

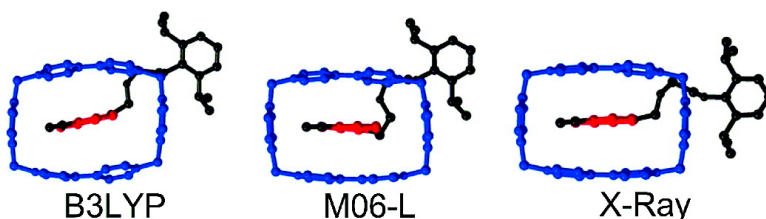
Communication

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Experimentally-Based Recommendations of Density Functionals for Predicting Properties in Mechanically Interlocked Molecules

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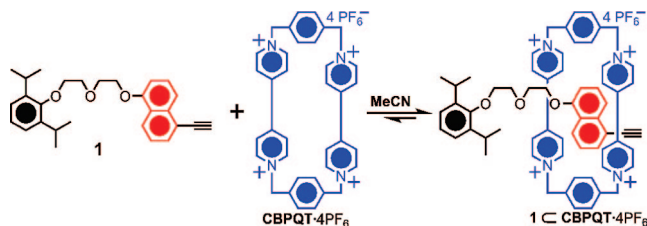
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Mechanically interlocked molecules, such as catenanes and rotaxanes, have evolved from simple structural curiosities into degenerate molecular shuttles and bistable switches, which are playing a central role in emergent molecular electronic devices.^{1,2} The specific molecular systems used by Heath, Stoddart, and co-workers involve a tetracationic cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) ring encircling another ring in the case of a [2]catenane or a dumbbell in the case of a [2]rotaxane. Recently, we developed³ a class of functionally rigid [2]rotaxanes which exhibit lower shuttling barriers (9.6 kcal/mol compared to 15 kcal mol⁻¹) than previous nonrigid molecular shuttles and switches.

These recent advances in molecular electronics have benefited⁴ from theoretical studies using quantum mechanics (QM) and force field (FF) calculations. We have been concerned with the accuracy of such calculations, particularly, the relative binding energies, geometries of superstructures, and charge transfer (CT) excitation energies. Consequently, we report here experimental thermodynamic and spectroscopic data on the [2]pseudorotaxane [1_CCBPQT]⁴⁺ (Scheme 1) which we use to assess the accuracy of common computational methods. We consider here the popular B3LYP,⁵ PBE,⁶ X3LYP⁷ functionals of density functional theory (DFT) and the Hartree–Fock⁸ methods along with the M06-class of DFT functionals (M06-L, M06, M06-2X, M06-HF) developed⁹ to improve the accuracy for describing medium range attractive interactions. All calculations were done with Jaguar 7.0 (release 207).¹⁰

Scheme 1. Formation of [2]Pseudorotaxane 1_CCBPQT·4PF₆⁻



Although B3LYP has been shown¹¹ to provide accurate energetics and structures for main-group and transition metal reaction mechanisms, we find that it leads to a poor description of the attractive medium-range interactions (London dispersion and π – π stacking) important in noncovalently bound systems.¹²

To obtain an experimental benchmark for comparing DFT methods, we analyzed an equimolar amount of **1** and CBPQT·4PF₆ at various concentrations over a 60 K range using ¹H NMR spectroscopy (see Supporting Information (SI)) to measure the binding. We obtained experimental values¹³ of $\Delta H = -4.9 \pm 1$

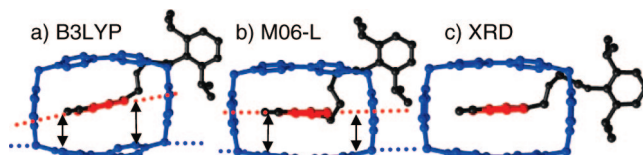


Figure 1. DFT-optimized superstructures using (a) B3LYP and (b) M06-L functionals, compared to (c) fragment of an X-ray diffraction (XRD) superstructure.

kcal mol⁻¹ and $\Delta S = -11 \pm 20$ cal mol⁻¹ K⁻¹ leading to $\Delta G = -1.6$ kcal mol⁻¹.

Starting with structures from crystallographic data¹⁴ we optimized the geometry using the 6-31G** basis set¹⁵ with the B3LYP,¹⁶ M06-L, and PBE functionals in the gas phase. Single-point energies were calculated using the 6-311++G** basis set. Solvent corrections were based on single-point self-consistent Poisson–Boltzmann continuum solvation calculations for acetonitrile ($\epsilon = 37.5$, $R_0 = 2.18$ Å) using the PBF¹⁷ module in Jaguar.

Figure 1 shows the optimized superstructures for [1_CCBPQT]⁴⁺ with B3LYP and M06-L compared to a fragment of an X-ray diffraction structure of a similar [2]rotaxane.¹⁴ B3LYP leads to a structure (Figure 1a) with the naphthyl (NP) and bipyridinium at an $\sim 14^\circ$ angle and at 3.6–3.8 Å from each other, while the M06-L geometry (Figure 1b) has them almost completely parallel at 3.4 Å, in agreement with experiment (3.3–3.4 Å). Thus, M06-L accommodates the NP unit inside the CBPQT⁴⁺ in good agreement with XRD, while B3LYP leads to repulsive medium-range interactions that dominate inside the tetracationic cyclophane, emphasizing [C–H···O] attractive interactions. The result is that B3LYP has a repulsive association $\Delta H = 24.2$ kcal mol⁻¹, while the PBE functional also predicts a repulsive interaction, $\Delta H = 16.6$ kcal mol⁻¹. Since Hartree–Fock leads to a strong repulsion (41.6 kcal mol⁻¹) at the distance for which experiment leads to -4.9 kcal mol⁻¹, the total correlation energy is 46.5 kcal mol⁻¹. This short-range electron correlation is what should be attained by DFT methods.

Using DREIDING¹⁸ empirical FF with various standard charge schemes also predicts that [1_CCBPQT]⁴⁺ is unbound (by 9.8 or 19.1 kcal mol⁻¹), showing the challenge these complexes are to theory.

The only DFT methods that predict the stability of [1_CCBPQT]⁴⁺ are the M06-class. Using M06-L optimized superstructures for [1_CCBPQT]⁴⁺, we performed single-point calculations with the hybrid functionals in the M06 suite. The M06 functional leads to a binding energy of $\Delta H = -27.5$ kcal mol⁻¹ in acetonitrile. As the percentage of Hartree–Fock (HF) exchange is increased in the series of functionals (27% for M06, 54% for M06-2X, and 100% for M06-HF), the binding energy becomes increasingly exothermic with M06-HF leading to $\Delta H = -30.8$ kcal mol⁻¹.

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Table 1. Comparison of Predicted¹⁹ ΔH in the Formation of [1 \subset CBPQT]⁴⁺ and [1 \subset CBPQT]·4Cl^a

geometry	SPE	[1 \subset CBPQT] ⁴⁺		[1 \subset CBPQT]·4Cl	
		MeCN	gas phase	MeCN	gas phase
B3LYP	B3LYP	24.2	-24.9	10.5	-23.4
B3LYP	M06-L	-20.3	-70.3	-38.6	-70.9
B3LYP	M06	-20.9	-70.8	-39.8	-75.4
B3LYP	M06-2X	-17.9	-68.3	-36.9	-77.9
B3LYP	M06-HF	-20.5	-74.9	-38.8	-88.2
M06-L	M06-L	-27.5	-75.2	-36.2	-58.4
M06-L	M06	-27.0	-74.0	-34.8	-59.3
M06-L	M06-2X	-28.1	-75.6	-33.3	-64.1
M06-L	M06-HF	-30.8	-82.1	-33.4	-72.9
M06-L	B3LYP	27.6	-18.6	23.9	0.8
M06-L	X3LYP	23.1	-23.3	18.7	-5.0
PBE	PBE	16.6	-34.5	16.1	-10.7
M06-L	HF	41.6	-6.7	41.1	1.6
DREIDING		QEeq charges 19.1		B3LYP charges 9.8	
experiment in MeCN		[1 \subset CBPQT]·4PF ₆		-4.9 ± 1	

^a All numbers have been corrected for ZPE and integrated specific heat using the B3LYP vibrational frequencies. See SI.

To evaluate the effect of the charge on the predicted binding energy, we optimized four Cl counterions around the previously optimized structures, leading to a neutral system. As shown in Table 1, we find the same trends. Including the “full” counterpoise correction²⁰ (7.4 kcal mol⁻¹ for M06, 6.2 kcal mol⁻¹ for M06-L, and 4.7 kcal mol⁻¹ for B3LYP all with the 6-311++G** basis set), the predicted association for M06, $\Delta H = -19.6$ kcal mol⁻¹ is still 14.7 kcal mol⁻¹ too strongly bound. These results indicate that M06 is too attractive at distances shorter than the equilibrium structures used in its parametrization. We recommend including such new experimental data in future optimizations of density functionals.

Using UV-vis spectroscopy, we measured $\lambda_{\text{max}} = 354$ nm ($\Delta E_{\text{CT}} = 3.50$ eV) for [1 \subset CBPQT]·4PF₆ in MeCN at 298 K. This absorption maximum can be compared to the excitation energies (Table 2) calculated using time-dependent DFT (TD-DFT) as implemented²¹ in Jaguar 7.0. Table 2 shows that TD-B3LYP predicts an excitation energy $\Delta E_{\text{CT}} = 1.33$ eV, TD-M06 $\Delta E_{\text{CT}} = 1.59$ eV, and TD-M06-HF²² $\Delta E_{\text{CT}} = 3.42$ eV. Thus M06-HF, which is expected to be the most accurate of the M06 family for CT excitation energies, is amazingly close to the experimental $\Delta E_{\text{CT}} = 3.5$ eV.

Table 2. Comparison of Predicted Charge Transfer and Excitation Energies for [1 \subset CBPQT]⁴⁺

method	charge transfer		CT excitation (eV)
	Mulliken	electrostatic	experiment 3.5 eV
B3LYP	-0.081	0.028	1.33
M06	0.047	-0.015	1.59
M06-HF	0.163	-0.030	3.42

Examination of the HOMO and LUMO from M06-HF for this transition shows the expected character of a hole on the DNP and an occupied LUMO on the CBPQT. This contrasts with B3LYP, PBE, and M06 where the HOMO is much more delocalized. Analyzing the charge distributions for M06-HF using electrostatically derived (ESD) charges leads to a net charge of -0.03 on **1**, whereas Mulliken populations lead to +0.163 (Table 2). This unreasonable result for the charge distribution from ESD is probably because of the large number of internal atoms far from the surface leading to an electrostatic potential that is insensitive to their charge distributions.

These investigations indicate that structural, optical, and binding properties of mechanically interlocked molecules and complexes are much more accurately predicted with the M06-class of functionals than with B3LYP, X3LYP, or PBE. In addition, TD-M06-HF leads to accurate CT excitation energies, making it useful for predicting optical spectra. Since the M06-L functional does not include HF exchange, it is faster for geometry optimization, making it an excellent choice for noncovalently bound systems where π - π stacking and medium-range interactions are vital. Lacking HF exchange should make M06-L practical for incorporation into periodic codes using plane wave methods.

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Supporting Information Available: Supplied are NMR spectra, thermodynamic properties, and XYZ coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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