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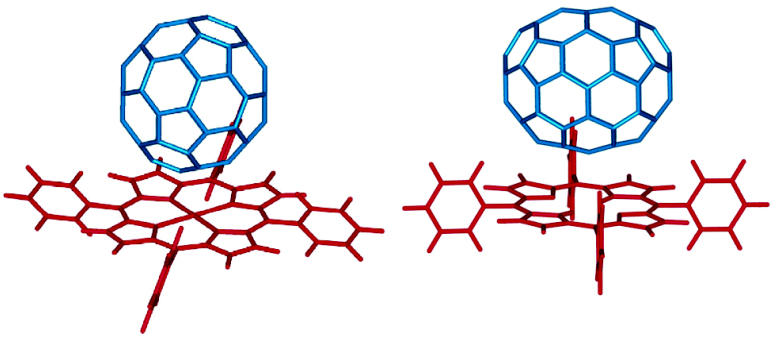

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Supramolecular Interactions between Fullerenes and Porphyrins

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Recent studies have shown that fullerenes and porphyrins or metalloporphyrins form supramolecular host−guest complexes, of which the majority contain closest contacts between one of the electron-rich 6:6 bonds of the guest fullerene and the geometric center of the host porphyrin or metalloporphyrin.[1−6] Contact distances are of the order of 2.7−3.0 Å, much longer than normal metal−olefin bonding distances commonly found in organometallic complexes. The nature of the fullerene−porphyrin interactions is not easily described in terms of conventional bonding arguments; instead, explanations that account for $\pi-\pi$ interactions or van der Waals forces are required to explain the supramolecular association.[1a,7] A recent study by Reed et al. found that a free-base porphyrin binds C_{60} somewhat more strongly than do metalloporphyrins,[1c] suggesting the importance of electrostatic interactions. Charge-transfer interactions between the host and guest have also been invoked in the literature.[5] Clearly, the nature of the fullerene−porphyrin interactions is still not clearly understood, and we report here high-level theoretical calculations to address more fully the nature of these interactions.

Our calculations employed the Perdew−Burke−Ernzerhof (PBE) density functional,[8] which has been used in the study of weak interactions.[9] In addition, the extended transition state method was used to decompose the interaction energy ΔE_{int} into electrostatic ΔV_{elstat}, orbital ΔE_{oi}, and Pauli-repulsion ΔE_{Pauli} terms.[10] All density functional theory (DFT) calculations have been performed using a double-ζ Salter-type (STO) basis set plus polarization functions (DZP) as included with ADF 2002.2.[11] The geometries of four supramolecular complexes were calculated and are shown in Figure 1.

The calculated distances (D_{cc}) between the geometric centers of the porphyrin ring and the electron-rich 6:6 bond of the fullerene are in accord with the experimental values (Table 1).[1a,2a] This level of theory was further tested by calculating the PBE/DZP binding energies for benzene−benzene, naphthalene−naphthalene dimers, and a naphthalene−anthracene complex. The binding energies obtained from the PBE/DZP level without correction for basis set superposition error (BSSE) agreed with those reported in the literature[12] (see Supporting Information). These results suggest that traditional BSSE corrections using the counterpoise method may not be applicable when using the PBE functional. There are some C_{60}/metalloporphyrin complexes where the 5:6 bonds of C_{60} have the closest contact with the metal centers.[3c,4] This experimental observation implies that the exceptional structural orientation of having a 5:6 bond located on the central metal ion also corresponds to a minimum in the potential energy surface.

The results in Table 1 show that the interaction energy for the C_{60}/porphyrin (**1**) is greater than that for the C_{60}/metalloporphyrin (**2**), in good agreement with the experimental observation that a free-base porphyrin binds C_{60} more strongly.[1c] For the two C_{70} complexes (**3** and **4**), the C_{70}/porphyrin (**3**) has only a slightly greater interaction energy than the C_{70}/metalloporphyrin (**4**). These results also show that the complexes having C_{70} as the guest (**3** and **4**) show a slightly larger degree of charge transfer and greater interaction energies. The interaction energies given here are smaller than those obtained by molecular mechanics calculations (−28.0 to −33.6 kcal/mol),[1a] but are greater than those obtained from BLYP calculations without BSSE corrections (−5.8 to −7.7 kcal/mol).[1a] It is possible that the force field used in molecular mechanics calculations may have overestimated the contribution to the total energy by the van der Waals interactions.

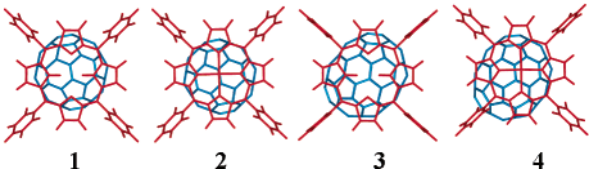

Figure 1. The PBE/DZP optimized structures of C_{60}/tetraphenylporphyrin (**1**, 1554 STOs), C_{60}/tetraphenylporphyrinato-zinc (**2**, 1576 STOs), C_{70}/tetraphenylporphyrin (**3**, 1684 STOs), and C_{70}/tetraphenylporphyrinato-zinc (**4**, 1706 STOs).

Table 1. The Closest Center-to-Center Distances (D_{cc} in Å), Interaction Energies in kcal/mol Together with the Three Energy Components, and VDD Atomic Charges of **1**−**4**

	1	**2**	**3**	**4**
D_{cc} (calcd)	2.743	2.770	2.908	2.864
D_{cc} (expt)[a]	2.756	2.720	2.884	2.814
ΔE_{int}	−17.33	−16.25	−18.39	−18.11
ΔV_{elstat}	−20.75	−29.51	−21.67	−26.67
ΔE_{oi}	−15.84	−18.51	−17.21	−18.93
ΔE_{Pauli}	19.26	31.76	20.49	27.50
$\sum\Delta Q_{fullerene}{}^{VDD}$	−0.12	−0.10	−0.14	−0.13
$\sum\Delta Q_{porphyrin}{}^{VDD}$	0.12	0.10	0.14	0.13

[a] The X-ray crystal structures were taken from refs 1a and 2a.

Table 1 also shows that for all complexes both the electrostatic and the orbital interaction terms are attractive, while the Pauli term, which accounts for the interactions between closed shells, is repulsive as expected. The orbital interaction energy arises mainly from charge transfer between occupied and unoccupied orbitals. The attractive electrostatic interactions are much greater for those complexes having a metalloporphyrin as the host molecule which has a greater charge separation because of the presence of a metal center. Pauli repulsive interactions increase significantly on going from the free-base porphyrin complexes to the metalloporphyrin complexes, while the orbital interaction energies change only moderately. The relative changes in the three components of the total interaction energy indicate that complexes with a metalloporphyrin host have a smaller ΔE_{int} because of increased repulsive Pauli interactions.

Electrostatic interactions contribute approximately 50−60% to the total attractive interactions. The other attractive interactions

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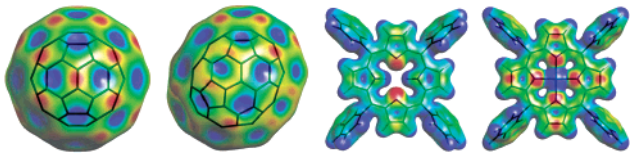

Figure 2. Molecular electrostatic potentials maps of C_{60}, C_{70}, tetraphenylporphyrin, and tetraphenylporphyrinato-zinc.

(ΔE_{oi}) either follow the same trend as the electrostatic interactions or change only slightly from one complex to another. This result suggests that correlation of the relative orientation of the guest and host molecules in the supramolecular complexes through examination of their molecular electrostatic potentials (MEPs) will be useful. The MEPs of the fullerenes and porphyrins were calculated at the PBE/6-31G(d,p) level at the optimized geometries shown in Figure 1 with Gaussian 98 and plotted using Molekel 4.2[13] (Figure 2). The MEP plots for C_{60} and C_{70} show that the positive electrostatic potential (shown in blue) corresponds to the center regions of the five- and six-membered rings, although the two-dimensional projection of the molecular structure onto the MEPs shown in Figure 2 obscures this feature somewhat. Along the 6:6 bonds, regions of negative potential (shown in red) are noticeable, although these are less obvious for C_{70} than for C_{60}. For the porphyrins, the negative potential is mainly associated with the nitrogen atoms, while in the free-base porphyrin the protonated nitrogen atoms display much less negative potentials because of the covalent N−H bonds.

The relative orientations of the guest with respect to the host in all four of the supramolecular complexes are mirrored in the MEPs of the guest and host molecules. The orientations adopted show that all four nitrogen atoms of the host are coincident with the centers of the four carbon rings (two five-membered and two six-membered) surrounding the closest contact 6:6 bond. The electron flow for the four complexes was studied using the Voronoi deformation density (VDD) method.[14] The results given in Table 1 indicate that the guest−host interactions are also associated with a charge transfer of about 0.10−0.14 electrons from the porphyrin moiety to the fullerene guest, consistent with the notion that fullerenes are normally the electron acceptors.[15] The majority of available crystal structures of fullerene−porphyrin complexes show this complementary orientation.

The host molecule in each of the supramolecular complexes studied has phenyl groups at the four *meso* positions. For comparison, calculations were also performed on complexes with unsubstituted porphyrins. The interaction energies for C_{60}/porphine, C_{70}/porphine, C_{60}/porphine-Zn, and C_{70}/porphine-Zn are all approximately 3.0−4.0 kcal/mol smaller than the corresponding fullerene-substituted porphyrin supramolecular complexes. This small difference in energy is derived from the four C−H$\cdots\pi$ interactions between the C−H bond on each phenyl group and the π system of the fullerenes. This estimation of the C−H$\cdots\pi$ interaction energy ($\sim$1.0 kcal/mol per C−H$\cdots\pi$) is consistent with other results reported in the literature.[16]

In summary, the fullerene−porphyrin interaction energies obtained for the four complexes reported here are in the range from −16 to −18 kcal/mol. The change in the interaction energies on going from fullerene−porphyrin to fullerene−metalloporphyrin complexes is not significant because the increase of the electrostatic attractive forces is offset by the increase of Pauli repulsive interactions. Attractive orbital interactions change moderately from one complex to another, and the relative orientation of the guest and host molecules can be understood in terms of the complementary nature of their molecular electrostatic potentials. Comparison with calculations for complexes that do not contain C−H$\cdots\pi$ interactions suggests that each such interaction contributes approximately −1.0 kcal/mol to the total interaction energy.

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Supporting Information Available: Cartesian coordinates of **1**−**4**, MEP maps, and calculations of arene dimers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Boyd, P. D. W.; Hodgson, M. C.; Chaker, L.; Rickard, C. E. F.; Oliver, A. G.; Brothers, P. J.; Bolskar, R.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 10487−10495. (b) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Burgess, M.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2000**, *122*, 10704−10705. (c) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2002**, *124*, 6604−6612. (d) Sun, Y.; Drovetskaya, T.; Bolskar, R. D.; Bau, R.; Boyd, P. D. W.; Reed, C. A. *J. Org. Chem.* **1997**, *62*, 3642−3649. (e) Sun, D.; Tham, F. S.; Reed, C. A.; Boyd, P. D. W. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5088−5092.

(2) (a) Olmstead, M. M.; Costa, D. A.; Maitra, K.; Noll, B. C.; Phillips, S. L.; Van Calcar, P. M.; Balch, A. L. *J. Am. Chem. Soc.* **1999**, *121*, 7090−7097. (b) Olmstead, M. M.; de Bettencourt-Dias, A.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1223−1225.

(3) (a) Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 9477−9478. (b) Nishioka, T.; Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *Macromolecules* **2000**, *33*, 9182−9184. (c) Zheng, J.-Y.; Tashiro, K.; Hirabayashi, Y.; Kinbara, K.; Saigo, K.; Aida, T.; Sakamoto, S.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1858−1861.

(4) Ishii, T.; Aizawa, N.; Yamashita, M.; Matsuzaka, H.; Kodama, T.; Kikuchi, K.; Ikemoto, I.; Isawa, Y. *J. Chem. Soc., Dalton Trans.* **2000**, 4407−4412.

(5) (a) Guldi, D. M.; Luo, C.; Prato, M.; Troisi, A.; Zerbetto, F.; Scheloske, M.; Dietel, E.; Bauer, W.; Hirsch, A. *J. Am. Chem. Soc.* **2001**, *123*, 9166−9167. (b) Guldi, D. M.; Luo, C.; Prato, M.; Dietel, E.; Hirsch A. *J. Chem. Soc., Chem. Commun.* **2000**, 373−374.

(6) Diederich, F.; Gómez-López, M. *Chem. Soc. Rev.* **1999**, *28*, 263−277.

(7) Schuster, D. I.; Jarowski, P. D.; Kirschner, A. N.; Wilson S. R. *J. Mater. Chem.* **2002**, *12*, 2041−2047.

(8) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.

(9) (a) Adamo, C.; Cossi, M.; Rega, N.; Barone, V. In *Theoretical and Computational Chemistry*; Eriksson, L. A., Ed.; Elsevier Science: Amsterdam, 2001; Vol. 9, pp 467−538. (b) Improta, R.; Barone, V.; Kudin, K. N.; Scuseria, G. E. *J. Am. Chem. Soc.* **2001**, *123*, 3311−3322.

(10) (a) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558−1565. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755−1759. (c) Bickelhaupt, F. M.; Baerends, E. J. In *Rev. Comput. Chem.*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley: New York, 2000; Vol. 15, pp 1−86. (d) Fonseca Guerra, C.; Bickelhaupt, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2092−2095.

(11) (a) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931−967. (b) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391−403.

(12) (a) Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887−10893. (b) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 104−112. (c) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem.* **1996**, *100*, 18790−18794. (d) Lee, N. K.; Park, S.; Kim, S. K. *J. Chem. Phys.* **2002**, *116*, 7910−7917.

(13) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.2*; Swiss Center for Scientific Computing, Manno, 2000.

(14) Fonseca Guerra, C.; Bickelhaupt, F. M.; Snijders, J. G.; Baerends, E. J. *Chem.-Eur. J.* **1999**, *5*, 3581−3594.

(15) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075−1119.

(16) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction*; Wiley-VCH: New York, 1998; p 2.

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