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The Nature of Noncovalent Interactions in Catenane Supramolecular Complexes: Calibrating the MM3 Force Field with *ab initio*, DFT and SAPT Methods

Tomekia M. Simeon*, Mark A. Ratner, and George C. Schatz

Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

Abstract

The design and assembly of mechanically interlocked molecules, such as catenanes and rotaxanes, are dictated by various types of noncovalent interactions. In particular, [C-H...O] hydrogen-bonding and π -stacking interactions in these supramolecular complexes have been identified as important noncovalent interactions. With this in mind, we examined the [3] catenane **2-4PF₆** using molecular mechanics (MM3), *ab initio* methods (HF, MP2), several versions of density functional theory (DFT) (B3LYP, M0X), and the dispersion-corrected method DFT-D3. Symmetry adapted perturbation theory (DFT-SAPT) provides the highest level of theory considered, and we use the DFT-SAPT results both to calibrate the other electronic structure methods, and the empirical potential MM3 force field that is often used to describe larger catenane and rotaxane structures where [C-H...O] hydrogen-bonding and π -stacking interactions play a role. Our results indicate that the MM3 calculated complexation energies agree qualitatively with the energetic ordering from DFT-SAPT calculations with an aug-cc-pVTZ basis, both for structures dominated by [C-H...O] hydrogen-bonding and π -stacking interactions. When the DFT-SAPT energies are decomposed into components, we find that electrostatic interactions dominate the [C-H...O] hydrogen-bonding interactions while dispersion makes a significant contribution to π -stacking. Another important conclusion is that DFT-D3 based on M06 or M06-2X provides interactions energies that are in near-quantitative agreement with DFT-SAPT. DFT results without the D3 correct have important differences compared to DFT-SAPT while HF and even MP2 results are in poor agreement with DFT-SAPT.

Keywords

catenanes; dispersion; MM3 force field; supramolecular complexes and DFT-SAPT

I. Introduction

[*n*] Catenanes and [*n*] rotaxanes are molecules consisting of *n* and *n*–1 macrocyclic mechanically interlocked components, with no inter-component covalent bonds.^{1–2}

Corresponding author: t-simeon@northwestern.edu, **Telephone number:** 847-467-4990, **Address:** WCAS Chemistry, TECH 2145 Sheridan Rd., K#148, Evanston Campus 3113, Evanston, IL 60208.

SUPPORTING INFORMATION

- XYZ coordinates for the MM3 Complexes denoted **^bI** and **^bII**
- XYZ coordinates for the Initial Complexes from crystal structure denoted **^bI** and **^bII**
- Table S.I:** Minimized MM3 interatomic distances and bond angles for Complexes **I** and **II**.
- Table S.II:** Calculated First-order DF-DFT-SAPT energies for *dimer* **^bI** and **^bII** components.
- Table S.III:** Calculated Second-order DF-DFT-SAPT energies for *dimer* **^bI** and **^bII** components.

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Superimposed noncovalent interactions along with mechanical bonds are responsible for holding the components together. Dismembering of either molecule (a catenane or a rotaxane) can occur only after cleaving an intracomponent covalent bond. The mechanically inter-locked components must be considered as independent, discrete molecules, rather than as assemblies of two or more molecules.

Functionalized catenanes have emerged as important functional molecular devices pioneered by Sauvage^{3,4-5,6} and Stoddart.^{2,7,8,9} The main driving force responsible for tailored functionalization are noncovalent interactions, and their fine tuning play very important roles in the architectures of interlocked molecules and molecular complexes. Two interactions, π -stacking and [C-H...O] hydrogen bonding (H-bonding), are considered to be primarily responsible for assembly processes in the catenane/rotaxane supramolecular complexes with high selectivity.¹⁰ Due to these interactions, catenanes have been used for sensing, functional molecular devices, (i.e. switches¹¹, shuttles¹² and rotors¹³), and template-directed synthesis.^{14,15,16}

Catenane complexes have been actively studied by both experimental^{17,18,19,20,21,22} and computational methods.^{23,24,25} The latter have been instrumental in exploring their structural dynamics and energetics, often filling gaps in experimental observation. In particular, molecular dynamics (MD) simulations and molecular mechanics (MM) have proven quite useful in studying the effects of rotaxanes with and without solvation, and in exploring major factors that determine the structural dynamics during packing.²⁶ Accurate description of noncovalent interactions is also important in biological problems, like protein folding²⁷ and nucleobase packing and stacking.^{28,29,30}

The relative strengths of H-bonding and π -stacking have been debated. Studies have indicated^{31,32,33}, and we will demonstrate in this paper, that both may be significant to catenane stability. Components of the [3] catenane **2-4PF₆** structures³⁴ where [C-H...O] H-bonding and π -stacking effects occur are shown in Figure 1 (for clarity solvent molecules are not shown). We note that the [C-H...O] H-bonding involves an adjacent positively charged pyridinium group which adds a significant electrostatic component to the H-bond, strengthening it relative to a conventional hydrogen bond between neutral partners. Also, the stacking interaction involves a π -electron rich “*host*” and a π -electron-deficient “*guest*” that also leads to a stronger than usual π - π interaction. These noncovalent interactions drive self-assembly, but they can be significantly altered with only minor structural variations as we shall see.

The goal of this paper is twofold: 1) to use high quality electronic structure results to determine [C-H...O] H-bonding and π -stacking interaction energies that can be used to calibrate the Molecular Mechanics 3 (MM3) force field,^{35,36,37} and 2) to use symmetry-adapted perturbation theory (DFT-SAPT), which is a method that treats intermolecular interactions at a higher level than DFT, to explore these same interactions for the [3] catenane thereby calibrating the DFT results, and providing a decomposition of the energy into components that can provide insight into the description of larger systems. Although MD simulations using empirical (MM) force-fields have been a common tool for analyzing similar systems in the past, there has been little done to calibrate the accuracy of these force fields for [C-H...O] H-bonding and π -stacking interaction energies, in part because the structures involved for catenanes are generally complex. Density functional theory methods provide these capabilities and we now have higher quality DFT functionals that include dispersion effects implicitly so the quality of the interaction energy calculation is now much better than in the past. Nevertheless, DFT approximations intrinsically lack the ability to recover the $-C_6/R^6$ dependence on the London dispersion interaction energy or the interatomic/molecular distance R . Hence, clarifying the accuracy of our DFT calculations is

of essential importance. In this work, we implemented Grimme's DFT-D3 method (denoted by the suffix "-D3") to provide an empirical dispersion correction for DFT,^{38,39} and the results are compared with DFT-SAPT results with a large basis for ultimate determination of the quality of these methods.

Williams and coworkers proposed that the contribution of the [C-H...O] H-bonds to the overall binding is four times higher than that associated with the π -stacking interactions, with interaction energies between -82 and -78 kcal mol⁻¹ and between -21 and -23 kcal mol⁻¹ for the [C-H...O] and π -stacking interactions, respectively, at the HF/3-21G(d) level of theory.³⁴ This is a low level of theory by today's standards which does not describe dispersion effects at all, and has an incomplete description of electrostatics, and important basis set superposition errors, so it is important to reevaluate these interaction energies with more modern methods. We use DFT-SAPT as the benchmark for these interactions, and we compare with a variety of DFT and wavefunction theory methods, and with DFT-D3.

Details of the structural models used to study [C-H...O] hydrogen-bonding and π -stacking interactions and the calculated geometric parameters are presented in Section II. Section III.A provides the results of our structural modeling, while the DFT-SAPT results are presented and compared with MM3 in III.B. In Section III.C we present *ab initio*, DFT and DFT-D3 results and study the effects of basis sets and different levels of treatment of electron correlation. In Section III.D we use molecular electrostatic potential maps (MEPs) to provide further insight on the spatial structure of nonbonded interactions. Finally in section IV, the main findings are summarized.

II.A Structural Parameters

The crystallographic structure of the [3] catenane consists of two macrocyclic polyethers and one tetra-cationic cyclophane (Figure 1).³⁴ A fragmentation scheme to understand the systems, first introduced in ref. ³⁴, is shown in Figure 2 (a and b), wherein the parent molecule is broken into two complexes, **I** and **II**.

The relative contribution of [C-H...O] H-bonding interactions to the overall complex binding is established in **I** by deleting the naphthalene units associated with the 1,5 dioxynaphthalene rings without altering the relative orientation of the remaining components. In **II**, where π -stacking interactions are considered, the polyether chains are removed. The π -electron deficient bipyridinium unit referred to as the "guest" is sandwiched between π -electron rich "hosts". For these model complexes, constrained geometry optimizations at the HF/3-21G(d) level of theory have been performed to account for the addition of hydrogen atoms to take care of dangling bonds (see Supporting Information (SI) for a complete description). The final geometries are then subjected to single-point calculations at the HF, MP2, B3LYP, M05, M05-2X, and M06, M06-2X levels of theory and using DFT-D3.^{38,39}

II.B Theoretical Methods

We have carried out MM3^{35,36,37} calculations on [3] catenane partitioned into the [C-H...O] H-bonding and π -stacked complexes **I** and **II** (ref. Figure 2 (a) and (b)) to calibrate against *ab initio* and DFT methods. Hartree-Fock (HF), MP2 and traditional DFT functionals are included in our calculations; however these are not expected to be accurate for this application. The M05 and M06 family of functionals^{40,41} have been shown generally to provide accurate geometries and energies for a variety of dispersion-dominated systems.^{42,43,44} These methods are more computationally efficient than the MP2 method traditionally used to investigate π -stacked systems and are often more accurate. We have

therefore calculated the complexation energies of **I** and **II** each containing the π -electron rich “host” and π -electron deficient “guest” using the M05, M05-2X, and M06 and M06-2X functionals.

Another direction of the DFT theory involves adding dispersion as an external term to the functional. Here we use the DFT-D3 method from Grimme et al, as the most recent version of this approach which has been shown to be successful in similar supramolecular assemblies.⁴⁵ Still another approach is to include a nonlocal correlation part to describe dispersion in a standard LDA or GGA exchange and correlation calculation.^{46–48} We have not considered this option here.

We have studied sensitivity to basis set size for each method, using the basis sets (BS) BS1, BS2, BS3 and BS4 to denote 6–31G(d), 6–31G(d,p), 6–311G(d) and 6–311G(d,p). The results generally show excellent convergence as basis set is increased, so no explicit basis-set superposition error effects have been considered. All calculations were done using QChem 3.1.⁴⁹

Following previous work on the influence of dispersion interactions in supramolecular complexes, we expect that dispersion could significantly contribute to stabilization in **I** and **II**. Given this, we have chosen the density functional theory-symmetry-adapted perturbation theory (DFT-SAPT)^{50,51,52} approach, as a higher level method by which to calibrate the HF, MP2, DFT, DFT-D3 and MM3 calculations. The specific implementation of DFT-SAPT that we use is in the Molpro quantum chemistry program.⁵³ To the best of our knowledge no systematic study has been reported accounting for the decomposition of the intermolecular complexation energy for a catenane supramolecular complex employing DFT-SAPT.

The DFT-SAPT calculations were invoked using the density fitting (DF) approximation referred to as DF-DFT-SAPT. It has been demonstrated that interaction energies from this method deviate by less than 1% from corresponding DFT-SAPT results.⁵⁴ Also, Tekin and Jansen found that the performance of DF-DFT-SAPT is superior to that of the complete basis set limit CCSD(T) interaction energies (within 0.05 kcal mol⁻¹) for systems where π -stacks and C-H $\cdots$ are dominant.⁵⁵ In the DF-DFT-SAPT method the DFT orbitals are used in evaluating the electrostatics and first-order exchange-repulsion corrections to the interaction energy, with the induction and dispersion contributions (along with their exchange counterparts) calculated from response functions. The asymptotically corrected PBE0(PBE0AC) exchange-correlation (xc) functional containing 25% of ‘exact’ exchange^{56,57,58,59} along with the adiabatic local density approximation (ALDA) xc kernel was used for the monomers in this calculation.⁶⁰ Recently, Kim and coworkers studied the nature of anion-templated interactions in crystal structures containing pyridinium moieties (similar to our complexes) and found that the overall energetics are not significantly altered with increasing basis set size, such as comparing aug-cc-pVDZ versus aug-cc-pVTZ.⁶¹ Indeed, the aug-cc-pVDZ basis set is accurate enough in DFT calculations, however the previous work has highlighted that the SAPT dispersion energy evaluated with the former basis set is underestimated by 10–20% in comparison to the aug-cc-pVTZ basis set.⁶² Thus, the correlation consistent basis sets, both in their regular cc-pVnZ and (diffuse function-) aug-cc-pVnZ augmented variants were considered abbreviated as VDZ, aVDZ, VTZ and aVTZ. The asymptotic correction for the PBE0AC xc potential requires knowledge of the sum of the ionization potential (IP) (called the *shift*) and the highest occupied molecular orbital (HOMO) energy; both were calculated for our complexes at the PBE0/aug-cc-pVDZ level of theory.⁵⁹

III.A Computational Results: Structures

Starting from the known crystal structure of the [3] catenane, we have generated equilibrium structures for **I** and **II** by minimizing energies using HF/3–21G (d) and using MM3. The resulting MM3 minimized structures and the atomic numeration scheme are presented in Figures 3 and 4. Table S.I (in Supporting Information) summarizes calculated bond lengths and angles for the crystal structure (labeled “initial”), HF/3–21G (d) (labeled “*ab initio*”) and MM3 derived parameters. The *ab initio* results are in very close agreement with those presented by Williams and coworkers.³⁴ Examining the MM3 and *ab initio* determined structural parameters shows fair agreement between the calculated values. Bond distances differ an average of 0.081 Å for N–O bonds and 0.037 Å for H–O bonds in **I** and for **II** NCH angles differ by 1.76° on average. Thus at least for the calculation of molecular geometries, we conclude that the standard MM3 force field is well parameterized.

Examining the MM3 minimized structure of **I**, we see that the [C–H...O] H-bonding between the methyl groups of bipyridinium and both polyethers of the host leads to an asymmetric structure which facilitates a *rocking* dynamic effect.⁶³ The variation of R_{H...O} distances (both shortening and lengthening) reflects the relative overall strength of these interactions, induced by polarization of the neighboring nitrogen. For the bipyridinium the methyl C–H bonds are lengthened, due to short distance interactions with the polyether oxygens. These interactions lead to distances (H3_a...O4_a and H2_b...O4_b) that are less than the sum of the van der Waals radii for these atoms (2.7 Å), which is indicative of [C–H...O] H-bonding. These distances are consistent with short range [C–H...O] H-bonding observed with aromatic C–H groups adjacent to positively charged nitrogen in heterocycles³⁰, demonstrating that neighboring positive partial charge can indeed significantly augment C–H...O interactions. Likewise, these short range contacts derive from polarization of the methyl group by the adjacent nitrogen which confers a partial positive charge on the carbon atom, thus enhancing [C–H...O] H-bonding.

The MM3 minimized structure of **II** (Figure 4) has the two outer naphthalenes aligned parallel to each other, while distortions from planarity occur in the bipyridinium; torsional angles, for example, are C3–C4–C9–C8 (31.05°) and C5–C4–C9–C8 (–149.05°), versus the initial parameters of 9.35° and –169.23°, respectively. There is also significant shifting of the bipyridinium such that the naphthalenes interact with only one pyridine ring. Ideally, during crystal packing H-bonding probably exists between the N⁺–CH protons and the 1, 5 dioxynaphthalene units. N⁺–CH...O hydrogen bonds thus make a major contribution to intermolecular complexation. This is notable since most catenanes contain both hydrogen bonds between the organic groups and either dipolar attractions between polar groups or π – π stacking forces between the units. Any vertical or horizontal shifting of bipyridinium is presumably avoided because of Pauli repulsion. In addition, the increased centroid distances of 4.31 Å (R2–cm) and 4.45 Å (R3–cm) indicates a well-balanced π – π stacking arrangement.

Two distinct structural details should be emphasized (i) the long axes of all three molecules are tilted away from their starting placement and (ii) there is a large angle between the nitrogeneous plane (a part of the “guest” bipyridinium unit) and the naphthalene plane. To account for the molecules tilting, we assume that since the major driving forces are the π – π stacking interactions, the more favorable interactions are actually the π – π attractions that overcome π – π repulsions, leading to a preference for an offset and slipped geometry. On the basis of this idea and looking at the drawings in Fig. 4, it is evident that the electronegative nitrogen cation can indeed enhance the π – π interactions, introducing a relative shift and increasing the perpendicular separation between the two naphthalene units.

III.B SAPT Calculations

SAPT provides the most rigorous approach of those that we have considered, both for evaluating E and for partitioning the energy into physically defined energy components. SAPT calculations are time consuming, however the complexes considered here are small enough that such calculations can be performed, even with aug-cc-pVTZ basis sets. In SAPT the total interaction energy (E_{tot}) is naturally partitioned into electrostatics (E_{el}), effective induction (E_i), effective dispersion (E_D), and effective exchange-repulsion (E_{ex}) energies. The density functional based theory (DFT) SAPT method combines DFT with SAPT using quantities calculated from Kohn-Sham density and linear response density matrices.^{64,65} Ideally, we envision our DFT-SAPT calculations serving as a benchmark for exploiting the design of solid state host-guest complexes, for instance, crystal structures containing pyridinium moieties. In the present work, we carried out calculations involving cc-pVDZ, cc-pVTZ, aug-cc-pVDZ and aug-cc-pVTZ basis sets, which we denote by VDZ, VTZ, AVDZ and AVTZ. The calculations in this paper were done as single point calculations for two variations on the structures **I** and **II**, in which **bI** and **bII** are structures minimized using the MM3 force field, while **bI** and **bII** match the reference structures of Williams and coworkers.³⁴ The DFT-SAPT results for these structures are presented in Tables I and II, and plotted in Fig. 5. Additional details of the DFT-SAPT results are presented in Tables S.II and S.III in Supporting Information. Note that structures **I** and **II** are both trimers (three fragments), and we have approximated the total SAPT energy by summing calculations for the two nearest neighbor dimer components. We found that the aug-cc-pVDZ and aug-cc-pVTZ dispersion energies show negligible differences for the trimer structures. The dimer structures show slight differences in dispersion energies between the two basis sets, so for calibration and benchmarking we conclude the VTZ basis set should be used.

Fig. 5 and Table II reveal that a VDZ basis without diffuse functions leads to an underestimation of the E relative to all other basis sets. It can be seen that, when passing from VDZ to the VTZ basis there is a significant increase in stabilization amounting to 13.3 kcal/mol in the case of [C-H...O] H-bonding in **bI** complexes. On the other hand, E_{ex} stabilization energies are smaller than for H-bonded systems and passing to a larger basis set is connected to a slightly smaller stabilization of 5.3 kcal/mol for **bII** complex.

It is well known that systems with diffuse charge distributions (such as are found in the electron-deficient pyridinium moiety) requires the use of diffuse basis functions. Dabkowska *et. al* demonstrated in biological complexes that the SAPT dispersion energy evaluated with aVDZ is underestimated by 10–20% in comparison to aVTZ.⁶² However, the changes in E and E_{disp} for **a,bI** and **a,bII** are not so large (about 1.0 kcal/mol) when going from aVDZ to aVTZ. Thus it seems that the aVDZ basis set is adequate for this work, which is an important conclusion given the significant computational effort associated with the larger basis set.

The results in Table I show that the electrostatic interaction makes the largest contribution to complexation for **a,bI**. The decomposition of E reveals the E_{el} contribution accounts to over 60–75% of the total E for complexes **a,bI**, whereas for **a,bII** the E_{disp} contribution is dominant. This result for **a,bI** is expected given that the polar C-H...O moiety interacts with the charged bipyridinium. Meanwhile, the exchange-repulsion contribution is short-range and small for **a,bI**. Typically in electrostatically dominated complexes there are significant contributions from induction, however Table I shows that E_i plays a secondary role in **a,bI**. In contrast to this, for **a,bII**, the electrostatic, exchange and induction energies are comparable in magnitude. The E_{el}/E_i ratio is 3.80 for **bI** compared to 0.84 for **bII**. Note also that induction is comparable in **a,bI** and **bII**; this means that induction arising from the

charged bipyridinium polarizing the two electron-rich naphthalene complexes is comparable to that of the bipyridinium polarizing the C-H...O.

In nonpolar molecules dispersion is usually the dominant attractive force. In the present application Table II shows that dispersion is much larger for **a,bII** than for **a,bI**, and in fact dispersion is the dominant contribution to the energy of **a,bII**, as also pointed out in ref.³⁴. The interactions associated with π - π interactions are associated with displaced-stacked geometries, such as parallel and angle-displaced geometries. The $E^{(2)}$ of **bII** is roughly 78% dispersion; whereas in **bI** dispersion makes a small contribution to the total energy.

The DFT-SAPT complexation energies have only modest deviations from the estimated MM3 complexation energies given in Table II. Indeed, for the largest basis set, the difference between MM3 and DFT-SAPT is -17.0 kcal/mol for **bI**, +7.4 kcal/mol for **bII**, +9.2 kcal/mol for **aI** and +7.1 kcal/mol for **aII**. While this agreement is not of chemical accuracy, the level of agreement provides confidence in the use of MM3 for empirical potential modeling of the catenane structures.

III.C DFT and Wavefunction Results

The complexation energies (E) for the structures **a,bI** and **a,bII** calculated using HF, MP2, B3LYP, for the meta-GGA DFT functionals [M05, M05-2X, M06 and M06-2X], for DFT-D3, and using the MM3 force field are summarized in Tables III and IV. Note that in general the “a” and “b” structures lead to similar results to each other for a given level of theory, however especially for the **aII/bII** comparison, there are important differences which reflect the conformational flexibility of the structures. Also note that our calculated E 's for **bI** and **bII** are in good agreement with ref.³⁴ for calculations at the same level of theory (HF/3-21G(d)) and the same structure (the “b” structure), being, within 0.2 and 3.2 kcal/mol. However it is clear from Table III that the HF/3-21G(d) results is poorly converged with respect to basis set, and for the **aII** structure that energy is off by over 20 kcal/mol compared to DFT-SAPT.

Table III shows that even for large basis sets HF theory severely underestimates the noncovalent interactions in **a,bI** and **a,bII** compared to DFT-SAPT, due to HF neglect of electron correlation. The MP2 results show stronger binding than HF, but for the largest basis set we considered, MP2 is in error by 10–25 kcal/mol, including overestimation of the binding for **bI**, underestimation for **bII**, and overestimation for **a,bII**. The average electron correlation energies (calculated differences between MP2 and HF) for **aI** and **bI** are -13.3 and -12.5 kcal/mol, and for **aII** and **bII** are -34.1 and -34.6 kcal/mol, respectively, for the largest basis sets. This three-fold difference in magnitude between the **a,bI** and **a,bII** structures accords with the more electrostatic character of the [C-H...O] H-bond. In principle, the proton donor is sp^3 -hybridized, and consequently the hydrogen-bonded C-H bond contracts due to electrostatic interaction with the neighboring proton acceptor. In general, the BS1 results are much different from BS2, BS3, BS4, so we ignore this basis in the following analysis. The qualitative differences between HF and the MP2 level of theory are not surprising for the latter basis sets for **a,bII**; the MP2 method is well-known to give questionable results for π - π stacking interactions, often exceeding 100% overestimation for dispersion in unsaturated systems. Hence, its usefulness for this type of structure is questionable. In the next few paragraphs, a number of standard DFT procedures which take into account dispersion are assessed.

Table III shows that for all the structures considered, the B3LYP method is particularly unsuited for describing the complexation energy, with substantial underestimation compared to DFT-SAPT except for **bI**. This is, of course, a well-known flaw with B3LYP. The M05

and M06 functionals show nonsystematic variation compared to DFT-SAPT for the different structures and different functionals. If we confine our discussion to BS4, then we find that for **bI**, the 2X functional are better but for **bII**, the 2X functional are worse. For **a,bII**, there are no systematic trends with choice of M0X functional and errors larger than 10 kcal/mol often occur. These conclusions are in contrast to what has been noted for other systems,⁴² where M06-2X is found to give the best results.

Traditional DFT provides acceptable E for hydrogen bonded complexes (such as **I**) which are dominated by electrostatic interactions, but in terms of the same protocol used for π -stacked complexes there is statistically no overall improvement. Doubling of the amount of Hartree-Fock exchange (X) (going from X=27 to 54) thus does not improve E for M06 versus M06-2X, although the former asymptotically yields no dispersion which is important for large complexes.

Now we consider the DFT-D3 results wherein many-body dispersion is explicitly included in the calculations. To study this, DFT-D3 calculations were performed for a number of representative DFT functionals (B3LYP, M05, M05-2X, M06, and M06-2X). The results are presented in Tables III and IV. Table III shows the B3LYP/DFT-D3 results, which show major differences from the corresponding B3LYP results. This indicates that dispersion interactions play a major role. In this case the DFT-D3 results are not systematically better than B3LYP compared to DFT-SAPT, which means that the B3LYP functional provides a poor reference for DFT-D3. Table IV shows DFT-D3 based on the M0X functional. Here we see results that are systematically closer to the DFT-SAPT results than the corresponding non-dispersion result, and much better than B3LYP/DFT-D3. There is some variation in the results with choice of functional, but this variation is smaller than for the non-dispersion results. The M06 results are generally better than M05, but M06 and M06-2X are on average about equally good. In the case of M06-2X, the differences between DFT-D3 and DFT-SAPT are -9.6, +2.2, -5.3, and +1.8 kcal/mol for **bI**, **bII**, **bI**, and **bII**, respectively, which is overall excellent agreement for these two quite different methods.

III.D. Potential Maps

Molecular electrostatic potentials [MEPs] are a powerful predictive and interpretive tool to rationalize trends in “host-guest” complexes and noncovalent interactions, such as [C-H...O] H-bonding and π -stacking. The MEPs of **bI** and **bII** obtained at the MP2/6-31G (d, p) level are plotted in Fig. 6. The strongest interactions occur in the most negative MEP region (indicated in red), and the weakest interactions take place in the less negative region shaded blue. We observe that there are slight differences in the MEPs between the two 1,5-dioxynaphthalene units in **bI**, but the similarities are striking. There is a significant area of negative electron density on the outer perimeter of both fragments and some of the peripheral oxygen atoms are more negative (shaded yellow). This indicates that there is a significant electron-deficient pocket (highlighted blue) between the nitrogen atoms of the bipyridinium unit. By contrast, the methyl groups of the bipyridinium unit are slightly negative (green regions) as induced by the charge-dipole interactions, with the oxygen atoms in the “host” units playing a crucial role in the binding. These phenomena in **bI** are also observed in **bII** with the two naphthalenes and “guest” component MEPs. Overall, for both **bI** and **bII**, the MEPs schemes are consistent with the importance of [C-H...O] H-bonding and π -stacking interactions in the binding between guest and host complexes, primarily because there are significant regions of electron depletion (repulsion) and accumulation (attraction).

IV. Summary

In this study, we have used *ab initio*, DFT, DFT-D3 and DFT-SAPT methods to study interactions in [C-H...O] H-bonded and π - π stacked complexes that appear in [3] catenane 2·4PF₆, and used the results to calibrate the MM3 force field. The MM3 results show reasonable though not quantitative agreement with DFT-SAPT, which enhances our confidence in using MM3 to model the important interactions of complex supramolecular structures, which are computationally expensive to study with electronic structure methods. The comparisons also show how *ab initio* and DFT results can be severely in error, especially for the π - π stacked complexes.

The minimized MM3 geometries of **bI** and **bII** show that the tilting and shifting of the bipyridinium has two distinct functions during template-designed synthesis: (i) the N⁺-CH...O hydrogen bonds make a major contribution to intermolecular binding in **bI** and (ii) π - π attractions overcome π - π repulsions in **bII**. These effects are notable since most catenanes contain only weak intermolecular interactions in the absence of these charge-enhanced hydrogen bond and π - π interactions. We have also demonstrated that many of the often-used electronic structure methods, including MP2 and the widely used B3LYP method make substantial errors in binding energies, often over 20 kcal/mol for these structures. The M0X functionals were generally better than MP2 and B3LYP, but errors with these methods were sometimes large and showed nonsystematic variation with choice of functional. On the other hand, the DFT-D3 approach when combined with M06 or M06-2X produced results that were in essentially quantitative agreement with DFT-SAPT, showing that this combination of meta-GGA with dispersion correction is well suited for benchmarking these structures.

Our studies have demonstrated that the original HF-3/21G work of Williams and coworkers³⁴ was based on calculations that missed important effects, especially dispersion interactions, in addition to basis set incompleteness problems. Curiously our best quality results (DFT-SAPT) are in reasonable agreement with the HF-3/21G(d) calculations due to a variety of accidental cancellations of error. However it is clear that M06-2X/DFT-D3 is to be preferred over all of the other methods we studied.

The DFT-SAPT analysis reveals that electrostatics dominates the interaction for complex **bI**, while dispersion is dominant in complex **bII**. While DFT-SAPT is not scalable to significantly larger systems, this comparison provides an important benchmark for further improvements in DFT functionals that can be scaled. In addition, the comparison between the VnZ and aVnZ basis sets demonstrates it is much better for a balanced description to increase the basis to VTZ size before adding diffuse functions. Improvements of both the E and the electronic contributions (E_{el} , E_{ex} , E_{ind} and E_{disp}) are not so large (1.6 kcal/mol for **bI** and **bII**) when augmenting the VTZ basis to aVTZ quality. So, we recommend for similar aromatic electronrich and electron-deficient supramolecular complexes minimized using a force field, one might compromise and do all DFT-SAPT calculations indiscriminately with the VTZ basis at the cost of augmenting with diffuse functions. With this in mind, it is clear that improved DFT methods for describing these weak interactions in applications to the modeling of supramolecular complexes and biological systems are useful for future calibration.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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FIG. 1. The crystallographic structure of [3] catenane illustrating regions of π -stacking and [C-H...O] hydrogen-bonding interactions. The color labels for the atoms are carbon (gray), oxygen (red), nitrogen (blue) and hydrogen (white).

FIG 2.

The fragmentation scheme for complexes **I** and **II** from the crystallographic structure of [3]catenane. The relative contribution of [C-H...O] hydrogen-bonded interactions to the overall complex is achieved by deleting the naphthalene units associated with the 1, 5 dioxynaphthalene rings for **I** while in **II** where π - π stacking interactions are considered, the polyether chains are removed. In both, the π -electron deficient bipyridinium unit “guest” is in between each “host”. The color labels for the atoms are carbon (gray), oxygen (red), nitrogen (blue) and hydrogen (white).

(a) Top View

(b) Side View

FIG 3.

Atomic numbering for complex **bI**. Color scheme for the atoms are carbon (gray), hydrogen (white), and nitrogen (blue).

(a) Top View

(b) Side View

FIG 4. Atomic numbering for complex **bII**. Color scheme for the atoms are carbon (gray), hydrogen (white), and nitrogen (blue).

Fig. 5. DFT-SAPT interaction energy contributions for bI and bII with VDZ, aVDZ, VTZ and aVTZ basis sets.

FIG 6. Complexes (a) $b\text{I}$ and (b) $b\text{II}$ MEPs. The MEPs were calculated at the MP2/6-31G (d, p) level of theory for the MM3 minimized structure.

TABLE I

First-order DF-DFT-SAPT electrostatic ($E_{el}^{(1)}$), exchange-electrostatic ($E_{ex}^{(1)}$) perturbation energies and the total energy $E^{(1)}$ (in kcal/mol) for **bI** and **bII** components.

Complex	$E_{el}^{(1)}$	$E_{ex}^{(1)}$	$E^{(1)}$	(HF)
bI				
cc-pVDZ	-68.5	9.2	-59.3	7.96
cc-pVTZ	-67.2	8.6	-58.7	-1.35
aug-cc-pVDZ	-66.4	9.6	-56.8	-3.22
aug-cc-pVTZ	-66.1	9.5	-56.6	-3.24
bII				
cc-pVDZ	-15.7	14.3	-1.34	-2.69
cc-pVTZ	-14.6	14.0	-0.63	-3.11
aug-cc-pVDZ	-13.8	13.9	0.13	-3.20
aug-cc-pVTZ	-13.7	13.7	0.03	-3.23

TABLE II

Second-order DF-DFT-SAPT induction ($E_{i,0}^{(2)}$), exchange-induction ($E_{i,Ex}^{(2)}$), total induction ($E_i^{(2)}$), dispersion ($E_{D,0}^{(2)}$), exchange-dispersion ($E_{D,Ex}^{(2)}$), total dispersion ($E_D^{(2)}$), and total second-order ($E^{(2)}$) and total complexation ($E^{(1)} + E^{(2)}$) energies for **bI** and **bII** components (in kcal/mol).

Complex	$E_{i,0}^{(2)}$	$E_{i,Ex}^{(2)}$	$E_i^{(2)}$	$E_{D,0}^{(2)}$	$E_{D,Ex}^{(2)}$	$E_D^{(2)}$	$E^{(1)} + E^{(2)}$	$E^{(1)} + E^{(2)} + (HF)$
bI								
cc-pVDZ	-23.6	3.6	-15.8	-18.6	1.1	-10.5	-81.1	-73.1
cc-pVTZ	-25.9	3.6	-17.0	-24.7	1.3	-14.0	-85.0	-86.4
aug-cc-pVDZ	-26.3	3.5	-17.2	-26.0	1.4	-14.8	-84.3	-87.5
aug-cc-pVTZ	-26.4	3.6	-17.3	-27.0	1.5	-15.6	-84.8	-88.0
MM3								-78.8
bII								
cc-pVDZ	-18.6	7.7	-14.1	-36.5	2.6	-17.5	-23.7	-26.4
cc-pVTZ	-21.9	7.8	-15.9	-44.8	2.9	-21.2	-28.6	-31.7
aug-cc-pVDZ	-22.5	7.5	-16.3	-46.0	3.0	-22.6	-29.2	-32.4
aug-cc-pVTZ	-22.6	7.7	-16.4	-47.3	3.1	-23.6	-30.1	-33.3
MM3							-26.2	

TABLE III

Calculated interaction energies for complexes **I** and **II**. Energies in kcal/mol.

Complex	Basis Set	HF	MP2	B3LYP	B3LYP/ DFT-D3	MM3/SAPT
<i>a</i>I	3-21G(d)	-86.5	-90.8	-86.0	-104.3	
	BS1	-68.7	-80.3	-68.1	-86.3	
	BS2	-69.0	-80.0	-68.2	-86.3	
	BS3	-70.7	-84.1	-70.9	-89.0	
	BS4	-70.0	-83.3	-70.4	-88.5	
						-87.6/-70.6
<i>a</i>II	3-21G(d)	-11.9	-28.8	-13.3	-40.2	
	BS1	-9.9	-35.4	-12.8	-39.0	
	BS2	-9.9	-35.7	-13.3	-38.9	
	BS3	-7.7	-41.8	-11.9	-39.1	
	BS4	-7.8	-41.9	-11.9	-38.6	
						-24.7/-32.1
<i>b</i>I	3-21G(d)	-78.6	-85.2	-79.9	-102.4	
	BS1	-65.2	-76.7	-65.9	-102.2	
	BS2	-65.5	-76.8	-66.0	-105.7	
	BS3	-66.7	-79.6	-68.0	-104.1	
	BS4	-66.1	-78.6	-67.4	-102.4	
						-78.8/-88.0
<i>b</i>II	3-21G(d)	-25.5	-44.1	-30.8	-39.6	
	BS1	-25.2	-52.6	-30.8	-39.6	
	BS2	-25.2	-52.0	-30.5	-39.6	
	BS3	-24.6	-58.3	-30.0	-39.2	
	BS4	-24.2	-58.8	-29.5	-39.6	
						-26.2/-33.3

^aDenotes MM3 minimized structures used for input for *ab initio* calculations.

^bDenotes structures taken from ref. 32.

TABLE IV

Calculated interaction energies for complexes **I** and **II**. Energies in kcal/mol.

Complex	Basis Set	M05	M05/ DFT-D3	M05-2X	M05-2X/ DFT-D3	M06	M06/ DFT-D3	M06-2X	M06-2X/ DFT-D3	MM3/SAPT
<i>a</i>I	3-21G(d)	-94.7	-104.5	-91.4	-97.7	-92.4	-92.4	-91.2	-91.9	
	BS1	-76.4	-84.3	-76.7	-84.0	-78.4	-76.6	-75.7	-76.0	
	BS2	-76.1	-84.4	-77.4	-85.5	-78.2	-76.8	-76.0	-76.4	
	BS3	-78.5	-87.0	-82.0	-88.9	-81.7	-80.8	-80.1	-80.7	
	BS4	-83.7	-86.5	-73.4	-80.2	-80.1	-80.1	-76.8	-80.2	
<hr/>										
<i>a</i>II	3-21G(d)	-34.9	-35.5	-25.4	-37.1	-46.6	-33.2	-35.8	-33.3	-87.6/-70.6
	BS1	-34.3	-35.0	-37.3	-34.3	-47.4	-32.9	-32.6	-30.9	
	BS2	-33.5	-35.2	-22.7	-34.3	-46.9	-33.2	-32.5	-31.0	
	BS3	-34.9	-35.7	-24.3	-37.6	-51.4	-36.8	-36.5	-35.1	
	BS4	-41.3	-35.3	-24.7	-36.7	-34.3	-36.1	-43.9	-34.3	
<hr/>										
<i>b</i>I	3-21G(d)	-85.1	-121.4	-83.9	-115.4	-81.7	-94.0	-83.5	-93.3	-24.7/-32.1
	BS1	-71.7	-100.7	-73.3	-101.0	-72.9	-94.0	-73.0	-94.7	
	BS2	-71.8	-100.6	-73.8	-101.1	-85.2	-98.6	-73.3	-98.4	
	BS3	-73.2	-103.9	-77.4	-106.5	-75.4	-96.8	-75.5	-96.7	
	BS4	-78.3	-102.3	-65.6	-104.7	-76.1	-94.0	-69.4	-93.3	
<hr/>										
<i>b</i>II	3-21G(d)	-49.3	-36.9	-41.9	-38.0	-49.6	-33.2	-50.1	-31.5	-78.8/-88.0
	BS1	-50.5	-35.2	-38.8	-35.3	-48.8	-33.5	-48.6	-33.5	
	BS2	-50.0	-35.5	-38.8	-35.3	-48.4	-36.9	-48.3	-35.7	
	BS3	-51.1	-35.7	-41.4	-38.8	-51.8	-36.3	-51.9	-35.0	
	BS4	-53.8	-35.4	-38.3	-35.3	-50.6	-33.2	-51.0	-31.5	
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										-26.2/-33.3

^aDenotes MM3 minimized structures used for input for *ab initio* calculations.

^bDenotes structures taken from ref. 32.