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Analysis of organophosphate–Zn metalloporphyrin interactions via UV–vis spectroscopy and molecular modeling

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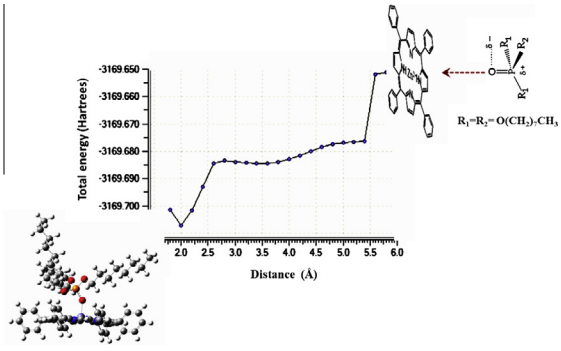
HIGHLIGHTS

- ZnTPP was spectrophotometrically titrated with a diverse suite of organophosphates (OP).
- Polarizability of OP substituents determines extent of ZnTPP λ_{Soret} shift.
- $A_{\lambda sor\text{-}b}$ for the OP bound ZnTPP varied with size and aromatic content of substituents.
- Ab-initio ZnTPP–OP energies reveal steric effects on binding.

GRAPHICAL ABSTRACT



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ABSTRACT

UV–vis absorption spectra of zinc tetraphenylporphine (ZnTPP) on interaction with six organophosphorus (OP) compounds in cyclohexane were compared using ab initio methods and the molecular and solvation ligand descriptors π^*, V_x, and σ. OPs with polarizable hydrocarbon substituents in the homologous series tri-ethyl, -pentyl, -octyl, and -phenyl phosphates and the toxicologically relevant methyl paraoxon (**1a–e**) each gave a red shift in the Soret band (λ_{sor}) of ZnTPP in the range of 8–10 nm. Sensitivity as $\Delta A_{sor\text{-}b}/\Delta ug$ OP for the spectral band of the ligand bound ZnTPP ($\lambda_{sor\text{-}b}$) decreased with increasing extent of alkyl and aromatic substitution. Calculated and combined energies for OP and ZnTPP examined as a function of distance (Å) between ligand and porphyrin center suggest increased steric crowding with increasing V_x, and aromatic content of the OP. Spectrally fitted $K_{1:1}$ and $\Delta A_{sor\text{-}b}/ug$ OP each vary exponentially with V_x/σ. Lack of a red shift in $\lambda_{sor\text{-}b}$ where ZnTPP was titrated with the toxic diethyl chlorophosphate (**1g**) is consistent with a model in which the magnitude of ΔE_{sor} is proportional to the donor capacity of the phosphoryl-O ligand.

Introduction

The development of sensing media for organophosphorus (OP) compounds is on going. Materials that have a recognition element, promote reversible OP binding and/or solubilization and elicit a strong signal on surface interaction are ultimately desired. In accordance with the first two criteria, substrates are frequently designed to mimic a known toxicological or metabolic process. For example, it is well known that toxic OPs bind and inhibit acetylcholinesterase (ACHe), the enzyme that facilitates neurotransmission and which is located in the neurosynaptic cleft [1]. There have been several efforts to utilize the natural enzyme [2,3] as well as substrates that mimic OP–ACHe interactions [4]. However, there

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are fundamental limitations including lack of reversibility and limited selectivity [5], and this has led researchers to make use of other substrates such as the Zn-hydrolases which are known to catalyze the hydrolysis of OPs in biological systems [6,7]. Synthetic versions of the Zn-based hydrolase active site as well as Zn^{2+} complexes have been used in the detection and/or catalytic breakdown of OPs [8–12]. A Zn^{2+} centered metalloporphyrin has also been recently explored as a sensing substrate for the nerve agent precursor dimethylmethyl phosphonate (DMMP) [13].

There is precedence for further exploring Zn^{2+} complexes, specifically Zn-metalloporphyrin as an OP detecting substrate. While the mechanism of OP–Zn interaction in the context of a porphyrin is different from that of the non-porphyrinic Zn-hydrolase, the unique spectroscopic properties of Zn-metalloporphyrins make them worthy of study. For example, UV/vis spectra of Zn^{2+}-porphine exhibit narrow Soret and Q bands that undergo distinct spectral shifts in response to axial ligand coordination [14,15]. The interactions of many small molecules, e.g. solvents and volatile organic chemicals (VOCs), with the tetracoordinate zinc tetraphenylporphine (ZnTPP, Table 1) have been studied fundamentally [15] and in a sensing context [16].

In this work, we explore a series of OPs of phosphate and chlorophosphate structure (Table 1a–e and 1g) as interacting ligands to ZnTPP. In particular, we examine via UV/vis spectroscopy and computational methods the varying optical response(s) of ZnTPP on binding individually with a homologous series of tri-O-alkyl and phenyl phosphates (**1a–d**) and two OPs of toxicological significance, the insecticide methyl paraoxon (**1e**) and the nerve gas surrogate diethyl chlorophosphate (DCP, **1g**). DCP is a toxic version of the alkyl phosphonate DMMP (**1e**) explored by Zhang and Coworkers [13]. Table 1 lists the specific OP structures used in this work along with DMMP [13] for comparison. Here we look specifically at OP–ZnTPP interactions via: (1) UV/vis spectrophotometric titration in a non-ligating solvent, (2) calculation of selected binding constants ($K_{1:1}$) from the UV/vis spectra, (3) ab initio computational modeling to understand the energetics of the binding process and to obtain computed binding energies for the individual OP–ZnTPP complexes, and (4) calculation of selected solvation parameters for the OP solutes which we use to interpret trends and relationships among the spectral and computational results. Note that many of our OPs (Table 1) are larger than the small solvents and VOCs (and even DMMP) whose interactions with ZnTPP have been previously studied [13]. Thus, we are able to examine trends in the effect of OP size, steric considerations and other selected solvation properties on the *sensitivity* of ZnTPP's UV/vis spectral response.

Experimental

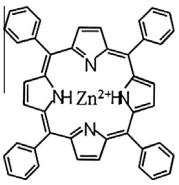
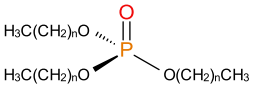
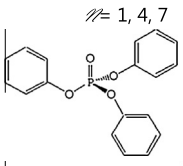
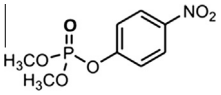
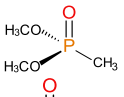
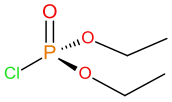
Chemicals and reagents

Zn(ll) meso-tetraphenylporphyrin (ZnTPP) was purchased from Frontier Scientific and used as received. Cyclohexane (99%), triethyl phosphate (99%), triphenylphosphate (98%) and diethylchlorophosphate (DCP > 97%) were obtained from Acros. Tripentyl and trioctyl phosphates were from TCI; di-methyl-4-nitrophenyl phosphate (methyl paraoxon) (98%) was purchased from Chem Service.

Solution preparation and spectrophotometric titration

Solutions of ZnTPP in the range of 0.25–0.88 μM were prepared in cyclohexane at concentrations yielding a Soret band with an

Table 1
ZnTPP structure; names, structures (**1a–g**) and calculated molecular and solvation parameters for OP compounds utilized and or discussed in this work.

	Compound name	Structure	π^{*}[a]	σ[b]	V_x[c]	R_2[d]
ZnTPP						
a	Triethyl phosphate		0.70	16.63	1.5343	0.26
b	Tripentyl phosphate		0.74	33.16	2.6615	0.25
c	Trioctyl phosphate		0.78	49.69	3.9296	0.23
d	Triphenyl phosphate		2.07	34.76	2.374	1.99
e	Methyl-4-nitro phenyl phosphate (methyl paraoxon)		1.71	21.60	1.6116	1.11
f	Dimethylmethyl-phosphonate (DMMP)[e]		0.53	10.43	0.9120	0.23
g	Diethylchloro-phosphate (DCP)		0.68	14.19	1.1753	0.25

[a] Unitless scaled solute dipolarity/polarizability (π^{*}).
[b] Molecular polarizability units of $(cm^{-24})^3$.
[c] Units of $cm^3\ mol^{-1}/100$.
[d] Solute excess molar refraction.
[e] Zhang et al. [13].