Journal of Inclusion Phenomena and Macrocyclic Chemistry **40:** 189–191, 2001.

Molecular Modeling on the Complexation of Cyclobis(paraquat-*p*-phenylene) with Tetrathiafulvalenes

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(Received: 31 October 2000; in final form: 3 May 2001)

Key words: inclusion complexation, cyclobis(paraquat-*p*-phenylene), tetrathiafulvalenes, molecular devices, *ab initio*

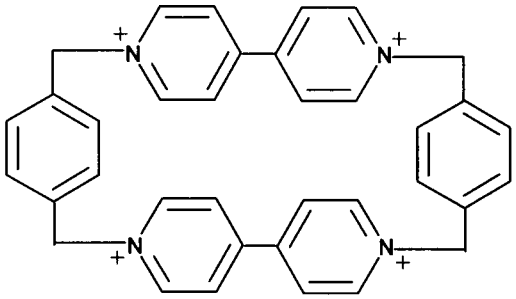
Abstract

PM3, HF/3-21g*, and B3LYP/6-31g* calculations on the inclusion complexation of cyclobis(paraquat-*p*-phenylene) with tetrathiafulvalenes show that *ab initio* methods are much more reliable in the modeling. The results, in agreement with the experimental observations, indicate that instead of the extended π-surface, the better electron-donor property of the pyrrolo-annelated tetrathiafulvalene makes it a better substrate than tetrathiafulvalene.

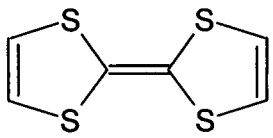
Introduction

The molecular recognition of cyclobis(paraquat-*p*-phenylene), $\mathbf{1}^{4+}$, has drawn great attention recently, due to its important applications in the design and synthesis of electrochemically and chemically switchable rotaxanes, photoactive rotaxanes, and other molecular devices [1]. Usually, the molecular recognition of $\mathbf{1}^{4+}$ was studied with methods including X-ray, NMR, UV, and IR, which, however, often have difficulties in providing a detailed understanding of the energetic and structural properties of the complexes. As a result, molecular modeling is often employed in the field, which is usually with molecular mechanics [2] and semi-empirical molecular orbital [3] calculations. Nevertheless, as the molecular recognition of $\mathbf{1}^{4+}$ involves some non-conventional intermolecular interactions such as charge–transfer interaction and π-π stacking, the *ab initio* approach should be apparently more desirable for the modeling, which, however, has not yet been performed before due to the large size of the system.

Among many guest compounds of $\mathbf{1}^{4+}$, tetrathiafulvalenes are especially interesting [4]. These molecules are efficient π-donors and hence represent good building blocks in synthetic supramolecular chemistry [5]. Recently, Becher *et al.* studied the complexation of $\mathbf{1}^{4+}$ with tetrathiafulvalene **2** and bis(2,5-dimethylpyrrolo)[3,4-*d*]tetrathiafulvalene **3** [6]. Though both the substrates were found to form stable inclusion complexes with $\mathbf{1}^{4+}$, it is interesting that **3** binds much more strongly with $\mathbf{1}^{4+}$ than **2**. As the behavior is potentially useful for the design of new molecular devices, it is interesting to see if molecular modeling can reproduce the experimental observations. Herein, in addition to the formerly used PM3 method, we also carried out *ab initio* calculations for the first time on the above systems.



1^{4+}



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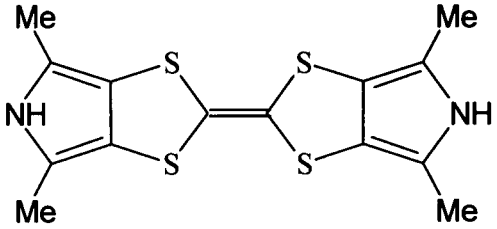

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Scheme 1.

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Methods

All the calculations were performed with GAUSSIAN 98. $\mathbf{1}^{4+}$ was optimized from the crystalline structure [7] with PM3, HF/3-21g*, and B3LYP/6-31g* methods in the gas phase or in acetone solution. The solvation effect was taken into account by using the Onsager solvation model based on the self-consistent reaction field (SCRF) method.

The complexes of $\mathbf{1}^{4+}$ with **2** and **3** were studied with PM3 in the gas phase and HF/3-21g* in acetone solution. They were optimized starting in a symmetric form with the center of symmetry inside the host. As all the structures were found to be true energy minima, no constraints were needed in the optimization. In addition, B3LYP/6-31g* single-point calculations in acetone solution were performed on all the HF/3-21g* optimized structures. Using a dual PII-450 PC with 256MB memory, it took three weeks to finish all the calculations.

Results and discussion

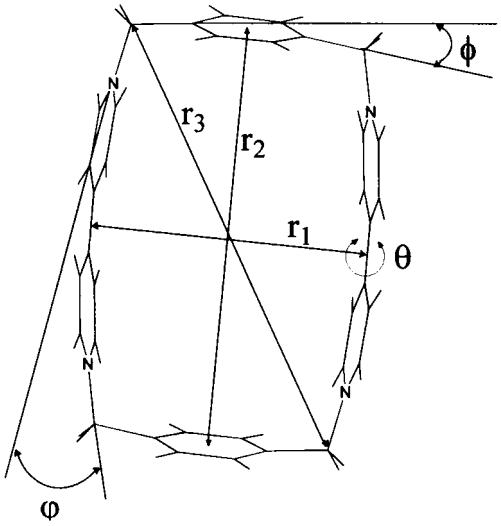
In Table 1 are listed the geometrical parameters of the crystalline and optimized structures of $\mathbf{1}^{4+}$. From Table 1, it can be seen that the optimized structures agree with the experimental one. The three distances, r_1, r_2, and r_3, are well reproduced by PM3, B3LYP/6-31g* (in vacuum), and HF/3-21g* (in acetone), which indicates that the cavity volumes of these structures are nearly the same.

According to Table 1, the bipyridinium torsion angle (θ) in the PM3-optimized $\mathbf{1}^{4+}$ is zero, different from the value in the other structures. As mentioned, the failure of PM3 in accounting for the steric hindrance between the bipyridinium ortho protons leads to such a value [3e]. In comparison, *ab initio* calculations provide better results.

On the other hand, though the experimental xylene bow angle (ϕ) has a nonzero value, all the theoretical methods predict that the value is zero. Presumably, the crystal packing may be contributing to the discrepancies, which pushes the two layers of bipyridiniums towards the center of the cavity. The effect can also be shown by the smaller experimental r_1 value.

All the PM3 (in vacuum) and HF/3-21g* (in acetone) optimized complexes reflect substantial inclusion of the substrates in the central cavity of $\mathbf{1}^{4+}$, (Figure 1) in which the tetrathiafulvalene moiety takes part in a face-to-face interaction with the paraquat units of the host. Interestingly, from Figure 1 it can be seen that although the PM3-optimized structure of the complex of $\mathbf{1}^{4+}$ with either **2** or **3** basically correspond to a C_{2h} geometry, in the HF/3-21g* structures the tetrathiafulvalene moiety is oriented with its long axis significantly inclined to the $N^+ \cdots N^+$ vector of each bipyridium residue. In fact, according to the crystalline structure of the complex of $\mathbf{1}^{4+}$ with **2** [4a], the tetrathiafulvalene molecule should be inserted into $\mathbf{1}^{4+}$ at an angle, which is energetically more favorable because it maximizes the π-π interaction between the host and guest subject to the spatial constraints of the receptor. Consequently, the present results clearly show that an *ab initio* method is more reliable than a semiempirical one in modeling the inclusion complexation of $\mathbf{1}^{4+}$.

Table 1. Geometrical parameters of $\mathbf{1}^{4+}$ given by theoretical methods and X-ray crystallography



	Exp.	PM3 (in vacuum)	B3LYP/6-31G* (in vacuum)	HF/3-21g* (in acetone)
r_1 (Å)	6.8	7.9	7.9	7.7
r_2 (Å)	10.3	9.8	9.9	9.9
r_3 (Å)	11.5	11.4	11.5	11.4
θ (deg.)	19	0	34	50
φ (deg.)	23	41	39	35
ϕ (deg.)	14	0	0	0

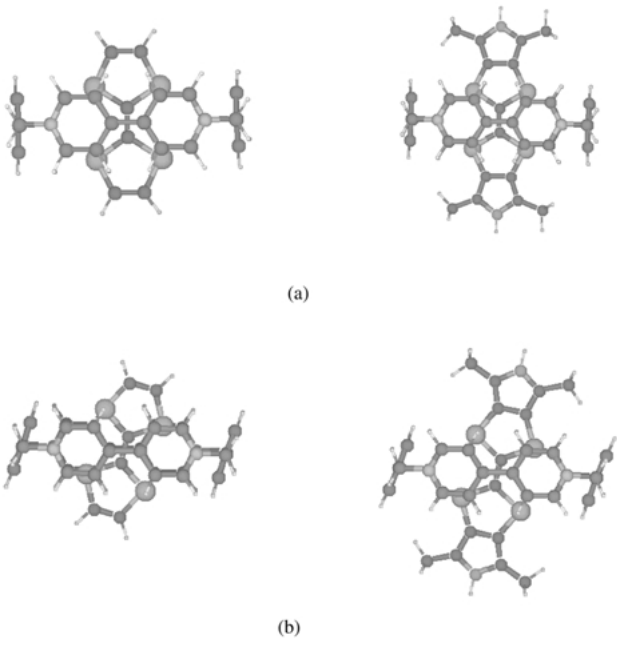


Figure 1. PM3 in vacuum (a), and HF/3-21g* in acetone (b) optimized structures of the complexes of $\mathbf{1}^{4+}$ with **2** and **3**.

Table 2. Stabilization energies upon complexation (kJ/mol)

Species	PM3 //PM3 (in vacuum)	HF/3-21g* //HF/3-21g* (in Me_2CO)	B3LYP/6-31g* //HF/3-21g* (in Me_2CO)
Complex of **2**	−14.35	−37.24	−62.35
Complex of **3**	−135.04	−464.1	−180.52

In Table 2 are listed the stabilization energies upon complexation for the two inclusion complexes. According to the results, it can be seen that calculations at different levels of theories all indicate that the complex of $\mathbf{1}^{4+}$ with **3** is more stable than with **2**, which well reproduces the experimental observations. It indicates that the three quantum mechanic methods are all at least qualitatively correct. However, it is also noteworthy that the difference between the numerical results at different levels of methods is not negligible. It suggests that in order to precisely quantitatively describe the non-covalent interactions in a supermolecule, methods at much higher level of theory than the present *ab initio* one used in this work might be required. Apparently, the usually used molecular mechanics approaches are far from being sufficient.

The reason that **3** binds more tightly with $\mathbf{1}^{4+}$ than **2** can be understood from the point of view of charge-transfer interaction, which is believed to be a driving force for the inclusion complexation of $\mathbf{1}^{4+}$. Apparently, as $\mathbf{1}^{4+}$ is a good electron-acceptor, a better electron-donor will be more favorably enclosed in the cavity. As known, the first oxidation potential well reflects the electron-donor property of a species, which can be calculated theoretically as the energy difference between the neutral form and radical cation of the species. Herein, the calculated first oxidation potentials of **2** and **3** at the PM3 level are 7.52 eV and 6.80 eV, respectively. According to them, **3** is a better electron donor than **2**, and in consequence binds with $\mathbf{1}^{4+}$ more strongly.

It should be mentioned that the extended π-surface of **3** can also be used to explain the above behavior [6], because the π interaction is also a known driving force of the complexation. However, from the structures of the complexes shown in Figure 1, the pyrrolo-rings of **3** are far away from the cavity of $\mathbf{1}^{4+}$. Because the π-π interaction is a short-range interaction, it does not seem likely that the above argument is correct.

Conclusion

PM3, HF/3-21g*, and B3LYP/6-31g* calculations were performed on the inclusion complexation of cyclobis(paraquat-*p*-phenylene) with tetrathiafulvalenes. The results, in agreement with the experimental observations, indicate that the better electron-donor property of the pyrrolo-annelated tetrathiafulvalene makes it a better substrate than tetrathiafulvalene itself.

Acknowledgements

We are grateful to the NSFC for the financial support. We also thank Prof. Stoddart for providing us with the crystalline structure data of $\mathbf{1}^{4+}$.

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