# Thermodynamic Studies of the Molecular Interactions of 2,4-Dichlorophenol and 2,4,6-Trichlorophenol with Free Bases *meso*-Tetraarylporphyrins

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The hydrogen bonded complexes of 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) with free base *meso*-tetraarylporphyrins [$H_2T(4-X)PP$] (X = OCH_3, CH_3, H, Cl) have been studied. The formation constants K and other thermodynamic parameters were calculated by UV-Vis spectrophotometry titration method. The formation constants show the following trend relative to X substituent of porphyrins:

$H_2T(4-CH_3O)PP > H_2T(4-CH_3)PP > H_2TPP > H_2T(4-Cl)PP$
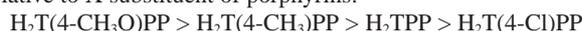
On the other hand, formation constants show that 2,4-DCP form more stable hydrogen bonded complexes than 2,4,6-TCP with free base porphyrins.

Key Words: Hydrogen-bonded complexes, Phenol derivatives, Free base porphyrins, Molecular adducts.

INTRODUCTION

Hydrogen bonds play a crucial role in many chemical, physical and biochemical processes and they are also very important in crystal engineering[1-3]. Hydrogen bonds usually designated as X-H···Y in which there is an X-H proton donating bond and an acceptor of protons (Y-center). Interaction of phenol derivatives (PD) such as 4-nitrophenol[4,5], 2,4-dichlorophenol (2,4-DCP)[6] and 2,4,6-trichlorophenol (2,4,6-TCP)[7], with biological systems are of interest[8]. Porphyrins with two N-H proton donating bonds and numerous nitrogen atoms as proton acceptor centers can form hydrogen-bonded complexes with some hydroxylated compounds. Last studies were demonstrated that hydrogen bended complexes of phenol derivatives with free base porphyrins has a 2:1 mol ratio of phenol derivatives to $H_2T(4-X)PP$[1,9].

In this work, the solution investigation for interactions of 2,4-DCP and 2,4,6-TCP with free base porphyrins are reported. The $H_2T(4-X)PPs$ are H_2TPP (*meso*-tetraphenyl porphyrin), $H_2T(4-Cl)PP$ (*meso-tetrakis*-(4-chloro phenyl)porphyrin), $H_2T(4-CH_3)PP$ (*meso-tetrakis*-(4-methylphenyl) porphyrin) and $H_2T(4-CH_3O)PP$ (*meso-tetrakis*-(4-methoxyphenyl) porphyrin).

EXPERIMENTAL

Benzaldehyde, *p*-substituted benzaldehydes, propionic acid, chloroform and phenols (Merck and Fluka) were used as received. Pyrrole (Fluka) was distilled before use. Chloroform solvent for UV-Vis measurements was distilled over K_2CO_3 before use. UV-Vis measurements were preformed using a Jasco V-530 UV-Vis spectrometer equipped with a LAUDA ecoline RE 104 thermostat.

Preparations: H_2TPP, $H_2T(4\text{-}Cl)PP$, $H_2T(4\text{-}CH_3)PP$, $H_2T(4\text{-}CH_3O)PP$ were prepared and purified by the usual methods[10].

UV-Vis measurements were carried out by a titration method at 5, 10, 15, 20 and 25 ± 1°C, in duplicated experiments. In a typical measurement, 2.5 mL solution of H_2TPP (2.5×10^{-6} M) in chloroform was titrated by 2,4-DCP (3 M). UV-Vis spectra were recorded over a range of 396-710 nm and about 10-15 wavelengths which show suitable variations of absorbance were selected. The formation constant K were calculated by the SQUAD program[11]. The other thermodynamic parameters for hydrogen-bonded complexes were obtained using the Van't-Hoff equation.

RESULTS AND DISCUSSION

By addition of phenol derivative to a solution of $H_2T(4\text{-}X)PP$, its colour changes to green. This change in colour is due to the hydrogen-bonded formations between phenol derivative and free base porphyrins. These interactions were studied by means of UV-Vis spectrophotometry.

Interaction of phenol derivatives with free base porphyrins leads to a fundamental change in the porphyrins electronic absorption spectra. The optical spectra of free base porphyrins slowly turn to new spectra during formation of hydrogen bonded complexes which differ from its original spectra (Fig. 1). For example, when a solution of $H_2T(4\text{-}CH_3O)PP$ in chloroform was interacted with 2,4-DCP, the original peaks of $H_2T(4\text{-}CH_3O)PP$ (λ; 420, 518, 555, 593 and 650 nm) were vanished and two new peaks at λ (455 and 688 nm) were appeared for adduct. A clear isosbestic point which seen at 428 nm along this interaction, Fig. 1, represents a reversible hydrogen-bonded formation in solution. Table-1 gives the original peaks of $H_2T(4\text{-}X)PPs$ and new peaks which produced by addition of phenol derivatives to a solution of porphyrin in chloroform.

The thermodynamic parameters are useful tools for studying these interactions and understanding the relative stability of corresponding hydrogen-bonded complexes. The formation constant K for complexes was determined at several temperatures by analyzing the concentration and the temperature dependence of UV-Vis absorption by a SQUAD program, (Table-2). Van't Hoff plots of formation constants (K) lead to other thermodynamic parameters, ΔH° and ΔS° (Table-3).
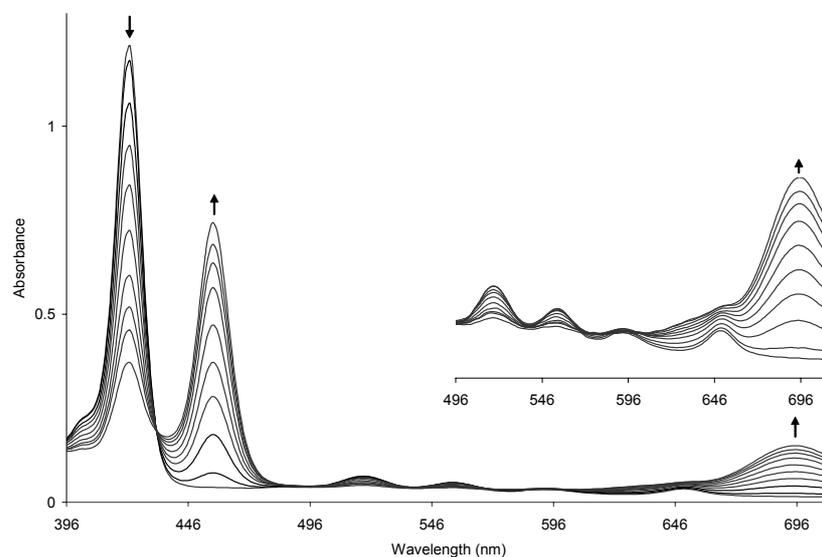
Fig. 1.   Titration spectra for interaction of 2,4-DCP with $H_2T(4\text{-}CH_3O)PP$ in chloroform. Bands appeared at 455 and 688 nm are related to adduct, isosbestic point at 428

TABLE-1

UV-VIS BANDS λ (CHCl$_3$/nm) OF $H_2T(4\text{-}X)PP$ AND THEIR HYDROGEN-BONDED COMPLEXES WITH PHENYL DERIVATIVES

H_2TPP	417	514	549	589	646
$(2,4\text{-}DCP)_2H_2TPP$	445	-	-	-	651
$H_2T(4\text{-}Cl)PP$	418	514	550	590	646
$(2,4\text{-}DCP)_2H_2T(4\text{-}Cl)PP$	448	-	-	-	658
$H_2T(4\text{-}CH_3)PP$	419	516	552	591	647
$(2,4\text{-}DCP)_2H_2T(4\text{-}CH_3)PP$	449	-	-	-	670
$(2,4,6\text{-}TCP)_2H_2T(4\text{-}CH_3)PP$	448	-	-	-	669
$H_2T(4\text{-}CH_3O)PP$	420	518	555	593	650
$(2,4\text{-}DCP)_2H_2T(4\text{-}CH_3O)PP$	445	-	-	-	688

The data in Table-1 show that the formation constant, K of the adducts undergo a regular increase from $H_2T(4\text{-}Cl)PP$, H_2TPP, $H_2T(4\text{-}CH_3)PP$, to $H_2T(4\text{-}CH_3O)PP$ for each phenol derivative. For example, at 20°C we have the following order of the formation constants (K):
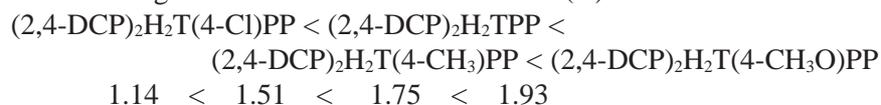
$(2,4\text{-}DCP)_2H_2T(4\text{-}Cl)PP < (2,4\text{-}DCP)_2H_2TPP <$
$(2,4\text{-}DCP)_2H_2T(4\text{-}CH_3)PP < (2,4\text{-}DCP)_2H_2T(4\text{-}CH_3O)PP$
1.14   <   1.51   <   1.75   <   1.93

TABLE-2
log K FOR HYDROGEN-BONDED COMPLEXES (DP)$_2$H$_2$T(4-X)PP
IN CHCl$_3$ AS SOLVENT

Free base porphyrin	Temperature (ºC)			
	10	15	20	25
(2,4-DCP)$_2$H$_2$T(4-Cl)PP	0.99 ± 0.02	1.08 ± 0.02	1.14 ± 0.02	1.20 ± 0.02
(2,4-DCP)$_2$H$_2$TPP	1.37 ± 0.01	1.43 ± 0.03	1.51 ± 0.03	1.60 ± 0.03
(2,4-DCP)$_2$H$_2$T(4-CH$_3$)PP	1.58 ± 0.03	1.69 ± 0.04	1.75 ± 0.04	1.86 ± 0.05
(2,4-DCP)$_2$H$_2$T(4-CH$_3$O)PP	1.72 ± 0.01	1.81 ± 0.03	1.93 ± 0.05	2.03 ± 0.02
(2,4,6-TCP)$_2$H$_2$T(4-CH$_3$)PP	0.67 ± 0.06	0.70 ± 0.05	0.76 ± 0.05	0.80 ± 0.05
(2,4,6-TCP)$_2$H$_2$T(4-CH$_3$O)PP	0.87 ± 0.02	0.92 ± 0.01	0.99 ± 0.02	1.02 ± 0.02

TABLE-3
THERMODYNAMIC PARAMETERS FOR HYDROGEN-BONDED
COMPLEXES (PD)$_2$H$_2$T(4-X)PP IN CHCl$_3$[a]

Complex	ΔHº	ΔSº	ΔGº
(2,4-DCP)$_2$H$_2$T(4-Cl)PP	19.9 ± 1.8	89.8 ± 6.4	-6.9 ± 0.1
(2,4-DCP)$_2$H$_2$TPP	25.7 ± 2.3	116.7 ± 7.9	-9.1 ± 0.1
(2,4-DCP)$_2$H$_2$T(4-CH$_3$)PP	30.1 ± 2.9	136.4 ± 9.9	10.5 ± 0.1
(2,4-DCP)$_2$H$_2$T(4-CH$_3$O)PP	35.2 ± 1.7	156.8 ± 5.8	11.5 ± 0.1
(2,4,6-TCP)$_2$H$_2$T(4-CH$_3$)PP	5.1 ± 1.4	65.9 ± 4.7	-4.5 ± 0.1
(2,4,6-TCP)$_2$H$_2$T(4-CH$_3$O)PP	17.5 ± 1.3	78.4 ± 4.6	-5.9 ± 0.1

[a]ΔHº (kJmol^{-1}), ΔSº (JK^{-1}mol^{-1}), ΔGº (kJmol^{-1}) at 25ºC

2,4,6-TCP shows no measurable interactions with H$_2$TPP and H$_2$T(4-Cl)PP under present experimental conditions. Also its interactions with H$_2$T (4-CH$_3$)PP and H$_2$T(4-CH$_3$O)PP are sizably weaker than corresponding interactions for 2,4-DCP. It might be raised from a high steric hindrance which coincident to interaction of 2,4,6-TCP with free base porphyrins.

Table-3 show the thermodynamic parameters ΔHº, ΔSº and ΔGº were obtained for interactions of phenol derivatives with free base porphyrins in chloroform.

The results are consisting with effect of basicity of free base porphyrin on these interactions. The free energy of hydrogen bonded complexes become more negative through the series H$_2$T(4-Cl)PP, H$_2$TPP, H$_2$T (4-CH$_3$)PP, to H$_2$T(4-CH$_3$O)PP which indicates formation of stronger hydrogen bonded complexes along this sequence.

On the other hand, interaction of a certain free base porphyrin with phenol derivatives depends on the type and the number of substituent on the phenol molecule. It is expected that hydrogen bonded formation for 2,4,6-TCP due to presence of three electron withdrawing Cl atoms become

more favourable than 2,4-DCP. Apparently the steric hindrance arises from addition of third Cl atom is more pronounced than its electron withdrawing property, so that its tendency to formation of hydrogen bonded complex with free base porphyrins is less than 2,4-DCP.

Adducts have positive values of ΔH^o and ΔS^o. A greater contribution of ΔS^o relative to ΔH^o leads to a negative value of ΔG^o in the following equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The positive value of ΔS^o may return to association between phenbol derivatives and free base porphyrin, which accompanied with releasing a large number of chloroform molecules that solvated the initial substances (Table-3). The results are dealing with endothermic aggregations between phenols and free base porphyrins in the selected range of temperatures.

The following sequence was obtained for interactions of $H_2T(4-X)PPs$ with phenol derivatives:

$$H_2T(4-CH_3O)PP > H_2T(4-CH_3)PP > H_2TPP > H_2T(4-Cl)PP$$

On the other hand 2,4-DCP show stronger hydrogen bonding with free base porphyrins than 2,4,6-TCP.

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