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Molecular complexation of *meso*-tetraphenylporphyrins with SO_2

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Abstract

When *para*-substituted *meso*-tetraphenylporphyrins were reacted with SO_2, only 2:1 (donor:acceptor) molecular complexes were produced. ^1H NMR, IR, UV–vis and elemental analysis indicated that the porphyrins act as electron donors and that two SO_2 molecules (as electron acceptors) are bound to the lone electron pairs of the pyrrolenine nitrogens in the porphyrin. Two d orbitals of the sulfur atoms accept the nitrogen lone pairs and the two SO_2 molecules are located above and below the porphyrin. There are two hydrogen bonds present between two pyrrole NH and SO_2 molecules.

Keywords: Porphyrin; Sulfur dioxide; Molecular complex; Donor; Acceptor

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1. Introduction

One of the most widespread of all naturally occurring prosthetic group is the class of highly colored pigments known as porphyrins. These tetrapyrrolic macrocycles play critical roles in a wide range of biological processes, including electron transfer, oxygen transfer, and photosynthetic processes.

This ubiquity reinforced by their visually appealing colors, has led Battersby to call the porphyrins the ‘‘pigment of life’’ [1]. There are three positions in porphyrins (α, β and *meso*). Two distinct patterns of substituent are illustrated by β-substituted porphyrins and *meso*-substituted porphyrins. The β-substituted porphyrins closely resemble naturally occurring porphyrins. The *meso*-substituted porphyrins have no direct biological counterparts but have found wide application as biomimetic models and as useful components in materials chemistry [2].

Para-substituted *meso*-tetraphenylporphyrins are a group of porphyrin derivatives where phenyl groups are placed in *meso*-positions. These derivatives are more reactive than *meta* and *ortho*-substituted because of less steric hindrance in *para*-substituted. *meso*-Tetraphenylporphyrins [H_2TPP] act as electron donors in reaction with some acceptors and produced some molecular complexes. In this situation, porphyrins give the lone electron pairs of pyrrolenine nitrogens to acceptors and produce 1:2 (porphyrin:acceptor) molecular complexes [3–9]. It is known that sulfur dioxide forms molecular complexes with the compounds containing nitrogen atoms such as amines and azaheterocycles [10].

In this work we present spectroscopic evidences of specific 1:2 molecular complexes of free base *p*-substituted *meso*-tetraphenylporphyrin derivatives (Fig. 1) as σ-electron donors, with SO_2 as electron acceptor. This article provides the first example of the molecular complexes of *meso*-tetraphenylporphyrins containing N → S dative bond.

2. Experimental

2.1. General procedure

All of the employed chemicals and solvents were obtained from Merck and Fluka and purified by distillation and dried over calcium chloride. In this work, at first, *meso*-tetraphenylporphyrins and three *para*-substituted derivatives were synthesized by literature methods [11]. SO_2 was prepared from

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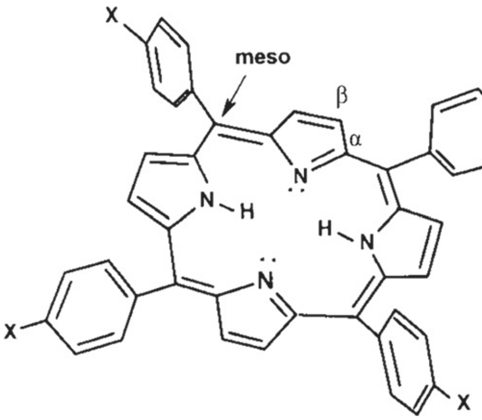

X=H, H_2TPP

X=OMe, H_2T(p-OMe)PP

X=Me, H_2T(p-Me)PP

X=Cl, H_2T(p-Cl)PP

Fig. 1. *meso*-Tetraphenylporphyrins.

burning of sulfur with oxygen [12], then sulfur dioxide was passed through the $CHCl_3$ solutions of the *meso*-tetraphenylporphyrins. After slow evaporation of the solvent at room temperature, the green residues of $[(SO_2)_2H_2T(p\text{-}X)PP]$ were obtained. The completion of the reaction was monitored by UV–vis spectra.

The results of elemental analysis for $[(SO_2)_2H_2T(p\text{-}X)PP]$ molecular complexes were consistent with $C_{44}H_{30}N_4O_4S_2$ ($[(SO_2)_2H_2TPP]$): calc. C, 71.1; H, 4.1; N, 7.5; S, 8.6; found C, 70.7; H, 3.9; N, 7.6; S, 8.2, $C_{48}H_{38}N_4O_8S_2$ ($[(SO_2)_2H_2T(p\text{-}OMe)PP]$): calc. C, 66.8; H, 4.4; N, 6.5; S, 7.4; found C, 65.7; H, 4.1; N, 6.0; S, 6.9, $C_{48}H_{38}N_4O_4S_2$ ($[(SO_2)_2H_2T(p\text{-}Me)PP]$): calc. C, 72.2; H, 4.8; N, 7.0; S, 8.0; found C,72.5; H, 5.0; N, 6.8; S, 8.1, $C_{44}H_{26}N_4O_4S_2Cl_4$ ($[(SO_2)_2H_2T(p\text{-}Cl)PP]$): calc. C, 60.0; H, 3.0; N, 6.4; S, 7.3; found C, 60.8; H, 3.2; N, 6.2; S, 6.9.

2.2. *Spectroscopic measurements*

The UV–vis spectra were recorded in $CHCl_3$ solution utilising an ATI UNICAM – UV/VIS Vision SOFTWARE V-2011 spectrophotometer (a 1 cm optical path length was employed). A Bruker 400 MHz spectrometer was used for ^1H NMR spectra of porphyrins and those molecular complexes in $CDCl_3$ solvent. For FTIR spectra, a Magna 550 Nicolet instrument was applied (using KBr pellets).

3. Results and discussion

The first evidence for formation of molecular complexes of *meso*-tetraphenylporphyrins and SO_2 was UV–vis spectra. Porphyrins have an intense soret band (400–420 nm) and 3–4 Q bands that are weaker intense than soret band. This clearly indicates that the spectra are essentially due to the electronic transitions within the porphyrin core, and they can be explained in terms of the four orbital models of porphyrins [13–17]. When acceptor is added to porphyrin, firstly, the intensity of soret band of the porphyrin decreases and in contrast the intensity of the soret band of the complex increases. Secondly, quantity of the Q bands is decreased and so those are shown red shift. When the molecular complexation of *meso*-tetraphenylporphyrins is completed, soret band of the porphyrin is omitted and soret band of the molecular complex is observed (435–455 nm) [3–9]. These evidences were observed when SO_2 was added to the $CHCl_3$ solution of the *meso*-tetraphenylporphyrins [$H_2T(p\text{-}X)PP$, X = H, OMe, Me, Cl]. The UV–vis spectra of H_2TPP and related molecular complex ($[(SO_2)_2H_2TPP]$) are shown in Fig. 2. The UV–vis data of the SO_2-porphyrin molecular complexes are listed in Table 1. The similar results are observed for 1:2 molecular complexation of *meso*-tetraphenylporphyrins with DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) [4], TCNE (tetracyanoethylene) [5], trialkylsilylchlorides [6], and borontrifloride [7]. The spectral red shift for $[(SO_2)_2H_2T(p\text{-}OMe)PP]$ molecular complex (30.5 and 42 nm) is much greater than the shifts in the other complexes (22.9–31 nm), Table 1. This difference could be attributed to a better π-resonance-type interaction caused by the lone pairs of the $p\text{-}OCH_3$ groups [3–5].

It is notable that *meso*-tetraphenylporphyrins are aromatic compounds and the ring current in magnetic fields caused the NH protons appear upfield about −2.75 ppm and the β-protons appear downfield at 8.84–8.86 ppm. Resonances due to the *meso*-phenyl protons consist of two doublets, one for *ortho* (8.08–8.24 ppm) and another for *meta* hydrogens (7.27–7.77 ppm). In the case of H_2TPP, the *meta* and *para* hydrogens overlap and give a doublet (7.75, 7.77 ppm). Upon formation of the molecular complex, the NH protons shift to downfield ($\Delta\delta = 1.46\text{–}2.71$ ppm) and β-protons shift to upfield

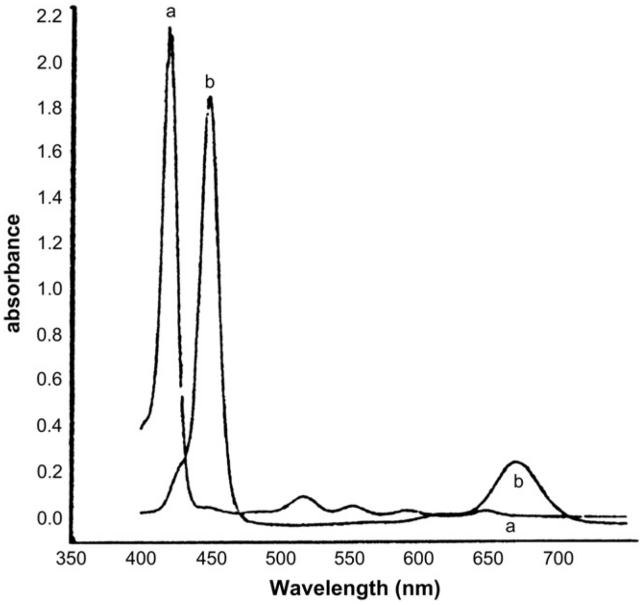

Fig. 2. UV–vis spectra of (a) H_2TPP and (b) $[(SO_2)_2H_2TPP]$ in chloroform.

Table 1
UV–vis spectral data of various $H_2T(p\text{-}X)PP$, $[(SO_2)_2H_2T(p\text{-}X)PP]$ molecular complexes

H_2T (p-X)PP	Porphyrin peaks					SO_2 molecular complexes		
	Soret	IV	III	II	I	Soret	II	I
X = H	416.7	516.8	551.5	592.0	648.0	439.6	605.0	675.3
$\Delta\lambda$						22.9		27.3
X = OMe	419.5	520.5	557.1	596.0	653.0	451.0		695.0
$\Delta\lambda$						30.5		42.0
X = Me	418.3	518.4	554.0	593.0	649.0	442.2		680.0
$\Delta\lambda$						23.9		31.0
X = Cl	418.0	517.4	551.4	592.0	648.8	443.0		677.0
$\Delta\lambda$						25.0		28.2

Table 2
^1H NMR data of various $H_2T(p\text{-}X)PP$, $[(SO_2)_2H_2T(p\text{-}X)PP]$ molecular complexes

	Compounds				
	NH	H_β	H_o	H_m	H_p or H_x
H_2TPP	−2.76	8.85	8.21, 8.24	7.75, 7.77	7.75, 7.77
SO_2 complex	−1.12	8.55	8.45	8.03	8.03
$\Delta\delta$	1.46	−0.30			
$H_2T(p\text{-}OMe)$	−2.75	8.86	8.11, 8.14	7.27, 7.31	4.10
SO_2 complex	−0.04	8.54	8.59, 8.54	7.58	4.16
$\Delta\delta$	2.71	−0.32			
$H_2T(p\text{-}Me)PP$	−2.77	8.85	8.08, 8.11	7.54, 7.56	2.70
SO_2 complex	−0.30	8.62	8.50	7.80	3.01
$\Delta\delta$	2.47	−0.23			
$H_2T(p\text{-}Cl)PP$	−2.86	8.84	8.12, 8.15	7.73, 7.76	–
SO_2 complex	−0.85	8.65	8.53	7.95	
$\Delta\delta$	2.01	−0.19			

($\Delta\delta = -0.19$ to -0.32 ppm) and overlap with *ortho*-protons, all phenyl protons shift to downfield and the *meta* and *para* protons in $[(SO_2)_2H_2TPP]$ give a signal in the 8.03 ppm region. All of the shifts are in direction of decreasing and increasing ring currents in the porphyrin core and phenyl ring, respectively. The ^1H NMR spectra of H_2TPP and its molecular complex ($[(SO_2)_2H_2TPP]$) are shown in Fig. 3. The changes of the ^1H NMR shifts upon the molecular complexation are due to tilting of the porphyrin core and contribution of phenyl rings in the ring current of the porphine macrocycle. ^1H NMR data of the *meso*-tetraphenylporphyrins and their molecular complexes with SO_2 are listed in Table 2. The ^1H NMR chemical shifts for $[(SO_2)_2H_2T(p\text{-}X)PP]$ are similar to the chemical shifts of the molecular complexation of the *meso*-tetraphenylporphyrins with DDQ, TCNE, and SiR_3Cl [4–6]. The very close correspondence among UV–vis and ^1H NMR spectral data of the $[(SO_2)_2H_2T(p\text{-}X)PP]$ compounds and those of the related $(DDQ)_2H_2T(p\text{-}X)PP$ [4], $(TCNE)_2H_2T(p\text{-}X)PP$ [5], $(SiR_3Cl)_2H_2T(p\text{-}X)PP$ [6] and H_4TPP^{2+} dication [18] proposed a similar porphyrin core structure in all these species, with noncoplanar pyrrole rings tilted alternatively up and down (Fig. 4). This conformation makes the lone electron pairs of the two pyrrole nitrogens more accessible for donating to empty d orbitals of the two sulfurs, analogous to electron donation to the acceptors in DDQ, TCNE, and SiR_3Cl. It is noteworthy that whilst the interaction of the *meso*-tetraphenylporphyrins with sulfur dioxide produced the corresponding green molecular complexed species in chloroform, it remained almost intact in the presence of H_2SO_3, under our experimental conditions. This test completely failed the probability of diprotonation of the porphyrins in our reaction system. Further, the UV–vis and ^1H NMR spectra of the $H_4T(4\text{-}X)PP^{2+}$ were quite sensitive to the concentration of CF_3COOH [3,7], but an excess SO_2 gas had no effect on the UV–vis and ^1H NMR spectra of $[(SO_2)_2H_2T(p\text{-}X)PP]$ molecular complexes. Furthermore, the integration of the pyrrolic NH hydrogen peak in 0.006 M $CDCl_3$ solution of the $[(SO_2)_2H_2TPP]$ molecular complex was 2.2, whereas for the H_4TPP^{2+} was 4.1. In other words, a diprotonated porphyrin species cannot form in our reaction system. The remarkable spectral correspondence between the $[(SO_2)_2H_2T(p\text{-}X)PP]$ and $H_2T(p\text{-}X)PP^{2+}$ suggested analogous saddled porphyrin core structures and π-system in these species.

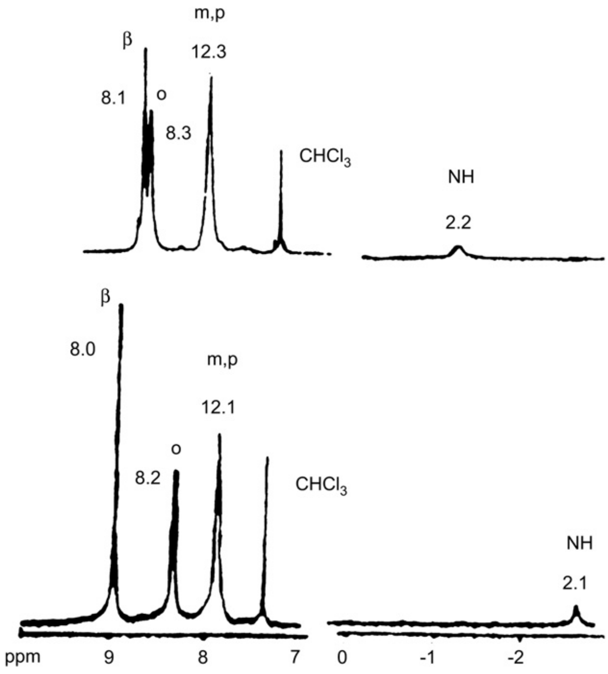

Fig. 3. ^1H NMR spectra of (a) H_2TPP and (b) $[(SO_2)_2H_2TPP]$ in $CDCl_3$.

meso-Tetraphenylporphyrins showed NH stretching band around 3320 cm^{-1} [19]. In free SO_2, two stretching bands

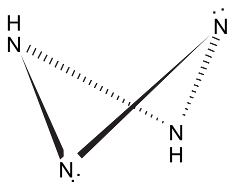

Fig. 4. The out-of-plane deformation of the porphyrin core causes two nitrogen atoms of pyrrole rings to be able to act as the electron donors to two molecules of SO_2.

appear at 1150 and 1360 cm^{-1} [20]. For the molecular complexes observed a new band around 820–830 cm^{-1} may be assigned to a stretching vibration of S–N bond formed between the porphyrins (as donors) and SO_2 (as acceptor). One d orbital of sulfur in SO_2 accepted one lone pair of the pyrrolenine nitrogen and produced a dative bond (N → S) between the porphyrins and sulfur dioxide. Formation of the dative bond caused the sulfur–oxygen bond in SO_2 to be a single bond. Molecular complexation between the porphyrins and sulfur dioxide caused a tilting of porphine core and sharing of phenyl rings in the π-resonance of core ring and extension of aromatic system in the porphyrins. This tilting is similar to diprotonation and molecular complexation of *meso*-tetraphenylporphyrins with various acceptors [3–9]. In the molecular complexes [$(SO_2)_2H_2T(p\text{-}X)PP$], it has been seen that stretching bands of the SO_2 decreased and were observed around 1100 and 1300 cm^{-1}. In molecular complexes, NH stretching band is completely lost. This effect may indicate the occurrence of intermolecular hydrogen-bonding between the pyrrolic hydrogens and the complexed SO_2 (Fig. 5). Such interactions should lead to further stabilization of the molecular complexes. The proposed out-of-plane conformation of the porphyrin pyrrole rings seems to provide a better orientation of NH groups for hydrogen-bonding. Addition of first SO_2 to porphyrin leads to a substantial distortion in the porphyrin nucleus structure, and this step makes the lone electron pairs of the pyrrolenine nitrogens and the pyrrole NH bonds more accessible for reactions with SO_2, thus facilitating the addition of second SO_2 to the porphyrin core, and achieving the final 2:1 complex.

In the porphyrins (Fig. 1) the NH groups of the pyrrolenines are not next to each other but for the molecular complexes of [$(SO_2)H_2T(p\text{-}X)PP$] (Fig. 5) two adjacent nitrogen atoms act as electron donors to acceptors. This structure is similar to the proposed structures for the 1:2 molecular complexation of porphyrins with DDQ, TCNE, SiR_3Cl, and BF_3 [4–8]. Furthermore, this structure is similar to the structure of diprotonated porphyrin ([H_4TPP^{2+}]·$2Cl^-$) [14]. In the diprotonated species two molecules of HCl are located above and below the porphyrin plane and two protons of HCl are connected to two adjacent nitrogens.

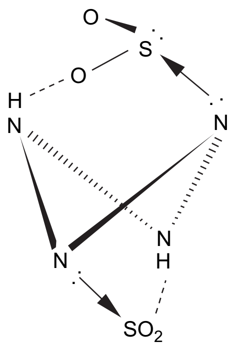

Fig. 5. Diagrammatic illustration of the proposed structure for a [$(SO_2)_2H_2T(p\text{-}X)PP$] molecular complex. In the middle the tetrahedrally tilted pyrrole nitrogens of a porphyrin core are shown.

4. Conclusions

When *para*-substituted *meso*-tetraphenylporphyrins were reacted with SO_2, only 2:1 (donor:acceptor) molecular complexes are obtained in which the porphyrins act as electron donors and two SO_2 molecules are bound to the lone electron pairs of the pyrrolenine nitrogens. Two d orbitals of the sulfur atoms accept the nitrogen lone pairs and the two SO_2 molecules are located above and below the porphyrin.

Acknowledgement

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