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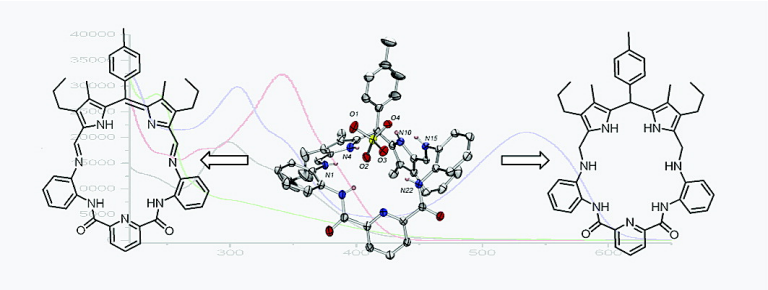

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Fine Tuning the Anion Binding Properties of 2,6-Diamidopyridine Dipyrromethane Hybrid Macrocycles

Jonathan L. Sessler,*,† Evgeny Katayev,†,‡ G. Dan Pantos,† Pavel Scherbakov,‡ Marina D. Reshetova,‡ Victor N. Khrustalev,§ Vincent M. Lynch,† and Yuri A. Ustynyuk*,‡

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Abstract: The synthesis, characterization, and anion-binding properties of a series of 2,6-diamidopyridine dipyrromethane hybrid macrocycles is presented. As part of this work, a new method for effecting the oxidation of dipyrromethane-based macrocycles in organic solvents has been developed. The macrocyclic frameworks presented here stand out because of their ease of synthesis and tunable anion-binding properties. Evidence for anion binding was obtained from UV−vis spectroscopic titrations carried out in acetonitrile. The results clearly indicate that by changing the flexibility, cavity size, and directionality of anion-binding moieties in the macrocyclic framework the anion selectivity may be changed dramatically. These results are in accord with density functional theory molecular modeling calculations performed on one member of the series.

Introduction

Anion recognition has emerged as an important theme in modern supramolecular chemistry.[1] The synthesis of artificial receptors with high affinity and selectivity for specific anions is an ongoing goal of researchers in the field. In addition to their academic interest, reflecting in part the inherent challenge of designing systems that can recognize anions of various shapes and charges with controlled specificity, there are a number of potential applications that are stimulating interest in this area.[2] These run the gamut from anion sensing to drug development and radioactive and nonradioactive waste remediation. Over the past 10 years many groups, including our own, have devoted considerable effort to the synthesis of novel anion receptors.[3] The focus of our attention has largely been on pyrrole-based systems whose properties can be potentially fine tuned. In this context, we recently reported the pyridine-2,6-dicarboxamide-dipyrromethane receptor **1** (Figure 1),[4] a system that shows promise as a sulfate anion receptor. In an effort to build on these findings, we have sought to prepare other pyridine-2,6-dicarboxamide dipyrromethane macrocyles and wish to report here the synthesis of compounds **2**−**4**. These systems display anion-binding properties very different from those of **1**.

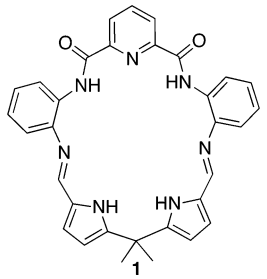

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Figure 1. Pyridine 2,6-dicarboxamide dipyrromethane receptor **1**[4].

Macrocycle **1**[4] displays high selectivity for tetrahedral anions over spherical, linear, or trigonal planar anions. It is thus a good candidate for sulfate extraction from nitrate-rich mixtures.[4]

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(1) (a) Bianchi, A.; Bowman-James K.; Garcia-España, E. *Supramolecular Chemistry of Anions*; Wiley−VCH: New York, 1997.

(2) (a) *Fundamentals and Applications of Anion Separations*; Moyer, B. A., Singh, R. P., Eds.; Kluwer Academic/Plenum Publishers: New York, 2004. (b) Camiolo, S.; Gale, P. A.; Sessler, J. L. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Steed, J. W., Eds.; Marcel Dekker: New York, 2004.

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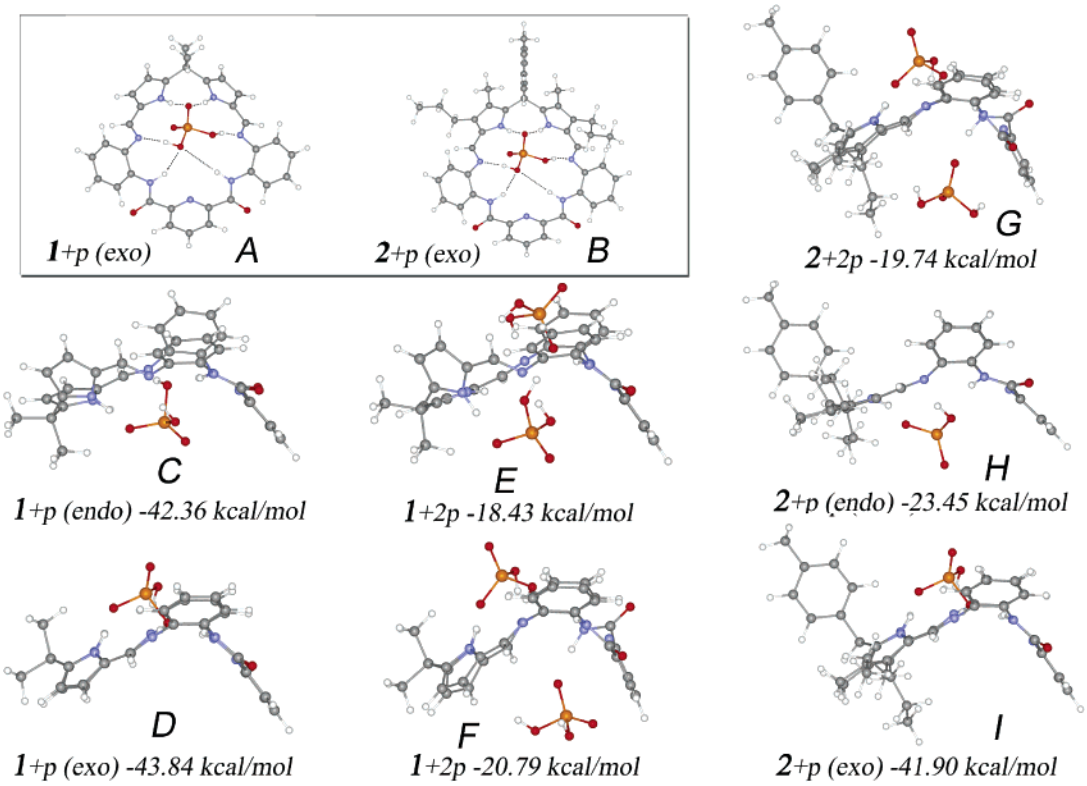

Figure 2. Optimized geometries and corresponding binding energies for the mono (+p) and bis (+2p) dihydrogenphosphate complexes of ligand **1** and **2**. The binding energies were calculated using $\Delta E = E°(\text{complex}) - E°(\text{host}) - nE°(\text{guest})$, where n = number of anions coordinated by the receptor.

However, it suffers from the disadvantage that it binds dihydrogenphosphate more strongly than hydrogen sulfate, albeit with a 2:1 binding stoichiometry. To design a better hydrogen sulfate receptor we performed density functional theory (DFT) calculations on a series of related macrocycles (see Results and Discussion section). Previous experience in the expanded prophyrin field coupled with the molecular modeling results led us to choose macrocycle **2** as our synthetic target. In this macrocycle, the pyridine-2,6-dicarboxamide backbone is retained, while the dipyrromethane subunit is modified. Such a modification, it was thought, would allow the basic structure of the system, and hence its anion-binding properties, to be further tuned via reduction and oxidation. As described below, this approach, which yields structures **3** and **4**, respectively, does give rise to receptor systems with substantially altered molecular recognition characteristics.

Results and Discussion

Anion−Receptor Complex Modeling Studies. The strong affinity for tetrahedral anions, such as sulfate and phosphate, displayed by **1** is most readily explained in terms of a geometrical complementarity between the hydrogen-bonding sites of the receptor and the bound tetrahedral anions. Such a conclusion, while not rigorously proved, is consistent with the prior findings of Bowman-James et al. made in the context of studying related macrocyclic frameworks.[5] However, such a generalized explanation fails to account for the relatively high affinity and 2:1 binding stoichiometry seen in the case of dihydrogenphosphate. The existence of two binding sites for this particular anion could reflect the inherent flexibility of **1**, especially within the dipyrromethane subunit, that, in turn, might allow NH hydrogen bond donors to orient is such a way that multiple, disparate NH−anion interactions are possible. To the extent such a rationalization is true, macrocycle **2** should display a greater selectivity for hydrogen sulfate relative to dihydrogenphosphate. This is because the conformation of **2** should be "frozen" as the result of substituting the β-positions of the pyrrole unit and "inserting" a tolyl group into the "meso-like" position of the dipyrromethane subunit.

To provide support for the above suggestions, we performed molecular modeling of macrocycles **1** and **2** and their respective dihydrogenphosphate complexes. Modeling studies were performed using DFT calculations in the gas phase. Optimized structures of the free ligands **1** and **2** appeared to be unsymmetrical. Ligand **2** can exist in two different conformations, where the tolyl and pyridine fragments are either in trans or cis positions relative to the *o*-phenylene rings. The modeling indicates the trans conformation has the lower energy. Therefore, all subsequent modeling studies were carried out starting with **2** in this conformation.

Optimization of the 1:1 dihydrogenphosphate complexes formed from receptors **1** and **2** revealed in both cases the existence of two binding sites for each ligand, an "endo" site (under the macrocycle) and an "exo" site (above the macrocycle), as shown in Figure 2. While the binding geometries are similar in both cases, the difference in energies between the

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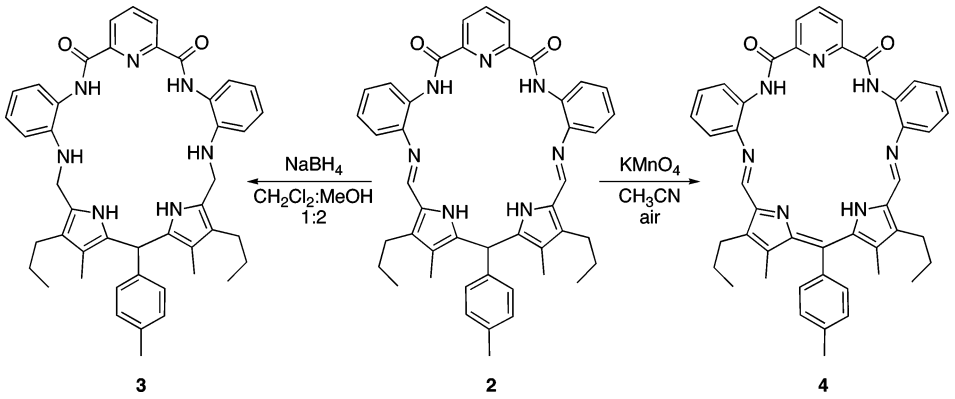
Scheme 1. Reduction and Oxidation of Macrocycle **2**



exo and endo coordination modes of **1** and **2** are 1.48 and 18.45 kcal/mol, respectively, in favor of the exo site (Figure 2). Interestingly, the modeling indicates that for both receptors only three oxygen atoms of the dihydrogenphosphate anion are involved in hydrogen-bonding interactions, (A and B in Figure 2, inset), while the fourth one is directed away from the binding sites. A similar arrangement is observed in the solid state of **2**·H_2SO_4, as inferred from the single-crystal X-ray diffraction analysis (vide infra).

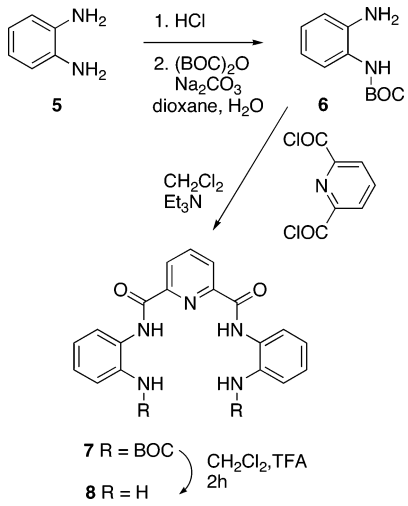
The structures **1**+p (C and D, Figure 2) and **2**+p(exo) (I) are characterized by strong hydrogen-bonding interactions between one of the OH groups of dihydrogenphosphate and the two amide NHs and an imine fragment. In the structure **2**+p-(endo) (H), a different binding mode is observed, where the two pyrrole fragments lie in the same plane and are coordinated to the bound dihydrogenphosphate anion, albeit weakly as the result of steric involving the methyl and tolyl substituents.

Optimization of the complexes containing two bound anions revealed two reasonable binding modes in the case of compound **1** but only one likely mode in the case of compound **2**. Of the 1:2 binding modes predicted for **1** and dihydrogenphosphate, structure F is the more stable, being 2.36 kcal/mol lower in energy than structure E. This prediction is not surprising since structure F incorporates the same binding mode for the "first" bound anion as does the most stable (predicted) 1:1 complex. The second bound dihydrogenphosphate anion in the 1:2 complex is calculated as being bound to one of the amide NH protons. The predicted structure of **2** (G) with two dihydrogenphosphate anions follows the same pattern.

The above results lead us to several key predictions. First, they underscore the fact that the dipyrromethane fragment in **1** is very flexible. In particular, the pyrrole rings can rotate along the C−C bond between the pyrrole ring and the *meso* carbon, with the net result that two coordination sites, exo and endo, are produced that differ little in energy both before and after $H_2PO_4^-$ complex formation. A second related prediction is that macrocycle **2**, being less flexible, gives rise to an exo coordination site that is lower in energy than the corresponding endo alternative, at least when bound to dihydrogenphosphate. Therefore, a 1:2 binding mode with dihydrogenphosphate is unlikely to be observed in the case of **2**. A third prediction arising from these calculations is that, because of the same steric considerations, receptor **2** will bind the first (and presumably only) equivalent of dihydrogenphosphate less well than **1**.

Synthesis. Precursor **8** is one of the key intermediates required for the synthesis of macrocycles **1**−**4**. In our initial work,[4] this species was prepared according to a literature procedure.[6] This method proved to be tedious and slightly inefficient (1 week reaction time; 23% overall yield; 2 steps from commercially available starting materials). We have now discovered what we believe is a better procedure. It is summarized in Scheme 2. Briefly, commercial *o*-phenylenediamine **5** was converted to the corresponding mono-BOC-protected derivative **6** by dissolving in a dioxane−water mixture containing 2 equiv of HCl, followed by the addition of $(BOC)_2O$ and Na_2CO_3. The mono-BOC-protected *o*-phenylenediamine **6** was then reacted with pyridine-2,6-dicarbonyl dichloride to yield intermediate **7**. After deprotection with trifluoroacetic acid in dichloromethane, intermediate **8** was obtained in high purity. By use of this procedure, we were able to synthesize compound **7** in three steps from commercially available precursors, in 1 day, in 80% overall yield.

Scheme 2. Improved Synthesis of Precursor **8**



The pyrrolic precursor **9** for the synthesis of macrocycles **2**−**4** was synthesized using standard conditions.[4] Specifically, ethyl 4-methyl-3-*n*-propylpyrrole-2-carboxylate was reacted with 4-methylbenzaldehyde in dichloromethane in the presence of methanesulfonic acid as a catalyst. The corresponding dipyrromethane derivative was subject to decarboxylation under basic conditions and subsequently formulated using triethyl orthoformate in trifluoroacetic acid. This gave **9** in 90% overall yield. The H_2SO_4 salt of macrocycle **2** was then synthesized by heating a methanolic solution of **8** and **9** at reflux for **15** min in the

(6) Picard, C.; Arnaud, N.; Tisnès, P. *Synthesis* **2001**, 1471−1478.

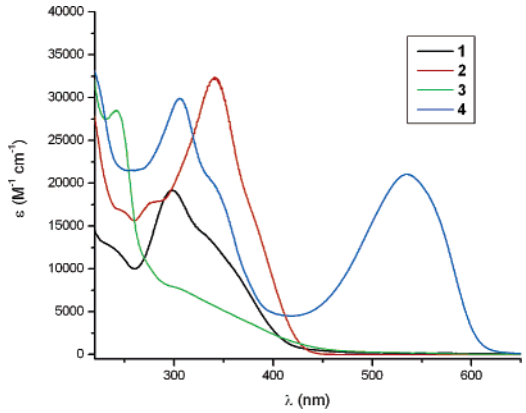


Figure 3. UV−vis spectra of macrocycles **1**−**4** in CH_3CN. **1**, λ_{max} [nm] (ϵ in M^{-1} cm^{-1}) 300 (19 000); **2**, λ_{max} [nm] (ϵ in M^{-1} cm^{-1}) 340 (32 000); **3**, λ_{max} [nm] (ϵ in M^{-1} cm^{-1}) 244 (28 000); **4**, λ_{max} [nm] (ϵ in M^{-1} cm^{-1}) 306 (30 000), 535 (21 000).

presence of 2.2 equiv of H_2SO_4. Compound **2** was obtained as the "free base" by quenching the reaction mixture with an excess of triethylamine. The overall yield for the last two, condensation and deprotection, steps was 90%.

For the synthesis of macrocycles **3** and **4**, the free base form of **2** was used as the starting material (Scheme 1). While the synthesis of **3** proved to be straightforward via reduction with $NaBH_4$ in a CH_2Cl_2−MeOH mixture, the oxidation of **2** to form **4** proved challenging. Initial attempts were made using the standard organic oxidizing agents, 2,3-dichloro-5,6-diocyanoquinone (DDQ) and chloranil. Although a wide range of reaction conditions were tested, neither DDQ nor chloranil yielded the desired macrocycle **4**. Rather, only starting material or decomposition products were obtained. Ferrocenium hexafluorophosphate, an oxidant that was used successfully in the synthesis of metal-free texaphyrin,[7] showed promise, as inferred from mass spectrometric analysis. However, it too failed to yield isolable quantities of **4** once the crude reaction mixtures were subject to workup and attempted purification. On the other hand, the use of manganese-based oxidants in acetonitrile allowed this transformation to be carried out successfully. For instance, in initial studies it was found that treatment of **2** with MnO_2 in CH_3CN at room temperature for 12 h yielded the desired product (**4**) in 35% yield. By use of similar conditions, but switching to a stronger oxidant, $KMnO_4$, improves the yield to 75%.

Compounds **2**−**4** were characterized using standard spectroscopic techniques (cf. Supporting Information). Here, the UV−vis spectral features proved especially diagnostic. Whereas macrocyles **1** and **2** give rise to very similar absorption profiles, with λ_{max} at 300 and 340 nm (Figure 3), the reduced macrocycle **3** displays a λ_{max} at 244 nm, while compound **4** displays two absorptions at 306 and 535 nm, respectively.

Proof for the proposed structures of macrocycles **2** and **4** came from single X-ray diffraction analyses of their diprotonated and neutral forms, respectively. X-ray diffraction analysis (Figure 4) revealed that **2**·H_2SO_4 adopts an up−down picket fence (Z-shape) structure, with the pyridine moiety and the 4-methylphenyl group acting as the "pickets". The two imine nitrogens, N1 and N15, are protonated and participate in hydrogen-bond interactions with the bound (formal) SO_4^- anion. Two of the

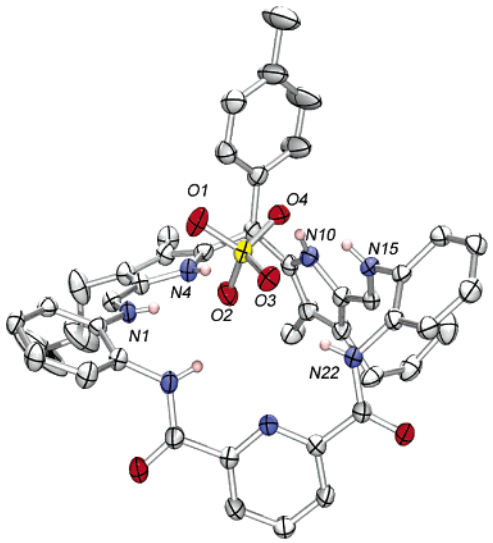


Figure 4. ORTEP−POVray rendered view of **2**·H_2SO_4. Solvent molecules and most hydrogen atoms have been removed for clarity. Thermal ellipsoids are scaled to the 50% probability level.

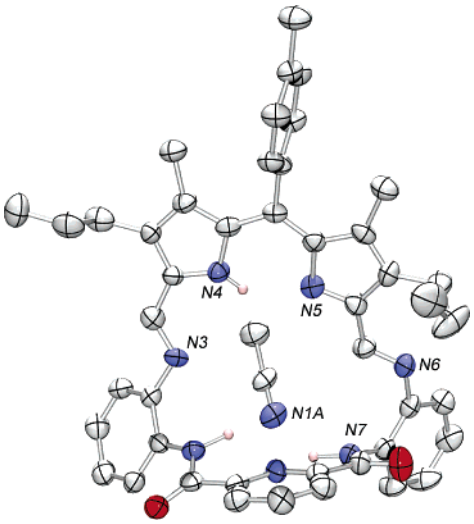


Figure 5. ORTEP−POVray rendered view of **4**. A molecule of CH_3CN is hydrogen bonded to one of the amide NH (N7). Most hydrogen atoms have been removed for clarity. Thermal ellipsoids are scaled to the 50% probability level.

oxygen atoms of SO_4^{2-} are hydrogen bonded in an unsymmetrical bifocal manner to a pyrrole NH and a protonated imine NH as follows: N1−O2 (2.709 Å, 178.0°), N4−O2 (2.789 Å, 155.84°), N10−O4 (2.753 Å, 150.28°), and N15−O4 (2.725 Å, 160.71°). The complex is stabilized by an aditional hydrogen bond between the amide NH proton and the SO_4^{2-} anion, N22−O3 (2.889 Å, 145.94°). An interesting observation is that the fourth oxygen atom of the sulfate anion is not involved in hydrogen-bonding interactions with atoms from the macrocycle but rather with a water molecule.

In the case of **4**, X-ray diffraction analysis (Figure 5) revealed an L-shaped structure in which the pyridine moiety is orthogonal to the plane formed by N3, N4, N5, and N6. The 4-methylphenyl group is also orthogonal both to the N3, N4, N5, and N6 planes and the pyridine ring. Interestingly, the two −CH═N− moieties adopt an endo−exo arrangement with respect to the inner macrocyclic core. There are two hydrogen bonds present in the molecule. One is between a pyrrole NH proton and the pyrrole

(7) Hannah, S.; Lynch, V. M.; Gerasimchuk, N.; Magda, D.; Sessler, J. L. *Org. Lett.* **2001**, *3*, 3911−3914.

Table 1. Affinity Constants (M^{-1}) for the Binding of Anions by Receptors **1**−**4** as Determined from UV−Vis Spectroscopic Titrations Carried out in CH_3CN at 23 °C[a]

receptor anion	**1**[b]	**2**	**3**	**4**
Br^-	*c*	*c*	*c*	2 760 ± 380
NO_3^-	*c*	*c*	*c*	*c*
Cl^-	2 000 ± 20	*c*	116 000 ± 11 000	*c*
CH_3COO^-	38 000 ± 3 000	12 600 ± 450	67 000 ± 9 900	*c*
HSO_4^-	64 000 ± 2 600	108 000 ± 17 000	47 00 ± 960	*c*
$H_2PO_4^-$	34 2000; 26 000[d]	29 000 ± 1 900	15 500 ± 1 750	*c*

[a] The anions studied were in the form of their tetrabutylammonium salts. The R^2 values for the curves fits used to determine the affinity constants range between 0.979 and 0.997. [b] Affinity constants reported in ref 4. [c] No apparent binding as reflected in the lack of changes observed in the UV−vis spectral titrations upon anion addition. [d] Stepwise, 2:1 (anion: receptor) binding observed; the values refer to those for the first and second binding events, respectively.

imine-like nitrogen, N4−N5 (2.709 Å, 138.67°), while the other is between an amide NH proton and a solvent (CH_3CN) molecule, N7−N1A (3.083 Å, 134.38°).

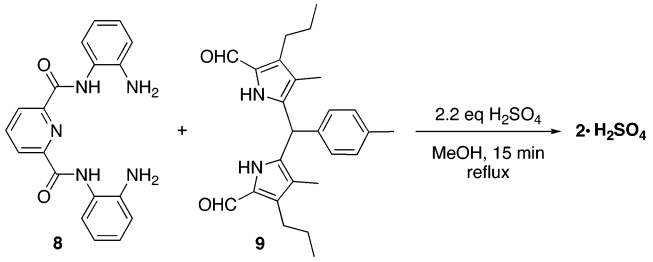
Anion-Binding Studies. Anion-binding studies were performed using UV−vis spectroscopic titrations. To maintain consistency with previously reported results, the measurements[3] were carried out in CH_3CN using the tetrabutylammonium salts of the anions being studied. Binding stoichiometries were determined using the Job plot method. Table 1 summarizes our findings.

An inspection of Table 1 reveals that the nature of the macrocycle and its geometry play crucial roles in modulating the observed anion affinities. Receptors **1** and **2** display selectivity for tetrahedral anions. However, the dihydrogen phosphate−hydrogen sulfate selectivity is reversed. This fact can be explained in terms of the different structures involved. Whereas macrocycle **1** possesses a larger cavity and, presumably, a more flexible geometry, due to the presence of the gem-dimethyl moiety, in receptor **2** the presence of the tolyl group in the *meso* position, acts as a "pseudo lid" for the macrocycle cavity. This group is also expected to freeze the conformation of the macrocycle as the result of steric interactions involving the methyl groups in the 4,4′ positions of the dipyrromethane subunit. Receptor **1** is also found to bind dihydrogenphosphate in a 2:1 anion:host mode,[4] while **2** binds this same anion with a 1:1 binding stoichiometry, as judged by Job plot studies (cf. Supporting Information). Such a change in stoichiometry is predicted based on these same geometric considerations and is supported by the DFT calculations (vide supra). The same reasoning, higher rigidity combined with higher steric demand, also provides a rationale for why **2** displays greater selectivity for hydrogensulfate, as compared to **1**, under identical conditions of study.[8]

Macrocycle **3** displays a relatively strong interaction with chloride anion and weaker interactions with the rest of the test anions. This selectivity reflects, we believe, the "hydrogen-rich" nature of this receptor, which makes its inner cavity better suited for the binding of smaller, spherical anions. System **3**, linked via a series of single C−C and C−N bonds, is also rather flexible. Thus, in contrast to its congeners, receptor **3** is not expected to provide as good control over the directionality of its hydrogen-bond donor moieties. Such features are expected to make it more suitable for the coordination of spherical anions.

(8) Another factor that could affect the anion binding selectivity of macrocycles **1** and **2** are the minor electronic effects resulting from the changes in the β-pyrrolic substitution patterns. However, on the basis of DFT calculations, we conclude that it is changes in the rigidity of the macrocycle that are mainly responsible for the observed differences in anion selectivity.

Scheme 3. Synthesis of Macrocycle **2** (H_2SO_4 Salt)



Macrocycle **4** is the most rigid of the anion receptors considered in this study. As observed from the single-crystal X-ray analysis (vide supra) the dipyrromethene unit is flat, a fact that is consistent with the presence of an extended conjugation pathway and a strong absorption band (at λ_{max} = 535 nm) in its UV−vis spectrum. On the other hand, as the result of oxidation, receptor **4** has fewer hydrogen bond donor atoms than **2** or **3**. Not surprisingly, therefore, it is a weaker anion-binding agent. In fact, receptor **4** binds only bromide in acetonitrile, and weakly at that. It displays no interaction with the other anions studied, as judged from the UV−vis titrations.

Conclusions

The pyridine 2,6-dicarboxamide dipyrromethane macrocyles **1**−**4** represent a new class of anion receptors with tunable properties. As the K_a values in Table 1 confirm, modifications in the basic structure of the macrocyclic can have a dramatic effect on the anion binding affinities and selectivities. The straightforward synthesis of these systems means they may find use in "real world" applications, including sulfate anion extraction protocols. On the other hand, their structural features also lead us to predict that they could serve as possible ligands for metal coordination. Studies along these lines are currently in progress.

Acknowledgment. This project was supported by the U.S. Department of Energy Office of Science (Grant No. DE-FG02-04ER63741 to J.L.S.), the National Science Foundation (CHE-0107732 to J.L.S.), and by the Russian Foundation for Basic Research (Grant Nos. 02-03-32101 and 05-03-32684 to Y.A.U.) and is part of an ongoing collaboration involving the Sessler research group at The University of Texas at Austin and those of Dr. Bruce Moyer at The Oak Ridge National Laboratory and Professor Kristin Bowman-James at the University of Kansas. We would like to acknowledge Dr. Dmitri Laikov for making available the quantum chemistry software "PRIRODA-04".

Supporting Information Available: General methods and materials, synthetic experimental, representative Job plots, UV−vis titrations, corresponding binding isotherms, and details of affinity constant determinations as well as X-ray crystallographic information including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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