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Multi-Point Interaction of Phosphates with Protonated Pyridylporphyrin. Discrimination of Monoalkyl and Dialkyl Phosphates[1)]

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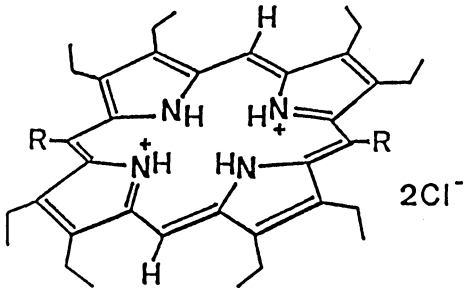
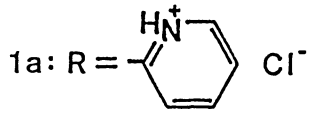
The rigid and unique polyammonium binding site of fully protonated 5,15-bis(2-pyridyl)octaethylporphyrin allows novel discrimination of monoalkyl phosphate vs. dialkylphosphate as well as oxy- and dicarboxylic acids vs. monocarboxylic acid; the former are readily bound with the protonated porphyrin via multi-point interaction, while the latter not.

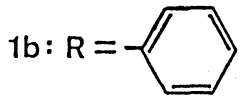
Discrimination of closely related structures based on multiple interactions is an important area of molecular recognition. A unique type of required multi-point binding sites of a high degree of rigidity are provided by porphyrin derivatives.[2-4)] The present work is concerned with multi-point fixation of phosphates.[5)] We report here that protonated pyridylporphyrin allows discrimination of monoalkyl and dialkyl phosphates.

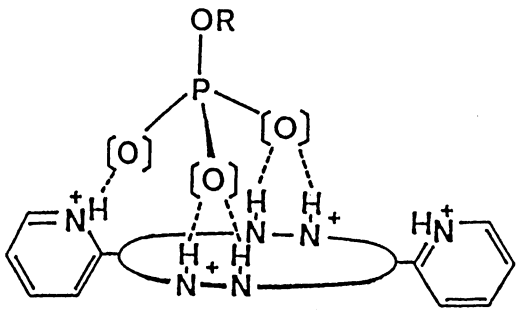
Treatment of a $CHCl_3$ solution of 5,15-bis(2-pyridyl)octaethylporphyrin [6)] with aqueous HCl gave tetraprotonated species **1a**; UV/VIS ($CHCl_3$) and ^1H NMR spectra (270 MHz, $CDCl_3$, 25 °C, TMS) of **1a** [7)] were characteristic of porphyrin diacids,[8)] thus confirming diprotonation of the porphyrin nitrogens. Similar treatment of the corresponding 5,15-diphenyl derivative as reference afforded diprotonated species **1b**.

Compound **1a** readily forms complex with monododecyl phosphate (**2**) in $CDCl_3$. The most convincing evidence for this came from ^{31}P NMR spectroscopy (162 MHz, 25 °C, 85% aqueous phosphoric acid as reference); the phosphorous signal for **2** (1×10^{-2} M) underwent an upfield shift of 4.18 ppm (from $\delta_P = 1.64$ to -2.54) upon addition of an equivalent amount of **1a** as a result of its strong ring-current effects (Fig. 1a).[9)] The ^1H NMR absorption for the OCH_2 moiety of **2** also exhibited an upfield shift of 0.97 ppm (from $\delta_H = 4.02$ to 3.05) as induced by an equivalent amount of **1a**. Addition of two equivalents of **1a** resulted in no further upfield shift. This result indicates that **1a** and **2** form a 1:1 complex. The ^1H NMR signals for **1a** were similarly affected by an equivalent amount of **2**; an upfield shift of 0.18 ppm for the $(NH)_4^{2+}$ moiety of the porphyrin skeleton (from δ_H = -0.62 to -0.80) and downfield shifts of 0.05-0.13 ppm for the pyridinium ring protons (from δ_H = 7.80, 8.15, 8.40, and 9.20 to 7.92, 8.28, 8.50, and 9.25, respectively). The UV/VIS spectrum of **1a**, on the other hand, showed no significant change in the presence of **2**. These results suggest that multi-point hydrogen-bonding interaction between N^+-H groups both in the $(NH)_4^{2+}$ inner cavity and the pyridinium moieties of **1a** and O=P-OH and P-OH groups of **2** as free acid [10)] is responsible for the complexation of **1a** and **2**, as schematically shown in structure **3** ([O] is =O or OH).[11)]

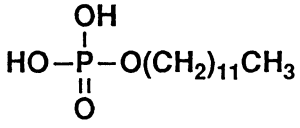








3: R = $(CH_2)_{11}CH_3$



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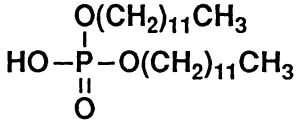

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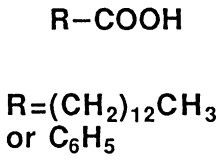

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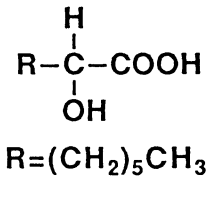

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Monododecyl phosphate (**2**) could also be bound with reference compound **1b** having no pyridinium moiety, but the affinity of **2** to **1b** was significantly lower than that to **1a** as judged by the extents of ^{31}P and ^{1}H NMR upfield shifts. Another interesting selectivity in view of multi-point interaction is between **2** having O=P-OH and P-OH groups and didodecyl phosphate (**4**) having only a O=P-OH group as guests. The ^{31}P NMR spectrum of **4** remained unaffected by the presence of an equivalent amount of **1a** (Fig. 1b), indicating that no complexation of **4** with **1a** was taking place. A loss of one hydrogen bonding site and an increase in steric bulkiness in going from **2** to **4** may be responsible for the failure of **4** to be bound with **1a**.

Selective binding via multi-point hydrogen bonding was also observed in the case of carboxylic acid systems. Monocarboxylic acids (**5**) having a O=C-OH group and 2-oxyacids (**6**) having O=C-OH and C-OH groups in close proximity may correspond respectively to **4** having a O=P-OH group and **2** having O=P-OH and P-OH groups. ^{1}H NMR spectroscopy showed that **6**, like **2**, is readily bound with **1a** in $CDCl_3$, while **5**, like **4**, is not.[12]

In summary, the rigid and unique polyammonium binding site of **1a** allows novel discrimination of *bifunctional* molecules and *monofunctional* molecules, i.e., monoalkyl phosphate **2** vs. dialkyl phosphate **4** as well as oxycarboxylic acid **6** vs. monocarboxylic acid **5**.

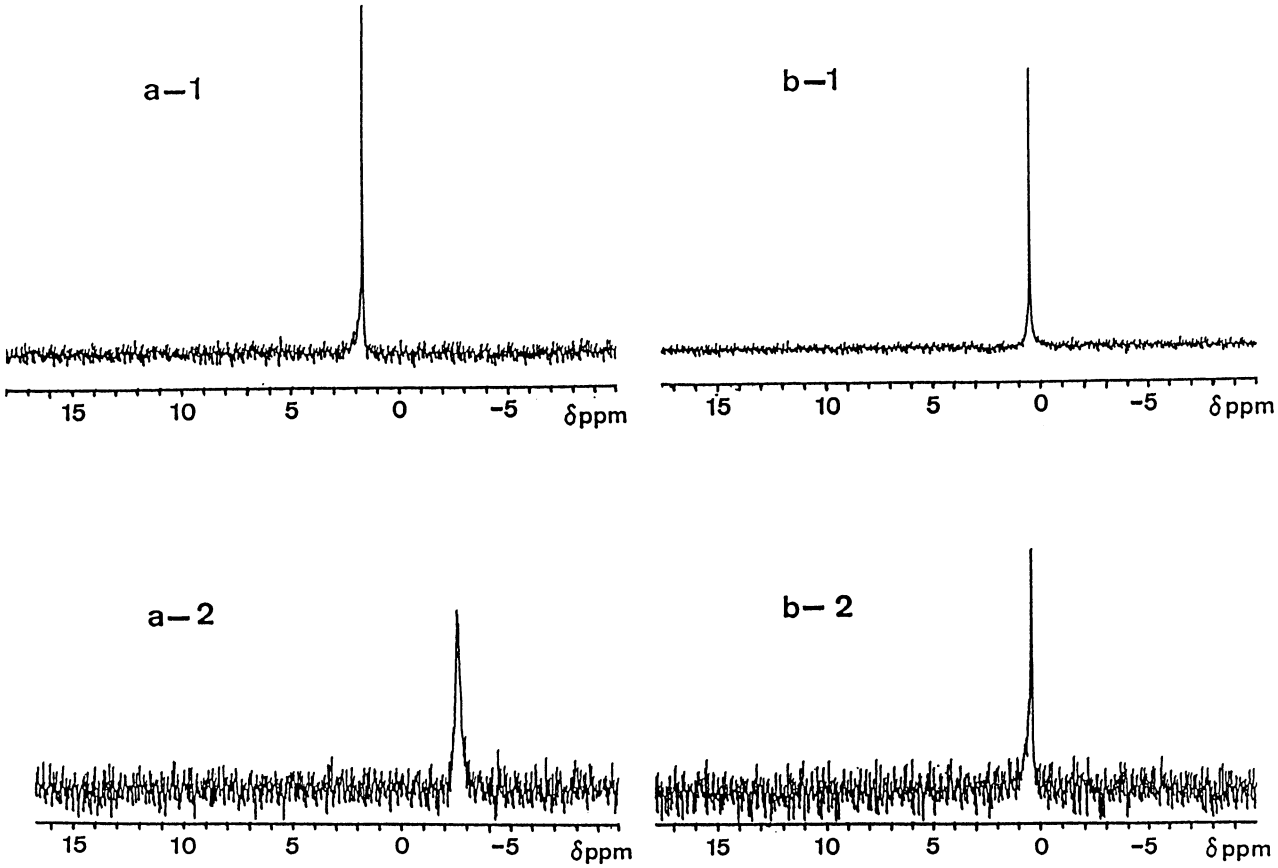

Fig. 1. ^{31}P NMR spectra of **2** (a) and **4** (b) (1 x 10^{-2} M) in the absence (a-1 and b-1) and presence (a-2 and b-2) of **1a** (1 x 10^{-2} M) in $CDCl_3$ at 25 °C with 85% aqueous phosphoric acid as an external reference.

Multi-point hydrogen bonding is plausibly responsible for the selectivity for **2** and **6**; the state of protonation in **1a** remains essentially unchanged during interaction, as revealed by UV/VIS and NMR spectroscopy. Further work is now under way to get deeper insight into the structures of complexes **1a**-**2** and **1a**-**6** and the origins of selectivity for these.

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7) λ_{max}[nm] = 441, 578, 624 and δ_H = -0.62 for four equivalent inner NH protons. The corresponding absorptions for octaethylporphyrin diacid dichloride are λ_{max}[nm] = 419, 554-559, 599 and δ_H = -2.07

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10) It is not likely that **2** is bound with **1a** as a counteranion with concomitant liberation of HCl [$(N^+$-H)(Cl^-) + P-OH] → [$(N^+$-H)$(P$-$O^-)$ + HCl], since phosphoric acid is weaker as acid than HCl.

11) The observed upfield shifts of the ^{31}P and ^{1}H NMR signals for bound **2** in structure **3** are reasonable in light of those for alkyl and amine ligands coordinated with Rh(III) porphyrins (Refs. 4 and 9).

12) The ^{1}H NMR signals of **6** (R = $(CH_2)_5CH_3$, 1 x 10^{-2} M) in $CDCl_3$ underwent chatacteristic upfield shifts (0.81 ppm for C<u>H</u>(OH) and 0.57 ppm for C<u>H$_2$</u>CH(OH)) in the presence of an equivalent amount of **1a**. In marked contrast, the ^{1}H NMR spectra of **5** (R = $(CH_2)_{12}CH_3$ or C_6H_5) as well as dodecanol having only a C-OH group were not affected by **1a** to any detectable extents under otherwise identical conditions.

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