

## Role of Face-to-Face and Edge-to-Face Aromatic Interactions in the Inclusion Complexation of Cyclobis(paraquat-*p*-phenylene): A Theoretical Study

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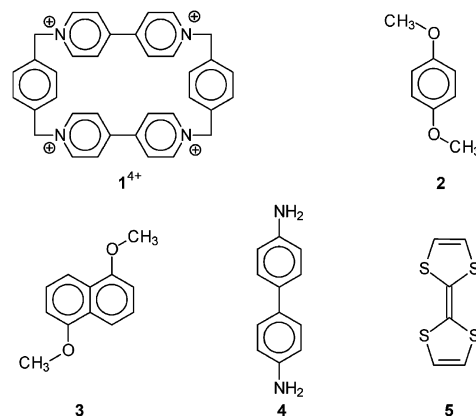
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**Abstract:** A B3LYP/6-31G(d,p) and MP2/6-31G(d,p)//B3LYP/6-31G(d,p) computational study of the gas-phase complexation of cyclobis(paraquat-*p*-phenylene) (**1**<sup>4+</sup>) with four typical aromatic guests, namely, 1,4-dimethoxybenzene (**2**), 1,5-dimethoxynaphthalene (**3**), benzidine (**4**), and tetrathiafulvalene (**5**), has been carried out. The structure of the host has been successively split into two responsible substructures, respectively, for the face-to-face and edge-to-face interactions with the guests. The sum of the two interactions calculated at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p)//B3LYP/6-31G(d,p) levels for each guest proved to be in good agreement with the overall binding energy of the host calculated at the corresponding level of theory. The results show that the binding of the complexes is primarily due to London dispersion interactions which require wave function-based correlation methods for an adequate description. Face-to-face interactions are about 1 order of magnitude more important than edge-to-face interactions in determining the overall binding energy. While edge-to-face interactions essentially depend on London dispersion forces, face-to-face interactions depend about one-half on electrostatic and frontier orbital contributions (the latter being more important) and the other half on London dispersion forces.

The design and creation of machine-like molecular assemblies has attracted considerable attention in recent years because of potential applications in the field of information processing and technology.<sup>1</sup> Many key advances in developing new nanoscale machines and devices have come from the outstanding contributions of Stoddart and co-workers, who have prepared a variety of catenanes, rotaxanes, pseudorotaxanes, molecular switches, and shuttles by exploiting the peculiar properties of the tetracationic host cyclobis(paraquat-*p*-phenylene), **1**<sup>4+</sup>.<sup>2</sup>

The receptor **1**<sup>4+</sup> has proved to have a strong affinity for a wide range of aromatic  $\pi$ -electron-rich substrates, which is increased by the presence of poly(ethyleneoxy) sidearms. A number of interactions were considered to be responsible for the observed binding energies,<sup>2</sup> among

CHART 1



them  $\pi$ - $\pi$  stacking between the  $\pi$ -electron-deficient and the  $\pi$ -electron-rich aromatic rings,<sup>3</sup> [C-H $\cdots\pi$ ] interactions between the hydrogen atoms attached to the aromatic guest and the *p*-xylyl spacers of the host,<sup>4</sup> as well as [C-H $\cdots$ O] hydrogen bonding between the protons  $\alpha$  to the pyridinium nitrogens on the cyclophane and the ethereal oxygens of the sidearms of the guest.<sup>5</sup> Recent investigations have shown that when polyether sidearms are present, the dominant interaction by far is the latter.<sup>6</sup> The presence of an aromatic core, however, is a necessary requisite for an effective guest, since it has been shown that simple polyether chains such as hexa(ethylene glycol) do not bind to **1**<sup>4+</sup>.<sup>7</sup> Despite the recognized importance of the aromatic nucleus in the guest structure, the driving forces that lead to its inclusion in the cyclobis(paraquat-

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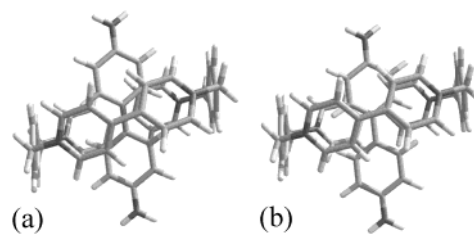
<sup>‡</sup> Università di Roma La Sapienza.

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*p*-phenylene) cavity and their relative importance are not completely understood. Here we report a computational study at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p)//B3LYP/6-31G(d,p) levels of theory of the gas-phase complexation of  $1^{4+}$  with four typical aromatic guests, namely 1,4-dimethoxybenzene (**2**), 1,5-dimethoxynaphthalene (**3**), benzidine (**4**), and tetrathiafulvalene (**5**), aimed at separating the face-to-face energy contributions from the edge-to-face ones. Previous computational studies of inclusion complexes of aromatic guests with the tetracation  $1^{4+}$  were mainly based on molecular mechanics<sup>8,9</sup> and quantum-mechanical semiempirical methods.<sup>7,10–15</sup> Owing to the large size of the structures involved, only a limited number of *ab initio*<sup>12,14–16</sup> and DFT studies,<sup>14,15</sup> and no post-Hartree–Fock studies have been reported in the literature. The present calculations are the most accurate not only in terms of basis set extension and treatment of correlation energy but also for taking into account the basis set superposition error by the counterpoise (CP) correction.<sup>17</sup>

The present work was carried out in two steps, the first at the B3LYP/6-31G(d,p) level and the second at the MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level;<sup>18</sup> the corresponding results will be discussed below.

**B3LYP/6-31G(d,p) Results.** Full optimized geometries at the B3LYP/6-31G(d,p) level were obtained for the host  $1^{4+}$ , the guests **2–5**, and the corresponding host–guest complexes (see Supporting Information). All the structures were optimized without symmetry constraints. The starting geometry of the host  $1^{4+}$  was from a previous study carried out at the HF/6-31G(d) level in which the results of a conformational search on  $1^{4+}$  have been



**FIGURE 1.** B3LYP/6-31G(d,p) optimized structures of the complex  $1^{4+}$ –**4**: (a) symmetric; (b) offset.

discussed.<sup>16</sup> The lowest energy conformation of  $1^{4+}$  has  $C_{2h}$  symmetry with the  $C_2$  axis passing through the 4–4' bond of the two paraquat units. The most stable conformations of guests **2** and **3** have a transoid structure of  $C_{2h}$  symmetry as illustrated in Chart 1: guest **4** is asymmetric with the benzene rings twisted about  $36^\circ$  and pyramidal amine groups (improper dihedral angles of about  $131^\circ$ ) and guest **5** has  $D_{2h}$  symmetry. The starting geometries of the host–guest complexes were obtained by inserting in the optimized structure of the host the optimized structure of the guests in an almost centrally symmetric arrangement as suggested by X-ray structures of  $1^{4+}$  complexes.<sup>19</sup> After geometry optimization, the guest was slightly shifted ( $\sim 0.5$  Å) along a direction perpendicular to the average plane of the host cavity, and the host–guest structure reoptimized. All the second geometry optimizations, with the exception of the complex  $1^{4+}$ –**4**, converged to the previous optimized structure having  $C_i$  symmetry. On the contrary the optimizations for the complex  $1^{4+}$ –**4** gave two distinct asymmetric structures of similar energy. One has the guest symmetrically placed at the center of the host (Figure 1a) whereas the other has the guest slightly offset from the centrally symmetric position (Figure 1b). Analogous results had been obtained previously by Jorgensen et al.<sup>9</sup> As expected the positive electrostatic field and the steric constraints of the host caused a reduction of both the twist angle of the aromatic rings of the benzidine guest ( $24^\circ$  and  $18^\circ$ , in  $1^{4+}$ –**4** sym and offset, respectively) and the degree of pyramidalization of the amine groups (improper dihedral angles both of about  $168^\circ$  in  $1^{4+}$ –**4** sym, and  $159^\circ$  and  $180^\circ$ , respectively, in  $1^{4+}$ –**4** offset).

Host–guest complexation in the gas phase is essentially a single-step event, to which an energy change corresponding to the complexation energy,  $\Delta E$  [ $\Delta E = E_{\text{complex}} - (E_{\text{host}} + E_{\text{guest}})$ ], is associated. CP corrected complexation energies are reported in the first column of Table 1.

It should be remarked that at this level of theory CP correction is very large ranging from 33% to 80% of the uncorrected complexation energies ( $\Delta E_{\text{unc}}$  in kcal mol<sup>-1</sup>:  $1^{4+}$ –**2**,  $-12.0$ ;  $1^{4+}$ –**3**,  $-12.7$ ;  $1^{4+}$ –**4** sym,  $-23.3$ ;  $1^{4+}$ –**4** offset,  $-23.9$ ;  $1^{4+}$ –**5**,  $-14.6$ ), pointing out the limited extension of the basis set.

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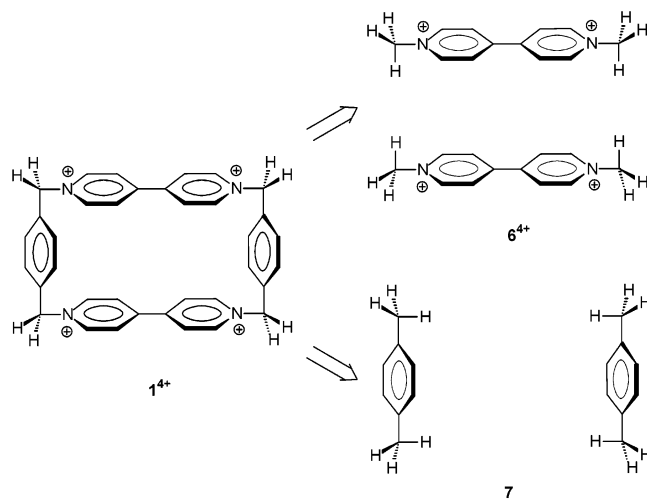
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**TABLE 1. Complexation Energies of the Host–Guest Complexes ( $\Delta E$ ) and the Corresponding Face-to-Face ( $\Delta E_{\text{ftf}}$ ) and Edge-to-Face ( $\Delta E_{\text{etf}}$ ) Contributions (their sum is also reported) Calculated at the CP-Corrected B3LYP/6-31G(d,p) Level of Theory<sup>a</sup>**

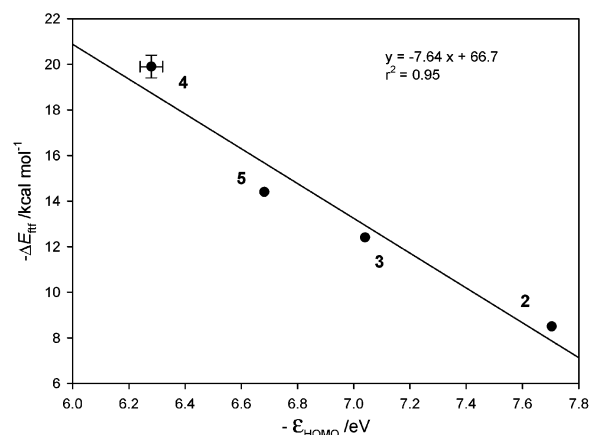
| complex                        | $\Delta E$ | $\Delta E_{\text{ftf}}$ | $\Delta E_{\text{etf}}$ | $\Delta E_{\text{ftf}} + \Delta E_{\text{etf}}$ |
|--------------------------------|------------|-------------------------|-------------------------|---|
| <b>1<sup>4+</sup>·2</b>        | -4.9       | -8.5                    | 3.2                     | -5.3  |
| <b>1<sup>4+</sup>·3</b>        | -2.5       | -12.4                   | 8.5                     | -3.9  |
| <b>1<sup>4+</sup>·4 sym</b>    | -15.2      | -19.4                   | 5.1                     | -14.3   |
| <b>1<sup>4+</sup>·4 offset</b> | -16.0      | -20.4                   | 5.4                     | -15.0   |
| <b>1<sup>4+</sup>·5</b>        | -7.6       | -14.4                   | 5.9                     | -8.5  |

<sup>a</sup> All data are in kcal mol<sup>-1</sup>.



**FIGURE 2.** Fragmentation of the receptor **1<sup>4+</sup>** carried out to separate the face-to-face from the edge-to-face interactions.

To establish the relative contribution of the face-to-face and edge-to-face aromatic interactions to the overall binding energy of the complexes, a series of single-point B3LYP/6-31G(d,p) calculations were performed on model substructures. These were constructed from the optimized geometries of the host **1<sup>4+</sup>** and of the corresponding host–guest complexes: for the evaluation of the face-to-face and edge-to-face interactions, the benzene units and the bipyridinium units of the host, respectively, were deleted; the deletions were carried out without altering the positions of the remaining atoms; after the deletions, the normal valence of each terminal carbon was restored by adding a hydrogen atom at the standard C–H bond distance. The procedure is illustrated in Figure 2 in the case of the host **1<sup>4+</sup>**, which gives rise to the assemblies **6<sup>4+</sup>** and **7**. An identical procedure was carried out starting from the host–guest complexes to generate the corresponding complexes of hosts **6<sup>4+</sup>** and **7**, respectively (see Supporting Information). Counterpoise corrected binding energies of hosts **6<sup>4+</sup>** and **7** with guests **2–5** were then computed by the B3LYP/6-31G(d,p) method yielding an estimate of the face-to-face (ftf) and edge-to-face (etf) contributions, respectively, to the binding energy of **1<sup>4+</sup>** (Table 1). The sum of the two contributions, also reported in Table 1, is in very good agreement with the gas-phase binding energies  $\Delta E$  of host **1<sup>4+</sup>** (mean absolute deviation = 0.9 kcal mol<sup>-1</sup>) thus suggesting that the two contributions are practically additive. It is interesting to note that while the edge-to-face interaction in the case of the guests **2–4** is of the type CH– $\pi$ , in the case of **5** it is of the type



**FIGURE 3.** Face-to-face  $\pi$ – $\pi$  stacking interactions  $\Delta E_{\text{ftf}}$  vs the HOMO energies of the complexed guests structures. Data for the guest **4** are reported as the mean of the symmetric and offset configurations with error bars representing the limit values of the two configurations.

[S $\cdots\pi$ ], but despite the different interaction type, the guests display a uniform behavior.

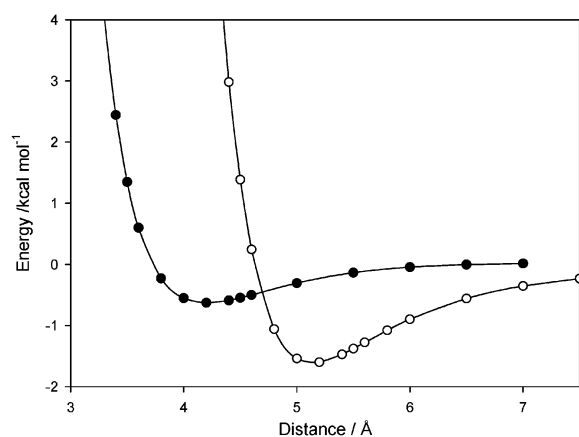
An intriguing result of this analysis is that edge-to-face interactions appear to be destabilizing. Although initially we were inclined to favor this conclusion, a deeper examination of the recent literature revealed that in the benzene dimer, the archetypal system for the study of CH– $\pi$  and  $\pi$ – $\pi$  interactions, the binding energy is primarily due to London dispersion forces, and that neither the Hartree–Fock theory nor current implementations of Kohn–Sham DFT are capable of describing these interactions.<sup>20,21</sup> Indeed both methods erroneously suggest that the interaction energy between two benzene molecules is repulsive for all three typical configurations of benzene dimer (sandwich, T-shaped, and parallel displaced) because of electrostatic and short-range exchange repulsions. As to the receptor **1<sup>4+</sup>**, these observations would explain the repulsive edge-to-face interactions and would suggest that the attractive face-to-face component is the result of favorable electrostatic and orbital interactions. With the aim at understanding if the calculated face-to-face interactions are mainly electrostatic or involve a significant degree of orbital interaction, the electrostatic potential<sup>22</sup>  $E_p$  calculated on the surface of the aromatic units ( $-E_p$  in kcal mol<sup>-1</sup>: **2**, 19.0; **3**, 20.8; **4 sym**, 23.2; **4 offset**, 23.9; **5**, 16.7) and the energies of the highest occupied molecular orbitals ( $-\epsilon_{\text{HOMO}}$  in eV: **2**, 7.70; **3**, 7.04; **4 sym**, 6.32; **4 offset**, 6.24; **5**, 6.68) were determined by single-point calculations performed at the HF/6-31G(d) level on the geometry the guests have in the corresponding complexes.<sup>23</sup> It is interesting to note that there is a satisfactory linear correlation (Figure 3)

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**FIGURE 4.** Adiabatic potential energy curves at the CP-corrected MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level for the sandwich (●) and T-shaped (○) configurations of the benzene dimer. Distance is referred to the centers of mass of the two molecules.

between  $\Delta E_{\text{tf}}$  values from Table 1 and the HOMO energies of the structures of the complexed guests. By contrast, no correlation is observed between the same energy differences and the electrostatic potentials. These observations indicate, in contrast to previous findings,<sup>24</sup> that the orbital interactions are more important than the electrostatic ones, as suggested by the strong charge-transfer bands observed experimentally in the visible spectra of the complexes that are evidence of orbital interactions.<sup>19c</sup>

**MP2/6-31G(d,p)//B3LYP/6-31G(d,p) Results.** To gain an understanding of the role played by London dispersion forces in the complexation of aromatic guests by cyclobis-(paraquat-*p*-phenylene), wave function-based correlation methods are required.<sup>20,21</sup> This prompted us to evaluate the CP-corrected MP2/6-31G(d,p) interaction energies on the geometries found at the B3LYP/6-31G(d,p) level. To establish whether this method is appropriate for the evaluation of  $\pi$ - $\pi$  and CH- $\pi$  interactions, we have carried out preliminary calculations on the benzene dimer in the sandwich and T-shaped configurations. From the corresponding potential energy curves, shown in Figure 4, a dissociation energy of the dimer,  $D_e$ , of 0.6 and 1.6 kcal mol<sup>-1</sup>, respectively, is obtained, which compares fairly well with the best estimates of Sherrill et al. obtained by state-of-the-art electronic structure methods ( $D_e = 1.8$  and 2.7 kcal mol<sup>-1</sup>, respectively),<sup>20</sup> and very well with the experimental dissociation energy from the ground vibrational level,  $D_0$ , of 1.6 ± 0.2 kcal mol<sup>-1</sup> obtained by Krause et al.<sup>25</sup>

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**TABLE 2.** Complexation Energies of the Host–Guest Complexes ( $\Delta E$ ) and the Corresponding Face-to-Face ( $\Delta E_{\text{ftf}}$ ) and Edge-to-Face ( $\Delta E_{\text{etf}}$ ) Contributions (their sum is also reported) Calculated at the CP-Corrected MP2/6-31G(d,p)//B3LYP/6-31G(d,p) Level of Theory, and Experimental Free Energies of Binding in Acetonitrile at 25 °C<sup>a</sup>

| complex                     | $\Delta E$ | $\Delta E_{\text{ftf}}$ | $\Delta E_{\text{etf}}$ | $\Delta E_{\text{ftf}} + \Delta E_{\text{etf}}$ | $\Delta G^\circ$  |
|-----------------------------|------------|-------------------------|-------------------------|---|-------------------|
| <b>1<sup>4+</sup>·2</b>     | -24.2      | -23.2                   | -2.8                    | -26.0   | -1.7 <sup>b</sup> |
| <b>1<sup>4+</sup>·3</b>     | -31.6      | -34.0                   | -1.5                    | -35.5   | -3.9 <sup>c</sup> |
| <b>1<sup>4+</sup>·4 sym</b> | -36.0      | -34.1                   | 0.0                     | -34.1   | -4.1 <sup>d</sup> |
| <b>1<sup>4+</sup>·5</b>     | -26.1      | -27.8                   | -2.0                    | -29.8   | -5.5 <sup>e</sup> |

<sup>a</sup> All data are in kcal mol<sup>-1</sup>. <sup>b</sup> Reference 19c. <sup>c</sup> Estimated value. See ref 26. <sup>d</sup> Reference 27. <sup>e</sup> Value at 27 °C. See ref 28.

CP-corrected MP2/6-31G(d,p)//B3LYP/6-31G(d,p) binding energies for the complexation of guests **2–5** by hosts **1<sup>4+</sup>**, **6<sup>4+</sup>**, and **7** are reported in Table 2, together with the corresponding experimental free energy changes ( $\Delta G^\circ$ ) for the complexation in CH<sub>3</sub>CN at 25 °C.<sup>7,19c,26–28</sup> Calculations were not carried out for configuration **1<sup>4+</sup>·4** offset, because DFT data in Table 1 did not show significant energy differences with respect to configuration **1<sup>4+</sup>·4** sym. In all of the cases CP correction is about 30% of the uncorrected complexation energies ( $\Delta E_{\text{unc}}$  in kcal mol<sup>-1</sup>: **1<sup>4+</sup>·2**, -34.9; **1<sup>4+</sup>·3**, -48.0; **1<sup>4+</sup>·4** sym, -48.5; **1<sup>4+</sup>·5**, -37.9). Comparison of  $\Delta E$  values in Tables 1 and 2 shows that *the binding of the complexes is primarily due to London dispersion interactions, which arise from favorable instantaneous multipole/induced multipole charge fluctuations.* Although the additivity between the face-to-face and edge-to-face interactions is now not so good (mean absolute deviation = 2.8 kcal mol<sup>-1</sup>, which is of the same order of magnitude as the edge-to-face interactions), the values of  $\Delta E_{\text{ftf}}$  and  $\Delta E_{\text{etf}}$  reflect the correct order of magnitude. This is justified by the fact that the edge-to-face interactions are now attractive and, considering the results on the T-shaped benzene dimer, of the expected magnitude.

The data in Table 2 show that face-to-face interactions are about 1 order of magnitude more important than edge-to-face interactions in determining the overall binding energy of the host–guest complexes. While edge-to-face interactions essentially depend on London dispersion forces, a comparison of  $\Delta E_{\text{ftf}}$  values in Tables 1 and 2 suggests that face-to-face interactions depend about one-half on electrostatic and frontier orbital contributions (the latter being more important) and the other half on London dispersion forces. Finally a comparison of the gas-phase binding energies  $\Delta E$  in Table 2 with the experimental free energies of binding in acetonitrile shows the lack of any correlation, indicating the importance of solvent effects in determining the strength and the order of binding in solution.

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**Supporting Information Available:** B3LYP/6-31G(d,p) optimized geometries, B3LYP/6-31G(d,p) and MP2/6-31G(d,p)//B3LYP/6-31G(d,p) energies, of the structures of the hosts **1<sup>4+</sup>**, **6<sup>4+</sup>**, and **7**, the guests **2–5**, and the corresponding complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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