Computational Studies of Inclusion Phenomena and Synthesis of a Novel and Selective Molecular Receptor for 1,4-Disubstituted Benzenes and 4,4′-Disubstituted Biphenyls

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A new tetracationic molecular receptor has been synthesized and studied by semiempirical molecular orbital theory. This novel macrocycle, $\mathbf{1}^{4+}$, derived from pentacyclo[5.0.0.0.^{2,6}0.^{3,10}0^{5,9}]undecane-8,11-dione (PCU-8,11-dione), structurally resembles cyclobis(paraquat-*p*-phenylene), $\mathbf{2}^{4+}$, in which a xylyl group has been replaced by a PCU unit. This derivatization effectively increases the size and flexibility of $\mathbf{1}^{4+}$ and changes its electronic, dynamical, and binding properties. A conformational search using Osawa's corner flapping technique and the PM3 semiempirical method identifies eight unique and low-energy $\mathbf{1}^{4+}$ conformers. The principal regions of structural variation occur in the bipyridinium torsion and in the ethylene bridges between PCU and the tetracationic unit. The inclusion complexes of $\mathbf{1}^{4+}$ with 1,4-disubstituted benzenes and 4,4′-disubstituted biphenyls have been studied by PM3. The first shell of solvation is approximated by the explicit inclusion of 12 acetonitriles in the computed supramolecular complexes. Binding of 1,4-disubstituted benzenes and 4,4′-biphenol is shifted from the $\mathbf{1}^{4+}$ geometric center. From the computations, host $\mathbf{1}^{4+}$ is predicted to have an enhanced binding preference for benzidine over 4,4′-biphenol, as compared to $\mathbf{2}^{4+}$. For all guests computed, $\mathbf{1}^{4+}$ binds more strongly than $\mathbf{2}^{4+}$. These properties can be exploited in the future design of supramolecular systems with potential applications as nanoscale devices.

Introduction

The design and creation of new nanoscale devices continues to be important in the chemical sciences and industry.[1] In particular, the development of molecular switches is driven by the potential applications of nanoscale devices in the field of information processing. Microscale molecular logic gates composed of rotaxane monolayers have been reported.[2,3] Many key advances in developing new nanoscale switches have come from Stoddart and co-workers.[4−6] Stoddart's tetracationic host cyclobis(paraquat-*p*-phenylene),[7] $\mathbf{2}^{4+}$, has been used to build a variety of catenanes,[8−12] rotaxanes,[13,14] pseudorotaxanes,[15−18] and molecular shuttles.[19,20] The goal is to develop a molecular system that functions as an electrochemical switch.[21,22] The rigid cavity of $\mathbf{2}^{4+}$ contains two π-electron-acceptor 4,4′-bipyridinium (paraquat) groups, which have been shown to bind a variety of π-electron donor guests. We have previously studied the inclusion complexes of $\mathbf{2}^{4+}$ with a series of 1,4-disubstituted benzenes and 4,4′-disubstituted biphenyls.[23,24] Within the cavity, the binding of 1,4-disubstituted benzenes is composed of strong electrostatic forces, whereas the binding of 4,4′-disubstituted biphenyls is primarily governed by guest polarizability. The versatile applications of $\mathbf{2}^{4+}$ raise questions as to how modifications on this molecular structure would affect binding properties.

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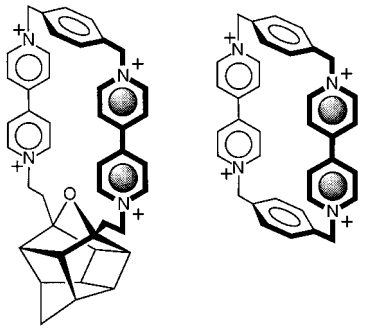

$\mathbf{1}^{4+}$ $\mathbf{2}^{4+}$

A fundamental understanding of the energy, structure, and dynamics of intermolecular interactions is crucial in the effective design of host−guest complexes.[25−27] To investigate the role of noncovalent interactions on complexation, a PCU-derived cyclophane, $\mathbf{1}^{4+}$, was synthesized. This novel host contains an ether linkage, which alters the electronic properties of the cavity, and two ethylene linkages, which change the size and flexibility of the molecule. Like host $\mathbf{2}^{4+}$, the newly synthesized $\mathbf{1}^{4+}$ contains two π-electron-deficient sites that can interact with a π-electron-rich guest by $\pi-\pi$ interactions[28−30] and a *p*-xylyl unit that can interact with the guest by forming weak noncovalent bonds such as [C−H···π].[31,32] The ether linkage in $\mathbf{1}^{4+}$ can also form weak nonconventional bonds with the guests, such as [C−H···O],[33−36] which are important to complexation. Therefore, a systematic conformational search of $\mathbf{1}^{4+}$ was performed to discover important molecular conformations and intramolecular interactions, which could affect the host's ability to bind guests. In addition, complexes of $\mathbf{1}^{4+}$ with a series of 1,4-disubstituted benzenes and 4,4′-disubstituted biphenyls were systematically studied by the PM3 semiempirical method to provide further insight into the nature and strength of the complexation forces for this novel molecular receptor.

Synthesis

Compound $\mathbf{1}^{4+}$ $(PF_6^-)_4$ was prepared by using the method shown in Scheme 1. The synthetic methodology employed for this purpose closely parallels that reported previously by Stoddart and co-workers[7] in connection with their preparation of $\mathbf{2}^{4+}$. Thus, diol **3**[37] was converted into the corresponding dibromide, **4**, which reacted subsequently with 4,4′-bipyridyl to afford **5**. Closure of **5** into $\mathbf{1}^{4+}(4Br^-)$ was achieved through its subsequent reaction with α,α′-dibromo-*p*-xylene at high dilution.[7] Finally, $\mathbf{1}^{4+}(4Br^-)$ was converted into the corresponding $(4PF_6^-)$ salt by anion exchange with NH_4PF_6. The product obtained, $\mathbf{1}^{4+}(4PF_6^-)$, proved to be stable under ambient conditions and also is nonhygroscopic.

Structural and Conformational Studies

Comparison of Macrocycles. All calculations were performed using the Spartan 4.1 software package[38] on an IBM RS/6000 model 591 workstation. The PM3 semiempirical molecular orbital method[39] was used with full geometry optimization to calculate the energies, geometries, and frequencies of all guests, hosts, and complexes. The PM3 semiempirical methodology has been shown to be a reasonable compromise between the computed accuracy of tetracation electronic effects and computational resources required for such large molecular systems.[23] The computed gas-phase structure of $\mathbf{2}^{4+}$ has been determined previously at several levels of theory. In particular, the gas-phase PM3 structure has been shown to reproduce available ab initio structures of $\mathbf{2}^{4+}$, in agreement with the reported X-ray crystal structure.[23,24] The computed structures of each host are shown in Figure 1. The greatest variation between $\mathbf{2}^{4+}$ and the crystal structure occurs in the dihedral between the bipyridinium units and in the cavity size. The discrepancies are small, considering the absence of counterions and solvent molecules in the calculations, which have been previously studied in detail.[23] The computations indicate that $\mathbf{2}^{4+}$ is a rigid and well-defined tetracation of high symmetry. In $\mathbf{1}^{4+}$, distances between the nitrogens of the bipyridinium units closer to PCU are longer than in $\mathbf{2}^{4+}$, resulting in an unsymmetrical and wider cavity. A CPK representation[40] shows how the hydrogens from the methylene groups, which point toward the center of the molecule in the $\mathbf{1}^{4+}$ conformers, effectively *decrease* the cavity volume, resulting in a binding cavity smaller than that of $\mathbf{2}^{4+}$. The lone pairs of electrons of the oxygen should also increase the electronic density within the cavity.

Conformational Search and Analysis. The two ethylene linkages provide $\mathbf{1}^{4+}$ with more flexibility, warranting a closer examination of the molecule's conformational space. A search of conformers was performed following Osawa's corner flapping technique using the PM3 semiempirical method.[41,42] A total of 879 trial conformers were generated of which 41 were retained by the program on the basis of structural dissimilarity and energetic considerations. After careful examination, eight unique conformers ($\mathbf{1a}-\mathbf{h}^{4+}$) were identified, as shown in Figure 2. Conformer $\mathbf{1a}^{4+}$ and $\mathbf{1b}^{4+}$ illustrate how the ethylene bridges allow the PCU subunit to switch orientation, producing a pair of enantiomeric structures. The ethylene unit bonds at each side of the PCU subunit can rotate and generate the major structural changes found in this set of conformers. The effects of these bond

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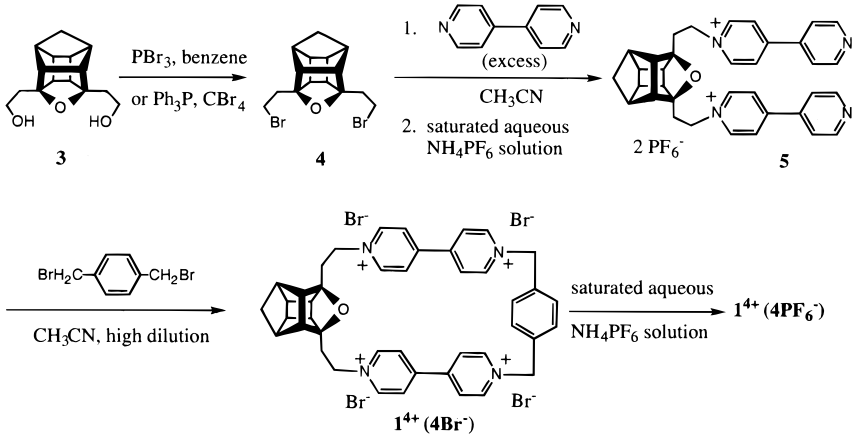
Scheme 1



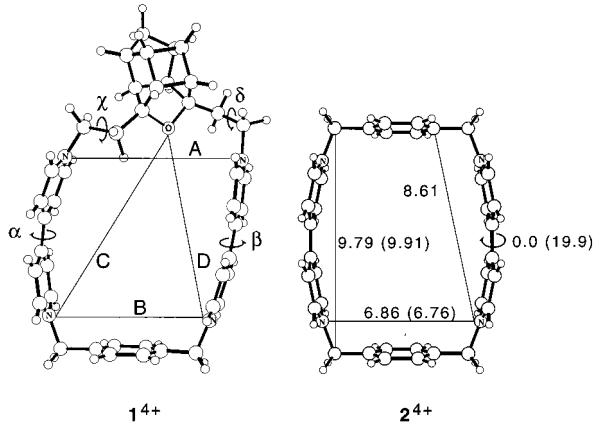


Figure 1. Comparison of computed and experimental parameters. Values for $\mathbf{1}^{4+}$ are listed in Table 1. X-ray data available for $\mathbf{2}^{4+}$ are shown in parentheses. Distances are in Å, and angles are in degrees.

rotations can be assessed by the changes of dihedrals χ and δ (see Figure 1) in the first four conformers $\mathbf{1a}-\mathbf{d}^{4+}$ (Table 1). The dihedrals χ and δ range from −179.0° to 153.7° and from 86.6° to 179.0°, respectively. In addition, a narrow range of dihedral angles for α and β reflects little structural variation in the torsion of the bipyridinium rings (−2.8° to 0.7° and −3.5° to 0.3°, respectively). As expected, the rigid PCU subunit does not deform significantly for any of the located conformers. The computations show that the PCU subunit tilts slightly as a result of the ethylene linkage rotations. The immediate bonds that connect the subunit to the rest of the macrocycle have an insignificant effect.

The last four conformers $\mathbf{1e}-\mathbf{h}^{4+}$ illustrate the second major structural change that occurs in $\mathbf{1}^{4+}$. The bipyridinium rings rotate along the bonds that connect them to the macrocycle. In these conformers the wide range of dihedrals for α and β reflect the structural variation (−41.8° to 119.7° and −5.4° to 40.2°, respectively). This can be clearly seen in $\mathbf{1h}^{4+}$, where the ring has rotated, changing both the electronic and physical nature of the cavity. The bipyridinium hydrogen is 1.81 Å from the PCU oxygen and the ∠CHO is 143°, allowing for the existence of a weak nontraditional hydrogen bond [C−H···O].[33−36] The combination of reduced steric and enhanced electronic effects allows the rings closest to the PCU subunit to have a greater change in their torsional rotation, again underscoring the additional flexibility provided by the two ethylene units.

Bipyridinium Torsions. To explore the potential energy surface associated with the torsion around the central bond of the PCU bipyridinium units, separate calculations on a simplified model, the 4,4′-bipyridinium molecule, were performed at several levels of theory. The 4,4′-bipyridinium molecule was geometry optimized with C_2 symmetry while constraining the dihedral to the desired value. Geometries and energies were computed with the semiempirical PM3, Hartree−Fock (HF), and the three parameter corrected Becke density functional (B3LYP)[43] methods. Figure 3 illustrates how the different levels of theory represent the rotation of the bipyridinium unit around its central bond. The Becke computations (B3LYP/6-31G*) include the effects of electron correlation and locate the energy minimum with a bipyridinium twist of 45°, while the uncorrelated HF method with the same basis set (HF/6-31G*) shows the minimum at 60°. Compared with other methods, PM3 behaves well between 30° and 90° but fails to account for the steric hindrance between the bipyridinium ortho protons and produces an artificial minimum at 0°. This could explain the small discrepancies between the computed and X-ray dihedrals of $\mathbf{2}^{4+}$ (Figure 1). Despite the shortcomings of PM3 at nearly coplanar bipyridiniums, the corner flapping method was able to locate structures $\mathbf{1e}-\mathbf{h}^{4+}$ consistent with the Hartree−Fock and density functional computations.

Inclusion Complexes. The possible supramolecular applications of $\mathbf{1}^{4+}$ depend on its binding properties. Inclusion complexes with several guests were optimized using the PM3 semiempirical method in a vacuum and in a solvent-approximated environment. Binding enthalpies (ΔH) were computed by subtracting the individual enthalpies of formation of the guests and the hosts from the enthalpies of formation of the complexes. Several conformations for inclusion complexes were found and were classified according to the location of the guest after energy minimization. When the guest is centered within the cavity, allowing for $\pi-\pi$ interactions, it is referred to as a π-complex. If the guest is only partially inside the cavity, with a substituent in the cavity center and the aromatic ring outside, then it is called a σ-complex. Table 2 lists the computed binding enthalpies for the π- or σ-complexes between 1,4-disubstituted benzenes and 4,4′-disubstituted biphenyls with both $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$. The binding energies for host $\mathbf{2}^{4+}$ indicate that σ-complexes are generally more stable than π-complexes. Since dif-

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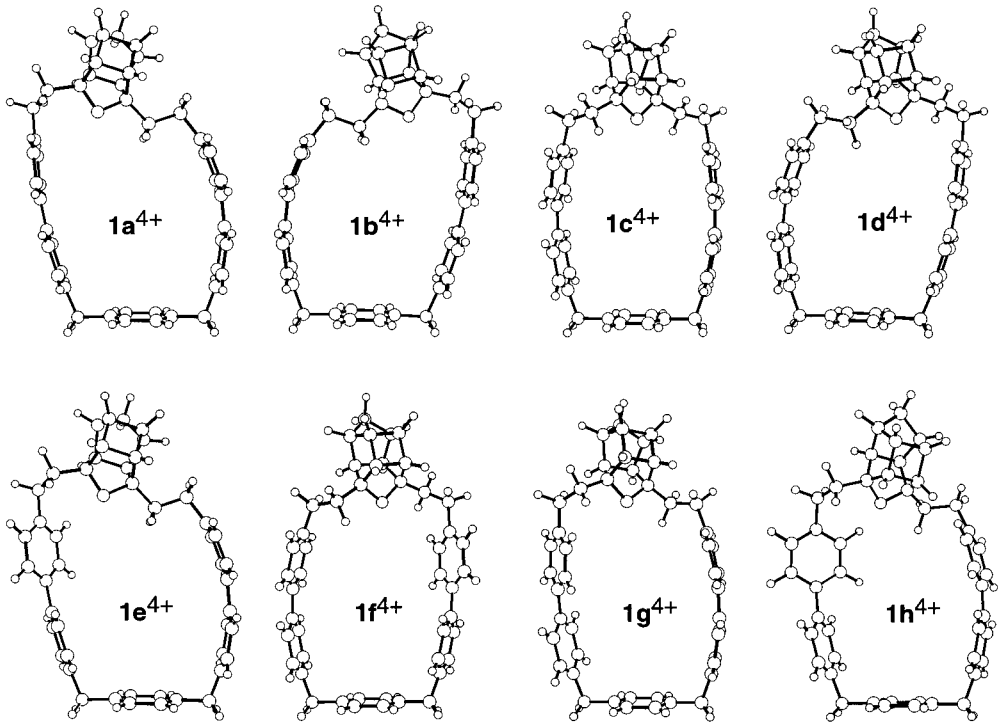

Figure 2. Different structures of $\mathbf{1}^{4+}$ obtained from the conformational search.

Table 1. Structural Parameters of Conformers 1a−h^{4+} [a]

	A	B	C	D	α	β	χ	δ	Δ*H*
1a^{4+}	7.64	6.93	8.31	9.72	0.8	0.3	87.0	179.0	0.00
1b^{4+}	7.65	6.93	9.72	8.31	0.7	0.9	−179.0	86.6	0.01
1c^{4+}	7.26	6.80	9.22	9.11	−2.8	−2.5	119.4	112.4	0.43
1d^{4+}	7.56	6.69	9.59	8.46	−2.3	−3.5	153.7	91.1	0.68
1e^{4+}	7.66	6.93	8.25	9.70	−41.8	0.1	86.5	177.5	0.74
1f $^{4+}$	7.24	6.82	9.45	8.92	−2.4	40.2	134.4	99.6	1.02
1g^{4+}	7.24	6.82	8.94	9.45	39.4	−2.1	100.8	133.0	1.08
1h^{4+}	7.37	6.86	8.59	9.34	119.7	−5.4	95.5	116.5	1.68

[a] Distances are reported in Å, and dihedrals are in degrees, as shown in Figure 1; energy differences (Δ*H*) are given in kcal/mol.

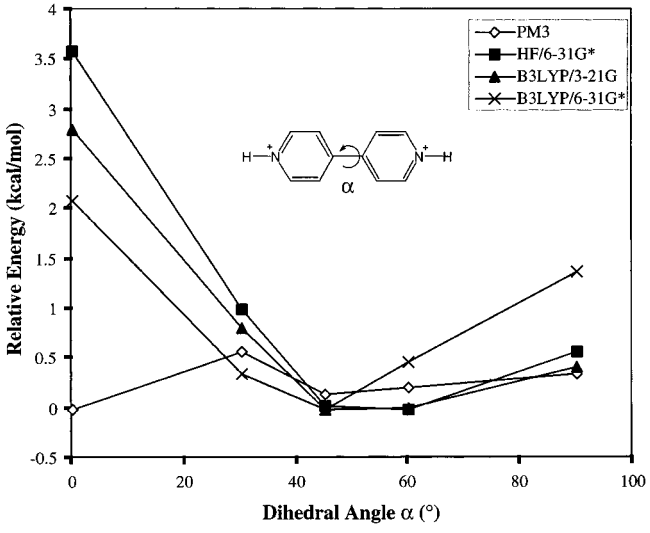

Figure 3. Effect of level of theory on the torsion of the central bond of the bipyridinium subunit.

ferent types of interactions operate in the σ- and π-complexes, energetic comparisons between the different guests will be made among complexes of the same type (σ or π).

Table 2. Binding Enthalpies (kcal/mol) of Complexes between Hosts 1^{4+} and 2^{4+} with a Variety of Guests

	aceto-nitriles[a]	Δ*H*(**1**$^{4+}$)	Δ*H*(**2**$^{4+}$)[b]	−ΔΔ*H*
4,4′-Disubstituted Biphenyls				
benzidine	0	-16.86^{π}	-14.91^{π}	2.0
	12	-5.25^{π}	-4.85^{π}	0.4
4,4′-biphenol	0	π, *c*	-7.54^{π}	
	12	π, *c*	-2.62^{π}	
	0	-12.14^{σ}	-12.11^{σ}	0.0
	12	-5.15^{σ}	-5.04^{σ}	0.1
4,4′-dimethoxybiphenyl	0	-14.36^{π}	-11.35^{π}	3.0
	0	-14.68^{σ}	-13.82^{σ}	1.0
	12	-6.33^{σ}	-5.52^{σ}	0.9
1,4-Disubstituted Benzenes				
benzene	0	π, *c*	-2.29^{π}	
	0	-7.43^{σ}	-5.35^{σ}	2.1
	12	π, *c*	-0.52^{π}	
	12	-2.37^{σ}	-1.67^{σ}	0.7
hydroquinone	0	π, *c*	-5.37^{π}	
	0	-9.70^{σ}	-6.79^{σ}	2.9
	12	-3.79^{σ}	-2.46^{σ}	1.3
p-xylene	0	π, *c*	-2.66^{π}	
	0	-9.18^{σ}	σ, *c*	
	12	$-3.97^{\sigma/\pi}$	-1.50^{π}	2.5
1,4-dimethoxybenzene	0	-12.30^{σ}	-7.93^{σ}	4.4
	12	$-5.72^{\sigma/\pi}$	-3.24^{σ}	2.5

[a] Twelve acetonitriles are used to mimic the effect of solvation. [b] Reference 24. [c] Complex not found. [π] Guest centered within the cavity. [σ] Substituent of guest centered in the cavity.

When a guest is present inside the cavity, the host's ability to adopt different conformations is restricted. In the complexes, the geometries of the hosts are closest to that of the **1d**$^{4+}$ conformer (Figure 2). This results in an entropic cost that could effectively decrease the free energy of binding. Yet, a previous correlation of 0.94 between the experimental free energies of binding and the computed binding enthalpies has been reported for complexes between host **2**$^{4+}$ and 4,4′-disubstituted biphenyls,[24] which suggests a negligible contribution from the entropic term. The expected entropic cost should be

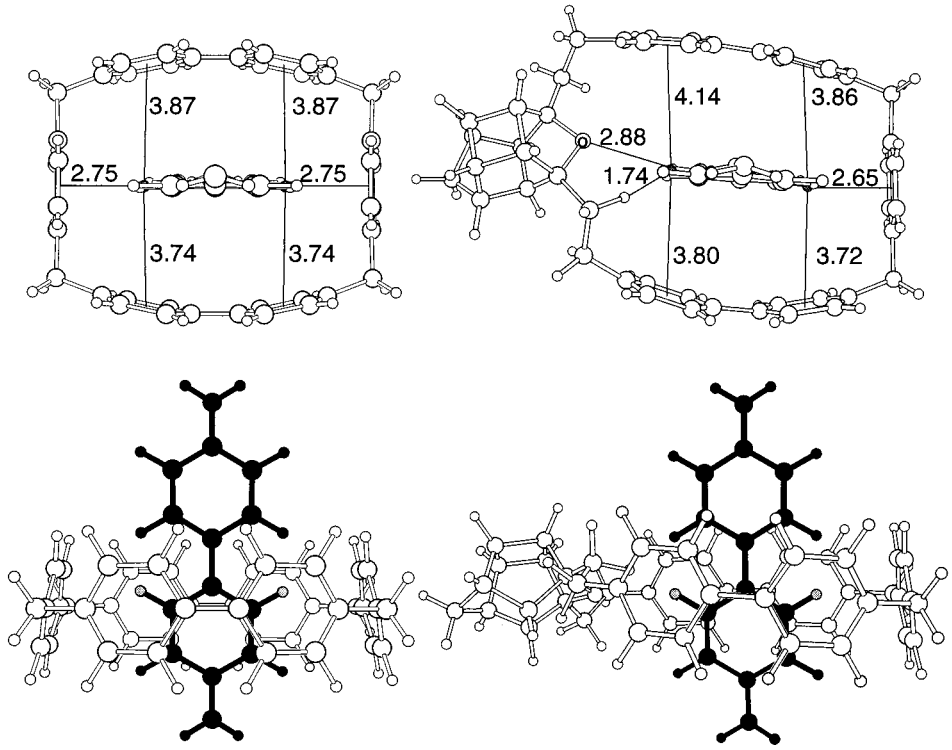

Figure 4. Geometries of host $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ complexed with benzidine. Distances (Å) shown are from the benzidine's β-protons (gray) to the centroid of the rings, the hydrogen, or the oxygen.

slightly greater for $\mathbf{1}^{4+}$ complexes, since host $\mathbf{1}^{4+}$ has a greater conformational flexibility. A qualitative understanding of binding should be retained as a result of the overall similarity of host $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$. A full and accurate account of entropic effects is beyond the qualitative intentions of this work.

The first major trend in the binding, as revealed by the computed complexes, is that $\mathbf{1}^{4+}$ forms stronger complexes with nitrogen-containing guests than with oxygen-containing guests. This trend was also observed with host $\mathbf{2}^{4+}$ in computational and UV−vis experimental studies,[23,24] but was further enhanced with the $\mathbf{1}^{4+}$ host. The nitrogen substituents are stronger electron donors to the π system than the corresponding oxygen substituents, which enhances the π-electron-rich nature of the guests. Thus, stronger binding in these π donor−acceptor complexes results. Although the methoxy substituent is a weaker electron donor group than the hydroxyl substituent, it results in stronger binding, revealing that interactions other than $\pi-\pi$ interactions are also contributing to the binding enthalpies. For example, a correlation between the binding strength of host $\mathbf{2}^{4+}$ with 4,4′- disubstituted biphenyls and the molecular polarizability of the guests was found in a previous theoretical study.[23] The higher molecular polarizability of 4,4′-dimethoxybiphenyl was proposed to explain the stronger binding enthalpy. Generally, nitrogen-containing guests remained centered within the $\mathbf{1}^{4+}$ cavity forming π-complexes, while oxygen-containing guests preferred to form σ-complexes in which the guests moved slightly out of the cavity, placing the oxygen lone pairs closer to the paraquat nitrogens furthest away from the PCU ether linkage. Although 4,4′-dimethoxybiphenyl formed both π- and σ-complexes with host $\mathbf{1}^{4+}$, 4,4′-biphenol only formed σ-complexes. Different orientations inside the cavity were used as starting geometries, but the 4,4′-biphenol always moved out of the cavity during optimization to form the σ-complex. Since a π-complex was formed between host $\mathbf{2}^{4+}$ and 4,4′-biphenol, interaction between the guest's oxygen and the paraquat acidic hydrogens is not the cause for this displacement from the cavity center. One explanation is that the higher electron density inside the cavity fills up some of the electron deficiency of the receptor's binding interior.

An analysis of the geometries of the complexes was performed to identify the presence of other stabilizing noncovalent interactions. The distances between the guest hydrogens and the ether oxygen are too long for the existence of nontraditional hydrogen bonds. Figure 4 illustrates the complexation of benzidine in the gas phase by hosts $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$. The separation between the ether oxygen in $\mathbf{1}^{4+}$ and the closest benzidine hydrogen (in gray) is 2.88 Å. Steric repulsion between the closest methylene hydrogen and the benzidine hydrogen (1.74 Å) prevents the benzidine from approaching the ether. This steric hindrance results in an enhanced [C−H$\cdots\pi$] bond between the opposite benzidine hydrogen and the xylyl aromatic centroid (2.65 Å). The side view in Figure 4 shows how the benzidine hydrogens are better aligned with respect to the pyridinium centroids in $\mathbf{1}^{4+}$, revealing a deeper insertion of benzidine in the host.

Host $\mathbf{1}^{4+}$ also binds 4,4′-disubstituted biphenyls more strongly than 1,4-disubstituted benzenes, as shown in Table 2. Indeed, when π-complexes are formed, $\mathbf{1}^{4+}$ binds 2−3 kcal/mol more strongly to the 4,4′-disubstituted biphenyls than $\mathbf{2}^{4+}$ in the gas phase. The $\mathbf{1}^{4+}$ host does not form stable π-inclusion complexes with benzene, hydroquinone, or *p*-xylene, whereas $\mathbf{2}^{4+}$ forms complexes in the gas phase. Despite the absence of π-complexes with $\mathbf{1}^{4+}$, strong σ-complexes have been located. Within a molecular device, the type of binding is not as important as the magnitude of the binding. When π or σ complex-

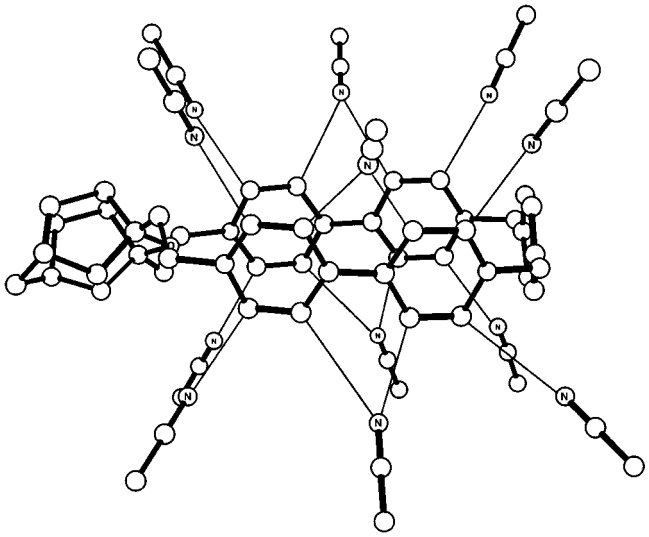

Figure 5. PM3 geometry optimized host $\mathbf{1}^{4+}$ complexed with 12 acetonitriles as the solvent model. The hydrogens are removed for clarity.

ation occurs in the gas phase, $\mathbf{1}^{4+}$ consistently binds all guests 1−4 kcal/mol more strongly than $\mathbf{2}^{4+}$.

Solvation is expected to affect these results, reducing the computed binding energies. In the case of $\mathbf{2}^{4+}$, computations with a first solvation shell of 12 acetonitriles reproduced the experimental free energies of binding to within 1 kcal/mol.[24] Since $\mathbf{1}^{4+}$ contains the same 12 acidic protons as $\mathbf{2}^{4+}$, the same solvation model of using 12 explicit acetonitriles was implemented. As shown in Figure 5, one acetonitrile was added for every α-proton, and four acetonitiles were placed to form bifurcated hydrogen bonds with the bipyridinium β-protons, for a total of 12 explicit solvent molecules. Previous PM3 calculations were carried out on $\mathbf{2}^{4+}$ with four chloride anions. A few structural deviations from the X-ray crystal structure, such as the cavity size, were corrected, but the counterions introduced more geometric and energetic error than that found with the simple $\mathbf{2}^{4+}$ model.[24] To avoid the computational artifacts observed earlier, the solvation model in this study utilized 12 acetonitriles without the four counterions. Solvation effects cause several of the guests to move deeper into the cavity, as in the case of *p*-xylene, since the solvated bipyridinium hydrogens can no longer interact as strongly with the guests. Reduced from the gas phase, host $\mathbf{1}^{4+}$ is computed to bind 1−3 kcal/mol more strongly to 1,2-disubstituted benzenes than $\mathbf{2}^{4+}$ in acetonitrile. The preference for benzidine over 4,4′-biphenol is diminished in solvent but retained for $\mathbf{1}^{4+}$ over $\mathbf{2}^{4+}$. For all guests computed, host $\mathbf{1}^{4+}$ binds more strongly than $\mathbf{2}^{4+}$.

Conclusion

Given the importance of new molecular receptors in the design and synthesis of switchable rotaxanes and other molecular devices, we report the synthesis and computational analysis of a novel molecular receptor, $\mathbf{1}^{4+}$, and its inclusion complexes with 1,4-disubstituted benzenes and 4,4′-disubstituted biphenyls. In comparison with receptor $\mathbf{2}^{4+}$, $\mathbf{1}^{4+}$ is a stronger binder of the 1,4-disubstituted benzenes and 4,4′-disubstituted biphenyls. The enhanced binding for benzidine over 4,4′-biphenol is important, since they are guests commonly used in the docking stations of rotaxanes.[3,4,21,44] These supramolecular properties will be exploited in our future collaborative efforts in the design of novel supramolecular structures to better understand fundamental issues in intermolecular complexation and create new materials for nanotechnology applications.

Experimental Section

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Phoenix, AZ.

3,5-[2′,2″-Bis(bromoethyl)]-4-oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (4). A solution of diol **3**[37] (300 mg, 1.25 mmol) in benzene (10 mL) was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise with stirring a solution of PBr_3 (146 mg, 0.54 mmol) in benzene (3 mL). After the addition of PBr_3 had been completed, the external cold bath was removed, and the reaction mixture was allowed to stir at ambient temperature for 12 h. Water (5 mL) was added to the reaction mixture, and the benzene layer was separated. The organic layer was washed with water (5 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated in vacuo. The residue thereby obtained was purified by column chromatography on silica gel by eluting with hexane. Pure **4** (285 mg, 61%) was thereby obtained as a colorless oil: IR (film) 2980 (s), 1428 (m), 1132 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.51 (d, J = 10.2 Hz, 1 H), 1.86 (d, J = 10.2 Hz, 1 H), 2.28−2.70 (m, 12 H), 3.39 (t, J = 7.0 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 28.2 (t), 36.2 (t), 43.3 (d), 43.5 (t), 44.0 (d), 47.5 (d), 58.1 (d), 95.0 (s). Anal. Calcd for $C_{15}H_{18}Br_2O$: C, 48.16; H, 4.85. Found: C, 48.53; H, 5.00.

Reaction of 4 with 4,4′-Bipyridine.[7] To a solution of dibromide **4** (400 mg, 1.06 mmol) in dry CH_3CN (20 mL) was added 4,4′-bipyridine (873 mg, 5.60 mmol), and the resulting mixture was refluxed for 24 h. At that time, TLC analysis of the reaction mixture indicated the complete absence of **4** in the reaction mixture. The reaction mixture was concentrated in vacuo, and water (1 mL) was added to the residue. To the resulting mixture was added saturated aqueous NH_4PF_6 (1 mL), whereupon crude **5** (238 mg) precipitated as a colorless microcrystalline solid. This solid material was isolated by suction filtration and then was used as obtained in the next synthetic step without additional purification or characterization.

Reaction of 5 with α,α′-Dibromo-*p*-xylene.[7] To crude **5** (238 mg, vide supra) under argon was added a solution of α,α′-dibromo-*p*-xylene (77 mg, 0.29 mmol) in very dry CH_3CN (50 mL), and the solution was refluxed gently under argon atmosphere for 24 h. The reaction mixture was concentrated in vacuo, and water (1 mL) was added to the residue. To the resulting aqueous suspension was added rapidly saturated aqueous NH_4PF_6 (1.5 mL), whereupon a light tan precipitate formed. The resulting solid was collected by suction filtration, washed with water (2 mL), and dried in vacuo. Repeated fractional recrystallization of this material from acetone−water mixed solvent afforded $\mathbf{1}^{4+}$ ($4PF_6^-$) (359 mg, 26% overall yield from **4**) as an off-white (i.e., ivory-colored) microcrystalline solid: mp 289−290 °C; IR (Nujol) 2983 (s), 1625 (w), 1180 cm^{-1} (m); ^{1}H NMR (CD_3CN) δ 1.55 (d, J = 10.1 Hz, 1 H), 2.12 (d, J = 10.1 Hz, 1 H), 2.38−2.78 (m, 12 H), 4.60 (t, J = 6.6 Hz, 4 H), 5.81 (s, 4 H), 7.56 (s, 4 H), 8.30−9.02 (m, 16 H); ^{13}C NMR (CD_3CN) δ 33.2 (t), 42.8 (d), 44.14 (t), 45.1 (d), 48.8 (d), 49.3 (d), 60.2 (t), 64.7 (t), 95.0 (s), 127.7 (d), 128.4 (d), 131.22 (d), 135.3 (s), 146.6 (d), 146.8 (d), 150.9 (s), 151.6 (s). Anal. Calcd for $C_{43}H_{42}F_{24}N_4OP_4$: C, 42.66; H, 3.50. Found: C, 42.73; H, 3.60.

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Supporting Information Available: Semiempirical energies and structures in SPARTAN archive format. This material is available free of charge via the Internet at http://pubs.acs.org.

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