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The Determination of the Protonation Constants of A New Macrocyclic Dinucleating Ligand, BDBPH

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Abstract: The protonation constants of a new dinucleating 24-membered hexaazadiphenol macrocyclic ligand, BDBPH， were determined by potentiometric measurement at 25.0°C and $\mu = 0.100\ \text{mol}\cdot\text{L}^{-1}$ (KCl). The species distributions of the deprotonated and protonated compounds in the pH range from 2 to 12 in aqueous solutions were also described.

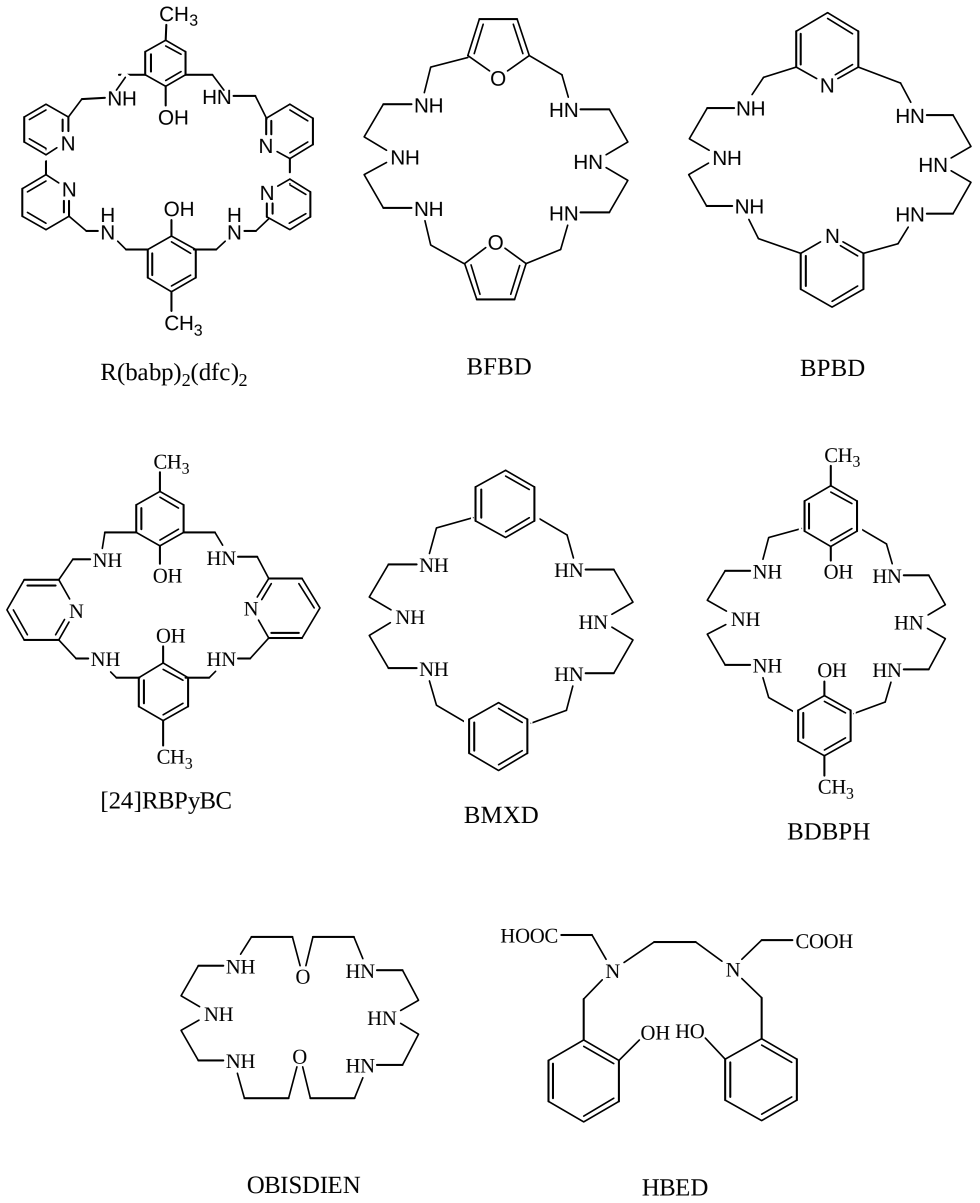
Keywords: Protonation constant, potentiometric measurement, macrocyclic ligand.

One of our current interests focuses on the design and synthesis of polyaza macrocyclic ligands, the determination of their protonation constants, and the stabilities of corresponding metal complexes. Two polyazadiphenol macrocycles, $R(babp)_2(dfc)_2$[1] and [24]RBPyBC[2], one octaazamacrocycle, BPBD[3,4], and several hexaaza macrocyclic ligands, BFBD[5], BMXD[6], and OBISDIEN[7], have been reported recently. We have also reported the synthesis of a new dinucleating 24-membered hexaazadiphenol macrocyclic ligand, 3, 6, 9,17,20,23-hexaaza-29, 30-dihydroxy-13, 27-dimethyl-tricyclo [23, 3, 1, $1^{11,15}$] triaconta -1(28),11,13,15(30),25,26-hexaene,BDBPH[8] (see **chart 1**). Here we present the protonation constants of BDBPH, and also discuss the species distribution in aqueous solution.

Potentiometric Equilibrium Measurements and Computation

Stock solution ($2.073\times10^{-3}\ \text{mol}\cdot\text{L}^{-1}$) of BDBPH for potentiometric work was prepared with double-distilled water, and the ionic strength of the solution was maintained at $0.100\ \text{mol}\cdot\text{L}^{-1}$ by the addition of KCl solution. A carbonate-free $0.1013\ \text{mol}\cdot\text{L}^{-1}$ KOH solution was prepared from a Dilut-it ampoule and standardized with potassium acid phthalate. Reagent grade potassium chloride was used as supporting electrolyte for all the experiments. The potentiometric equilibrium measurements were carried out with a Corning Model 350 digital pH meter. The potentiometric cell was fitted with glass and calomel electrodes in a water-jacketed reaction vessel maintained at 25.0 ± 0.1^{0}C, and was calibrated with standard aqueous HCl and KOH solution to read $-\log [H^+]$ directly. The measurements were carried out under an atmosphere of Argon gas. The equilibrium constants were determined with the program BEST[9], and the species distribution diagrams were obtained with the program SPE and SPEPLOT[9].

Chart 1 Structures of new macrocyclic dinucleating ligands



R(babp)$_2$(dfc)$_2$ BFBD BPBD

[24]RBPyBC BMXD BDBPH

OBISDIEN HBED

Protonation Constants of BDBPH and Discussion

The highest Log K^H of BDBPH could not be determined accurately by titration because of the weak acidity of one phenolic group. The Log K^H value had to be measured by the UV/Vis spectrophotometric method previously described[10]. The potentiometric equilibrium curve of BDBPH is found to have two inflections at $a = 3$ and $a = 4$ (where a = moles of base added per mole of the ligand). From $a = 0$ to $a = 3$ and from $a = 4$ to $a = 8$, there are two extensive buffer regions. The first buffer region corresponds to the completion of the neutralization of the three most acidic substituted ammonium ions. Between the first and the second inflections, one other substituted ammonium ion is neutralized. The buffer region at higher pH values corresponds to the dissociation of three substituted ammonium groups and one phenolic group in sequential overlapping steps. At pH<2, the ligand exists in the fully protonated form, H_8L^{6+}. As pH is increased, the ligand loses its protons from amino nitrogens to become H_7L^{5+}, H_6L^{4+}, H_5L^{3+}, H_4L^{2+} and H_3L^{+} species respectively. The neutral ligand H_2L reaches its maximum concentration (59.8%) at pH 10.6. When the pH is above 9.3, one of the two phenolic hydroxies begin to be deprotonated to form HL^-, which reaches its maximum concentration (56.8%) at pH 11.5. Under more alkaline conditions, the two phenol groups finally deprotonate to the free ligand dianion L^{2-} (pH > 12). The eight Log K^H values are listed in **Table1**.

To our knowledge, there is only one example of protonation constant studies of polyazadiphenol macrocyclic ligand, [24]RBPyBC[2], which also has the 24-membered ring. For comparison, the successive constants of [24]RBPyBC, BPBD, BFBD, BMXD, OBISDIEN, and an acyclic ligand containing a combination of similar functional groups, HBED[10], are also included in **Table 1**.

Table 1 Successive protonation constants of BDBPH, [24]RBPyBC, HBED, BPBD, BFBD, BMXD, and OBISDIEN (μ=0.100 mol·L^{-1}KCl, 25.0°C)

	n =	1	2	3	4	5	6	7	8
$^a \mathrm{Log}K_n^H$	BDBPH^b	11.9^c	11.04	10.03	9.47	7.14	4.49	3.57	3.30
	[24]RBPyBC	12.1^c	11.3^c	9.18	8.92	6.65	4.52		
	HBED	12.6^c	11.0^c	8.44	4.72	2.53	1.70		
	BPBD	9.25	8.49	7.55	6.98	4.11	3.26		
	BFBD	9.44	8.68	7.63	6.46	3.84	3.18		
	BMXD	9.51	8.77	7.97	7.09	3.79	3.27		
	OBISDIEN	9.62	8.89	8.29	7.62	3.82	3.30		

a: $K_n^H = [H_nL^{(n-2)+}] / [H_{n-1}L^{(n-3)+}][H]$ for BDBPH, [24]RBPyBC, and HBED

$K_n^H = [H_nL^{n+}] / [H_{n-1}L^{(n-1)+}][H]$ for BPBD, BFBD, BMXD, and BISDIEN

b: Estimated error = ±0.02~0.04

c: Determined by the spectrophotometric method

HBED is a well-known bis (o-hydroxybenzyl) ligand which has a very high stability constant with Fe (III) and other metal ions with high charges. Because there are two γ-amino groups adjacent to each phenolate in BDBPH and in [24]RBPyBC exhibiting electron-withdrawing effects, instead of only one γ-amino group in HBED, it is reasonable that the first protonation constants of BDBPH (Log K_1^H = 11.9) and

[24]RBPyBC ($\text{Log}\,K_1^H$ = 12.1) are 0.7 Log unit and 0.5 Log unit lower than that of HBED ($\text{Log}\,K_1^H$ = 12.6), respectively. Besides, the two phenol groups in BDBPH and [24]RBPyBC are somewhat more separated than those of HBED, the differences between the first two protonation constants of BDBPH($\text{Log}\,K_1^H - \text{Log}\,K_2^H = 0.9$) and between those of [24]RBPyBC ($\text{Log}\,K_1^H - \text{Log}\,K_2^H = 0.8$) are smaller than those of HBED ($\text{Log}\,K_1^H - \text{Log}\,K_2^H = 1.6$). The first two protonation constants between BDBPH and [24]RBPyBC are fairly close because of the similar environments of the phenolates in the two ligands. The considerable differences between the following four protonation constants of the two macrocyclic ligands, can be ascribed to the lower basicities of the amino nitrogens in [24]RBPyBC as compared to BDBPH, due mainly to the electron-withdrawing effects of pyridine groups.

It is noted that there are two larger differences between the fourth and the fifth stepwise protonation constants (2.33 log unit) and between the fifth and the sixth stepwise protonation constants (2.65 log unit) for BDBPH. This results can be explained as the minimization of electrostatic repulsion between positive charges in protonated species of the polyaza macrocycle. The third and the fourth protons occupy the positions of diethylenetriamine groups separated by two phenolic ring bridges, respectively, that is, the ligand with positive amino groups adopts a conformation in which the positive groups are as far apart as possible in order to achieve minimum electrostatic repulsion. But in the fifth and the sixth protonated species, the last hydrogen ion must be situated at one diethylenetriamine group on which there has been another positive charge, the electrostatic repulsion between the two positive charges are obviously stronger, which leads to much lower protonation constant.

The overall logarithm protonation constants, $\sum \text{Log}\,K_n^H$, of BPBD, BFBD, BMXD, and OBISDIEN, are 39.64, 39.23, 40.40, and 41.54, respectively. The overall logarithm of the last six protonation constants of BDBPH, $\sum \text{Log}\,K_n^H$ (n=3~8), is only 38.00, less than those of above ligands. This indicates that the overall basicities of these five hexaazamacrocycles containing diethylenetriamine moieties follow the order of OBISDIEN > BMXD > BPBD > BFBD > BDBPH, and reflects the fact that the magnitude of the electron-withdrawing effect increases in the order of aliphatic ester < phenyl carbon < pyridine nitrogen < furan oxygen < phenolic carbon.

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References

1. Z. Wang, J. Reibenspies, A. E. Martell, *Inorg. Chem.*, **1997**, *36*, 629.
2. Z. Wang, *Ph. D. Dissertation*, Texas A&M University, College Station, TX, August **1997**.
3. D. Chen, A. E. Martell, *Tetrahedron*, **1991**, *47*, 6895.
4. Q. Lu, R. Carroll, J. Reibenspies,A. E Martell, *J. Mol. Struc.*, **1998**, *469*, 121.
5. Q. Lu, R. J. Motekaitis, J. Reibenspies, A. E. Martell, *Inorg. Chem.*, **1995**, *34*, 4958.
6. D. A. Nation, J. Reibenspies, A. E. Martell, *Inorg. Chem.*, **1996,** *35*, 4597.
7. R. J. Motekaitis, A. E. Martell, *Inorg. Chem.***,** **1992,** *31***,** 5534.
8. G. Q. Shangguan, A. E. Martell, Z. R. Zhang, *Chinese Chemical Letters*, **2000**,*11*(7), 573.
9. A. E. Martell, R. J. Motekaitis, *The Determination and Use of Stability Constants*, 2nd Ed., VCH Publishers Inc., New York, **1992**.
10. R. J. Motekaitis, A. E. Martell, M. J. Welch, *Inorg. Chem.*, 1990, *29*, 1463.

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