6</sub> H <sub>3</sub> -P	2	8.43	–	–	8.32	8.27	[6a]			
	1	8.44	–	–	ca 8.28	ca 8.28	[6a]			
	3	8.42	–	–	8.34	overlpd	[8a]			
<b>average</b>		<b>[8.43]</b>	–	–	<b>[8.31]</b>	<b>[8.28]</b>		<b>0.01</b>	<b>–0.34</b>	<b>–0.14</b>
<b>S<sub>i(av)</sub>[Cl]</b>								<b>0.05</b>	<b>–0.12</b>	<b>–0.09</b>
3-Br-C <sub>6</sub> H <sub>4</sub> -P	4	8.38	–	7.95	7.64	8.16	[7]			
	3	8.37	–	7.97	7.65	8.15	[7]			
	2	8.37	–	7.98	7.66	8.15	[7]			
	2	8.37	–	7.98	7.66	8.15	[7]			
	1	8.37	–	8.00	7.68	8.15	[7]			
<b>average</b>		<b>[8.37]</b>	–	<b>[7.98]</b>	<b>[7.66]</b>	<b>[8.15]</b>		<b>0.22; 0.28</b>	<b>–0.04</b>	<b>0.00</b>
4-Br-C <sub>6</sub> H <sub>4</sub> -P	4	8.06	7.90	–	7.90	8.06	[11]			
	4	8.05	7.88	–	7.88	8.05	[15]			
	4	8.08	7.91	–	7.91	8.08	[16]			
	4	8.08	7.91	–	7.91	8.08	[17]			
<b>average</b>		<b>[8.07]</b>	<b>[7.90]</b>	–	<b>[7.90]</b>	<b>[8.07]</b>		<b>0.20</b>	<b>–0.08</b>	<b>–</b>
3-Br-4-NO <sub>2</sub> - -C <sub>6</sub> H <sub>3</sub> -P	1	ca 8.60	–	–	8.28	8.31	[7]			
	2	8.62	–	–	ca 8.30	ca 8.30	[7]			
	2	8.62	–	–	8.28	8.31	[7]			
	3	8.61	–	–	ca 8.31	ca 8.31	[7]			
	4	8.60	–	–	ca 8.30	ca 8.30	[7]			
<b>average</b>		<b>[8.61]</b>	–	–	<b>[8.29]</b>	<b>[8.31]</b>		<b>0.19</b>	<b>–0.36</b>	<b>–0.11</b>
<b>S<sub>i(av)</sub>[Br]</b>								<b>0.22</b>	<b>–0.16</b>	<b>–0.05</b>
3-I-C <sub>6</sub> H <sub>4</sub> -P	4	8.59	–	8.15	7.50	8.19	[7]			
	3	8.58	–	overlpd	7.52	overlpd	[7]			
	2	8.58	–	overlpd	7.54	overlpd	[7]			
	2	8.58	–	overlpd	overlpd	overlpd	[7]			
	1	8.58	–	overlpd	overlpd	overlpd	[7]			
<b>average</b>		<b>[8.58]</b>	–	<b>[8.15]</b>	<b>[7.52]</b>	<b>[8.19]</b>		<b>0.43; 0.45</b>	<b>–0.18</b>	<b>0.04</b>
4-I-C <sub>6</sub> H <sub>4</sub> -P	4	7.90	8.10	–	8.10	7.90	[10]			
	4	7.89	8.07	–	8.07	7.89	[18]			
	4	7.91	8.09	–	8.09	7.91	[19]			
	4	7.93	8.11	–	8.11	7.93	[17]			
<b>average</b>		<b>[7.91]</b>	<b>[8.09]</b>	–	<b>[8.09]</b>	<b>[7.91]</b>		<b>0.39</b>	<b>–0.24</b>	<b>–</b>
3-I-4-NO <sub>2</sub> - -C <sub>6</sub> H <sub>3</sub> -P	1	8.93	–	–	8.29	8.34	[7]			
	2	overlpd	–	–	8.30	8.34	[7]			
	2	overlpd	–	–	8.29	8.34	[7]			
	3	8.92	–	–	8.30	8.34	[7]			
	4	8.91	–	–	ca 8.32	ca 8.32	[7]			
<b>average</b>		<b>[8.92]</b>	–	–	<b>[8.30]</b>	<b>[8.34]</b>		<b>0.50</b>	<b>–0.35</b>	<b>–0.08</b>
<b>S<sub>i(av)</sub>[I]</b>								<b>0.44</b>	<b>–0.26</b>	<b>–0.02</b>

<sup>a</sup>P stands for porphyrin; <sup>b</sup>data for the same compounds or/and for the same substitution pattern are grouped in the table;

<sup>c</sup>SM – substitution multiplicity: 1 stands for mono-substitution with functionalized phenyl ring, 2 – for bis-, 3 – for tris-, and 4 – for tetrakis-;

<sup>d</sup>overlpd = overlapped; <sup>e</sup>in brackets [...] the average data for the same substitution pattern (used for calculations of S<sub>i</sub>);

<sup>f</sup>for all calculations involving NO<sub>2</sub> group the data from Table 2 were used;

<sup>g</sup>N/a – not available (for all instances in the table).

As it was mentioned earlier, the list of compounds available for these calculations was rather limited. On the other hand, we previously described many derivatives that contain (alongside the halogens) a variety of other substituents, especially including the nitro group.<sup>[6-8]</sup> Thus, if we knew values  $S_o$ ,  $S_m$ , and  $S_p$  of  $\text{NO}_2$  group for phenyl moiety in porphyrin system, we could determine parameters for halogens more precisely by using a larger platform of data.

There are three types of *meso*-nitrophenylporphyrins that can be taken into account: 2-nitrophenyl-, 3-nitrophenyl-, and 4-nitrophenyl-substituted derivatives. However, only for the latter case there is a number of reports published in the literature. Although there were some other papers concerning these mono-substituted nitroporphyrins, their spectra were not provided or they were described not enough detail, or the interpretation was evidently wrong. Such spectra were rejected. For multisubstituted moieties the situation is definitely more complicated and it is not so easy, or almost impossible, to reconsider whether the chemical shifts were determined and assigned correctly. To be sure the calculations, for these derivatives we used sets of data from our laboratory only.<sup>[7]</sup>

It should be also mentioned that in many papers not all of the chemical shifts in the spectra were assigned to the corresponding protons or were assigned incorrectly. We have done this herein and the spectra are given in Table 2. On the basis of these data we calculated approximative values of increments for  $\text{NO}_2$  group:  $S_o=0.95$ ,  $S_m=0.27$ , and  $S_p=0.32$  (Table 2). Using this set of parameters and including the available examples of compounds in which both halo- and nitro- substituents are present in phenyl rings, the final increments for halogens were determined (see Table 1). They could be treated as increments ready to use for assignment the chemical shifts in *m*-TPP derivatives that contain such substituents in *meso*-phenyl rings.

This approach has been already applied for some porphyrins, by us<sup>[7,8a,8b]</sup> and by Sun,<sup>[9]</sup> for elucidation of single structures. Moreover, we corrected the wrong assignment and the structure elucidation in the earlier published paper

(in *J. Org. Chem.* **1989**, *54*, 2753–2756).<sup>[8b]</sup> Interestingly, Sun *et al.* used for analysis a set of parameters determined for benzene ring that in our opinion cannot be taken into account due to a large field effect of aromatic porphyrin moiety affecting the phenyl ring (Figure 1). This changes the situation and the values should be different as compared to the single benzene ring.<sup>[4b]</sup>

During the selection of the literature material to be used in this work we found that in some spectra, *e.g.* for 5,10,15,20-tetrakis(4-iodophenyl)porphyrin (Lindsey<sup>[10]</sup>), the protons were not assigned, or the spectra were solved incorrectly (*e.g.*, 5,10,15,20-tetrakis(4-bromophenyl)porphyrin; reverse assignment of H-2/6 and H-3/5; Radzuan.<sup>[11]</sup> In such cases, we used the data after correction. For all instances we also assumed that any other substitution pattern in the remaining phenyl rings (positions 10-, 15-, and 20-) does not influence on the chemical shifts of the analyzed phenyl ring (in position 5-). This is very likely because they are far away from this ring. Finally, only the spectra recorded in  $\text{CDCl}_3$  were reconsidered herein and the chemical shifts are relative to residual proton signal in the deuterated solvent ( $\text{CDCl}_3$ ;  $\delta=7.26$  ppm).

One can find in Tables 1 and 2 that differences between some calculated numbers for the same  $S_i$ -elements are considerable, *e.g.*,  $\Delta S_m[\text{F}]=0.19$ ,  $\Delta S_m[\text{Cl}]=0.34$  (the largest one),  $\Delta S_m[\text{Br}]=0.32$ ,  $\Delta S_m[\text{I}]=0.17$ ,  $\Delta S_p[\text{I}]=0.12$ . These deviations appeared for disubstituted phenyl rings in which both groups remain in *ortho*-relation, thus causing mutual steric interactions and generating larger changes in values of parameters. The above abnormal  $S_m$  increments (especially in 3,4-disubstituted ring with  $\text{NO}_2$  group in position 4-) could be also an effect of disturbances in the inner (local) magnetic field that strongly influences on the chemical shifts. In this case, the  $S_m$  values were calculated involving 3-X substituent and H-5 proton, with  $\text{NO}_2$  group between them. On the other hand, it can be also a secondary error effect because we used in these calculations  $S_{i(\text{av})}[\text{NO}_2]$  increments that were previously determined from the available in the literature experimental data.

**Table 2.** Chemical shifts and calculated  $S_o$ ,  $S_m$ ,  $S_p$  for  $\text{NO}_2$  group (in *meso*-phenyl substituted porphyrin systems).<sup>a</sup>

Ph in porphyrin	SM	H-2	H-3	H-4	H-5	H-6	Lit.	$S_o$	$S_m$	$S_p$
<b>P</b> ( <i>m</i> -TPP)		8.15	7.70	7.70	7.70	8.15				
2- $\text{NO}_2$ - - $\text{C}_6\text{H}_4$ -P	4	–	8.67	7.97	7.97	8.45	[17]	0.97	0.27; 0.30	0.27
3- $\text{NO}_2$ - - $\text{C}_6\text{H}_4$ -P	1	9.01	–	8.61	7.88	8.48	[9]			
	3	9.01	–	8.60	7.87	8.45	[9]			
	4	9.09	–	8.72	8.00	8.57	[17]			
	4	9.09	–	<i>ca.</i> 8.73	8.00	<i>ca.</i> 8.57	[20]			
<b>average</b>		[9.05]		[8.67]	[7.94]	[8.52]		0.90; 0.97	0.24	0.37
4- $\text{NO}_2$ - - $\text{C}_6\text{H}_4$ -P	1	8.40	8.64	–	8.64	8.40	[17]			
	4	8.40	8.66	–	8.66	8.40	[21]			
	4	8.38	8.63	–	8.63	8.38	[22]			
	1	8.41	8.64	–	8.64	8.41	[22]			
	1	8.40	8.64	–	8.64	8.40	[23]			
<b>average</b>		[8.40]	[8.64]	–	[8.64]	[8.40]		0.94	0.25	–
$S_{i(\text{av})}[\text{NO}_2]$								0.95	0.27	0.32

<sup>a</sup> for explanations see footnotes to Table 1.

Nowadays, these types of structure problems (correct assignment of the chemical shifts) could also be done by other methods, *e.g.* 2D NMR homo- and heteronuclear experiments. However, for larger molecules they are time consuming and sometimes more expensive. Thus, the authors used to solve the spectra without these additional investigations. This simplified procedure resulted in many mistakes in the published papers (some assignments were unacceptable). It was the reason of preparation this work and it may be helpful for porphyrin chemists.

## Conclusions

Porphyrins structures are rather complex, thus, such package of increments may receive future attention in the interpretation of porphyrin spectra. Herein, we presented the calculated values for halogens and (by chance) for NO<sub>2</sub> group which was helpful to get more reliable data  $S_i[X]$ .

Now, we are planning to prepare more general complete tables for a large spectrum of substituents; not only for *meso*-TPP derivatives, but also for various types of porphyrins. The expanded and updated version of these tables will require reconsideration of many derivatives, some of them have to be synthesized. This allows preparation of more consistent system for NMR chemical shifts prediction in porphyrin moieties. It should be of great value to chemists working in this area. We are in the midst of these studies.

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