FULL PAPER

Modeling of Supramolecular Properties of Molecular Tweezers, Clips, and Bowls

Frank-Gerrit Klärner[1], Jens Panitzky[1], Dorin Preda[2], and Lawrence T. Scott[2]

[1]Institut für Organische Chemie, Universität Essen, D-45117 Essen, Germany. Tel: +49-201-1833081; Fax: +49-201-1834252; E-mail: Klaerner@oc1.orgchem.uni-essen.de

[2]Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467-3860, USA

Abstract The electrostatic potential surface (EPS) is calculated for molecular tweezers, clips, and bowls at different levels of theory (semiempirical AM1, *ab initio* HF/6-31G*, and density functional theory pBP/DN**). According to these calculations, the molecular electrostatic potential (MEP) on the concave side of the molecular tweezers and clips is suprisingly negative for hydrocarbons. This finding seems to be a general phenomenon in nonconjugated π-electron systems with concave-convex topology and it explains the receptor properties of the molecular tweezers and clips. Analogous calculations performed for the conjugated aromatic molecular bowls show different results. The DFT calculations predict that in these systems the more negative MEP lies on the concave side similar to the findings for the nonconjugated molecular tweezer- and clip-systems, whereas the AM1 calculation leads to the opposite result that the MEP is more negative on convex side of the bowl-systems.

Keywords Electrostatic potential surfaces, Quantum mechanical calculations (AM1, *ab initio*, DFT), Artificial receptors, Supramolecular chemistry
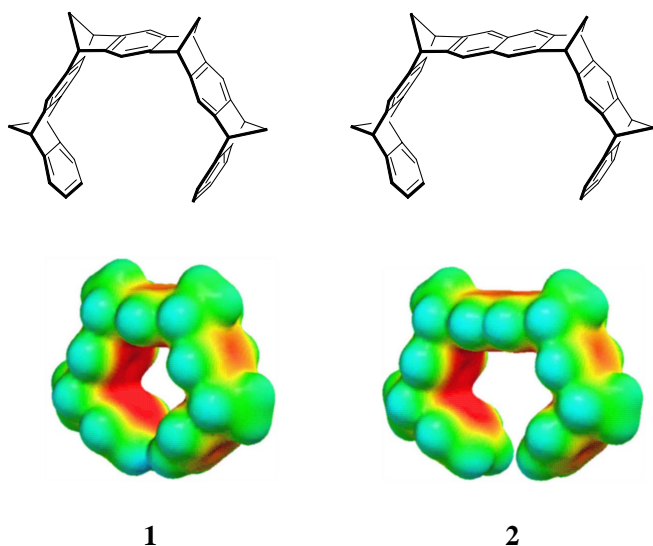
Introduction

The noncovalent interactions of arenes with other aromatic units (π-π or arene-arene interactions) [1] or with positively charged ions (cation-π interactions) [2] are important in the processes of molecular recognition and self-assembly. The design of efficient synthetic receptors with the ability to bind

Correspondence to: F.-G. Klärner

Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

substrates selectively requires precise control of both their topological and electronic properties. Besides the frequently used cyclic and, hence, well preorganized receptors of the cyclophane-type, noncyclic receptors with cavities of flexible size have proven to be effective [3]. Most recently, the synthesis and some supramolecular properties of the hydrocarbons **1** and **2** (the numbering of the molecules is shown in Scheme 1) were reported [4]. These receptors can be regarded as molecular tweezers that selectively bind electron-deficient aromatic and aliphatic substrates as well as organic cations, whereas electron rich neutral and anionic substrates are not bound by them within the limits of NMR detection. In most cases the formation of the receptor-substrate complexes was determined with the method of ^{1}H NMR titra-

Figure 1 *Semiempirically calculated (AM1) electrostatic potential surfaces (EPSs) of the molecular tweezers 1 and 2. The color code spans from –25 (red) to +25 kcal mol⁻¹ (blue)*

tion. To explain these findings, the electrostatic potential surfaces (EPSs) of the tweezer molecules were calculated with the semiempirical AM1 method (Figure 1) and compared with those of the substrate molecules calculated with the same method (Figure 2) [5].

The molecular electrostatic potentials (MEPs) of **1** and **2** were found to be surprisingly negative for pure hydrocarbons on the concave side of each molecule (Figure 1) whereas the potentials on the convex sides of **1** and **2** are less negative, corresponding to those of tetraalkyl substituted arenes (*vide infra*). When analogous calculations were performed for the aromatic substrates (Figure 2), the complementary nature of their electrostatic potential surfaces (EPS) to those inside the cavity of receptor **1** and **2**, respectively, became evident. The result of the calculations, that the MEP on the concave side (inside the cavity) of tweezer molecule **1** or **2** is much more negative than that on the convex side, can be rationalized in the following way: The electrostatic potential at a certain site corresponds to the energy of interaction of a positive test charge with wave functions of all nuclei and the electrons of the investigated molecule and is inversely proportional to the distance from the test charge [6]. This can be

Figure 2 *Semiempirically calculated (AM1) electrostatic potential surfaces (EPSs) of various potential substrates. The color code spans from –25 (red) to +25 kcal mol⁻¹ (blue) and from +50 (red) to +130 kcal mol⁻¹ (blue) for the N-methyl-pyrazinium cation*
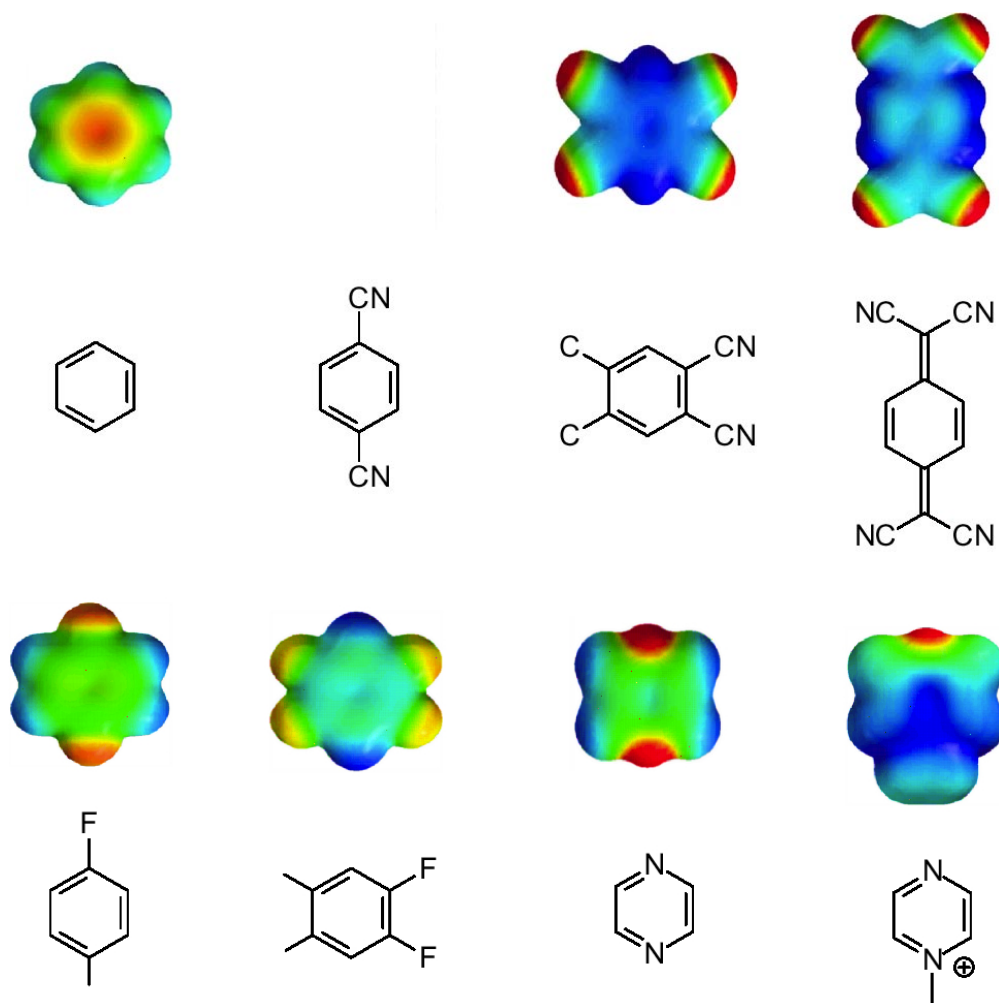
Scheme 1a *Molecular structures used for the EPS calculations - Nonconjugated arenes*

3   **4**   **5**   **6**

7   **8**   **9**   **10**

11   **12**   **13**
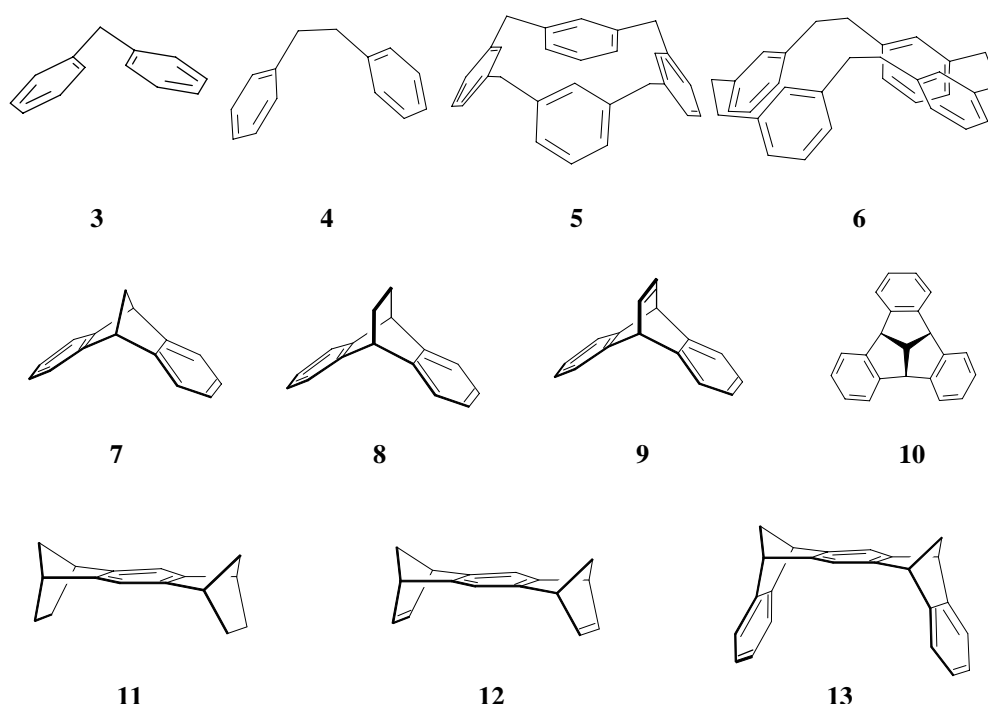
Scheme 1b *Molecular structures used for the EPS calculations - Nonconjugated-conjugated arenes (molecular clips)*

14   **15**   **16**
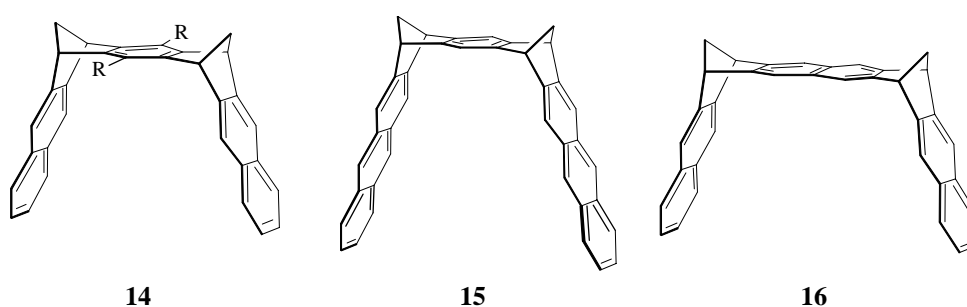
R	
H	**14a**
NH$_2$	**14b**
OMe	**14c**
OH	**14d**
OAc	**14e**

illustrated with the "idealized" π-electron system which assigns a negative charge to the π-orbital of a sp^2 C atom and the positive charge to the σ frame work (Figure 3) [7]. If two nonconjugated "idealized" π-electron systems are in one plane and the distance between them is large enough, a positive test charge does not "feel" both isolated π-electron systems at the same time, and the electrostatic potential is not influenced by the introduction of the second π-electron system. If, on the other hand, the molecule is bent, as it is the case with tweezer **1** or **2**, the two π-electron systems approach one another on the concave side, and the potential becomes more negative on this side at the same distance from the first π-electron system. To show this effect, the participating π molecular orbitals do not have to be significantly unsymmetrical with respect to the plane between the concave and

convex sides of the molecule and do not have to undergo a rehybridization.

To find out whether or not the topology-dependent EPS is a specific property of the molecular tweezers **1** and **2** or universal principle for nonconjugated π-electron systems with concave-convex topology, corresponding calculations were performed on **1**,**2**, and fragments of the molecular tweezers as well as on other arene-units used in synthetic receptors. As a check on the semiempirical AM1-method, *ab initio* calculations using HF/6-31G* and DFT calculations using pBP/DN** were carried out and compared with the AM1 calculations. By the use of these theoretical methods we have, furthermore, investigated the EPSs of the molecular clips **14**-**16** which contain benzene-, naphthalene-, and anthracene-units, respectively, and the EPSs of the geodesic polyarene bowls

Table 1 *Comparison between the minimum and maximum molecular electrostatic potentials (MEPs) calculated for various small molecules with optimized geometries at different levels of theory*

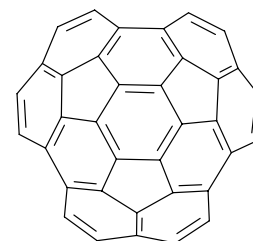| Compound | MEP [kcal·mol^{-1}] | | | | | |
| | HF/6-31G* | | MP2/6-31G* | | pBP/DN** | |
	max.	*min.*	*max.*	*min.*	*max.*	*min.*
CO	19.87	-14.37	20.83	-13.92	10.44	-19.41
NH_3	34.84	-53.47	35.14	-53.67	28.73	-54.79
H_2O	58.73	-46.22	59.01	-46.29	50.11	-46.38
CH_3OH	57.44	-44.98	58.42	-45.30	46.35	-47.10
CH_2O	34.49	-38.69	35.52	-39.56	19.43	-36.09
CH_3OCH_3	15.51	-40.68	16.32	-41.50	12.11	-44.39
$CH_2=CH_2$	17.41	-20.40	17.74	-21.03	13.20	-26.83
oxirane	22.38	-41.89	23.58	-42.92	15.90	-41.73
furan	27.89	-27.20	29.09	-28.12	23.66	-29.48
pyrrole	57.08	-30.73	57.56	-31.37	49.47	-41.89
cyclopentadiene	18.79	-20.91	18.95	-21.42	13.61	-34.45

17-**22**, which consist of continuously conjugated arene-units. Considerable work has been reported on the "fullerene fragments" **17-22** since the early 1990s [7,8,9,10].

Computational methodology

All calculations were performed with SPARTAN 5.1.3 [11] at the semiempirical AM1 [12], *ab initio* HF/6-31G* [13], and DFT pBP/DN** [14] level. All geometries were fully optimized. Owing to the prohibitive computational time the geometries of the larger molecules optimized either by DFT or AM1 calculations were used for single-point calculations at the HF/6-31G* and pBP/DN** level, respectively. Here, we are interested in electrostatic potential surfaces (EPSs) to visualize the supramolecular properties of various potential host-guest systems. Since experimentally the EPS cannot be measured directly, however, we have used experimentally accessible dipole moments to judge the relative reliability of one level of calculation over another for describing overall charge distribution. Accordingly, the chosen DFT method

Scheme 1c *Molecular structures used for the EPS calculations - Conjugated arenes (molecular bowls)*
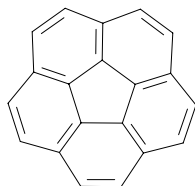
17
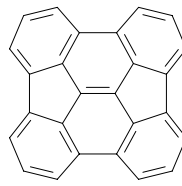
18
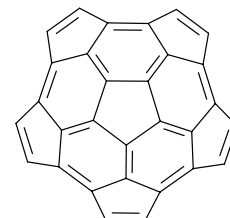
19
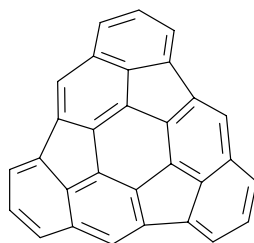
20
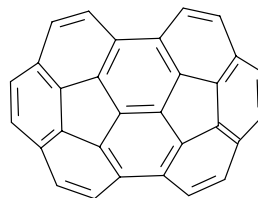
21

22

Table 2 *A comparison between the most negative molecular electrostatic potentials (MEPs) on the concave and convex side of nonconjugated arenes calculated with the semiempirical AM1,* ab initio *HF/6-31G*, and DFT pBP/DN***

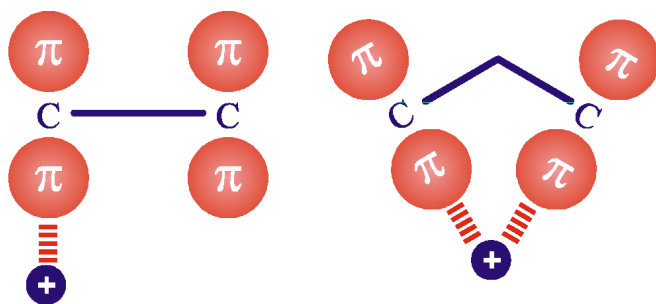| Compound | MEP [kcal·mol⁻¹] | | | | | |
| | AM1 | | HF/6-31G* [a] | | pBP/DN** | |
	concave	*convex*	*concave*	*convex*	*concave*	*convex*
benzene	-20.65		-16.50		-36.35	
toluene	-22.11		-22.39		-39.20	
3	-25.42	-22.10	-24.05	-21.08	-42.90	-37.50
4	-22.14	-22.10	-25.19	-22.24	-45.50	-39.30
m-xylene	-23.09		-23.29		-41.56	
5	-28.81	-19.96	-28.12	-20.90	-41.14	-29.30
6	-30.12	-22.29	-32.98	-25.12	-60.09	-41.52
o-xylene	-23.32		-23.38		-41.30	
7	-29.70	-22.0	-25.09	-22.33	-46.77	-39.35
8	-29.24	-22.5	-24.51	-21.71	-45.06	-40.50
9	-27.60	-24.5	-24.78	-23.26	-44.50	-41.75
10	-33.53	-22.0	-25.07	-21.12	-46.70	-37.70
durene	-25.60		-25.10		-45.10	
11	-26.51	-26.5	-21.09	-24.11	-48.61	-46.80
12	-29.42	-25.0	-26.77	-23.28	-50.41	-44.50
13	-31.07	-22.0	-27.19	-23.42	-51.75	-41.10

[a] *single-point calculations with geometries optimized by pBP/DN** calculations*

should be superior to the *ab initio* and semiempirical method [15,16,17]. A comparison of the minimum and maximum MEP values calculated for various small molecules with fully optimized geometries either at the *ab initio* or DFT level of theory shows, however, the same tendency in all cases (Table 1), although the absolute values calculated for one and the same molecule differ from each other quite substantially depending on the method employed. Therefore, we use the EPS calculations only in a very qualitative fashion to visualize the electrostatic surfaces of the molecules for an understanding of their supramolecular properties.

Tables **2** and **3** list, for some selected compounds with concave-convex topology, the most negative molecular elec-

Figure 3 *Schematic representation of a positive test charge with a nonconjugated "idealized" π-electron systems with linear (left) and concave geometry (right). The π-electron systems are negatively, the π framework positively charged*

trostatic potentials (MEPs) on the two faces of each molecule calculated either by the AM1, *ab initio*, or DFT method. It is important to note that absolute MEP values, even when calculated with one and the same method, are only comparable for molecules with identical substitution patterns, as each additional alkyl substituent decreases the MEP of an arene. Therefore, the MEP values of toluene, m- and o-xylene, and durene as examples for mono-, di-, and tetraalkyl-substituted benzene derivatives are included in Table 2. The results obtained with the *ab initio* and DFT method for the nonconjugated aromatic compounds generally corroborate the AM1 calculations. All three methods predict that, in each compound, the most negative MEP value is localized on its concave face, except in the cases of 1,2-diphenylmethane **4** and the bisnorbornasubstituted benzene **11**. In these cases the AM1 calculations show no preference for one face over the other, whereas the *ab initio* and DFT calculations result in more negative MEP values on the concave face of **4** and either on the convex or concave face of **11**.

The influence of neighboring π systems on the EPS of the concave side of the molecule becomes evident in the comparison with **11**-**13**. Contrary to **11** the MEPs of **12** and **13** are calculated by all three methods to be more negative on the concave face due to the additional nonconjugated double bonds in **12** and the two additional terminal benzene rings in **13**, whereas the MEP values on the convex sides of **12** and **13** are less negative comparable to that of durene. The difference between the MEP values on the concave and convex face is calculated by all three methods to be further increased from compound **13** (the central building block of **1**) to the

Table 3 *A comparison between the most negative molecular potentials (MEPs) on the concave and convex side of the molecular tweezers **1,2** and clips **14-16** calculated with the semiempirical AM1,* ab initio *HF/6-31G*, and DFT pBP/DN***

| Compound | MEP [kcal·mol⁻¹] | | | | | |
| | AM1 | | HF/6-31G* [a] | | pBP/DN** | |
	concave	*convex*	*concave*	*convex*	*concave*	*convex*
1[b]	-35.48	-22.0	-40.06	-27.81	-54.49	-43.85
2[c]	-33.30	-24.0	-36.28	-28.28		
14a	-30.86	-21.47	-25.44	-22.96	-49.95	-39.70
14b[d]	-32.51	-23.08	-26.47	-21.16	-54.99	-44.93
14c[d]	-19.64	-18.39	-16.41	-17.22	-47.19	-38.79
14d[d]	-24.03	-15.61	-19.87	-15.11	-48.34	-38.79
14e[b],[c]	-9.33	-1.22	-10.10	-1.97	-36.91	-26.85
15[b]	-30.11	-21.23	-32.07	-25.51	-49.40	-39.73
16[b]	-29.09	-20.87	-30.97	-26.04	-46.15	-38.30

[a] single-point calculations with geometries optimized by pBP/DN** calculations

[b] HF/3-21G$^{(*)}$-single-point calculations with geometries optimized by pBP/DN**

[c] HF/3-21G$^{(*)}$-single-point calculation with a geometry optimized by AM1. The DFT calculation was not feasible with the basis set pBP/DN**

[d] the MEP was determined in the center of the middle benzene ring

molecular tweezer **1**. The replacement of benzene-units by naphthalene- or anthracene-units in the molecular tweezer **1** or clip **13** leading to the tweezer **2** and clips **14-16** decreases the difference between the MEP values on the concave and convex side of the molecule (Table 3). Preliminary experiments with the molecular clips **14c,e** show that these receptors are less selective than the molecular tweezers **1** and **2** with respect to the geometrical and electrostatic properties of the substrates [18]. Substituents such as NH_2, OH, and OAc at the central benzene-unit of the molecular clips **14b,d,e** have no large effect on the MEP difference between the MEPs on the concave and convex face of these systems in agreement with the calculation of Dougherty et al. [19] for the corresponding benzene derivatives. The methoxy methyl groups in the gas-phase equilibrium geometry of compound **14c** are calculated to point toward the concave face. The positive MEP of the methyl hydrogen-atoms obviously compensates the negative MEP of the cavity at least partially.

The EPS of the total molecule can be best visualized by the color code as shown in Figures 1, 2, and 4-6. A close inspection of the EPS of **7**, for example, leads to the conclusion that in case of the AM1 and DFT calculation the most negative MEP is in the center of the concave side of **7**, and in the case of the *ab initio* calculation there is a double minimum close to the center of each benzene ring. These small differences, however, do not change the predicted properties of the molecular tweezers and clips as selective receptors for electron-deficient substrates. Also in the substructures **3,4,8**, and **9**, which are present in many cyclophanes and other macrocyclic receptors[1,2] employed for the complexation of neutral and cationic substrates, more negative MEPs are calculated for the concave side of the molecule. Further examples are calix[4]arene **5** and homocalix[4]arene **6** [20], and trisbenzotriquinacene **10** [21].

Contrary to the nonconjugated aromatic systems examined in Tables 2 and 3 the EPS calculations of the molecular

Figure 4 *The EPS of **7** calculated by AM1 (left), HF/6-31G*(geometry optimized by pBP/DN**) (middle) and pBP/DN** (right). The color code spans from –25 (red) to +25 kcal·mol⁻¹ (blue) for the AM1 and HF/6-31G* calculations and from -35 (red) to +10 kcal·mol⁻¹ (blue) for the pBP/DN** calculation*
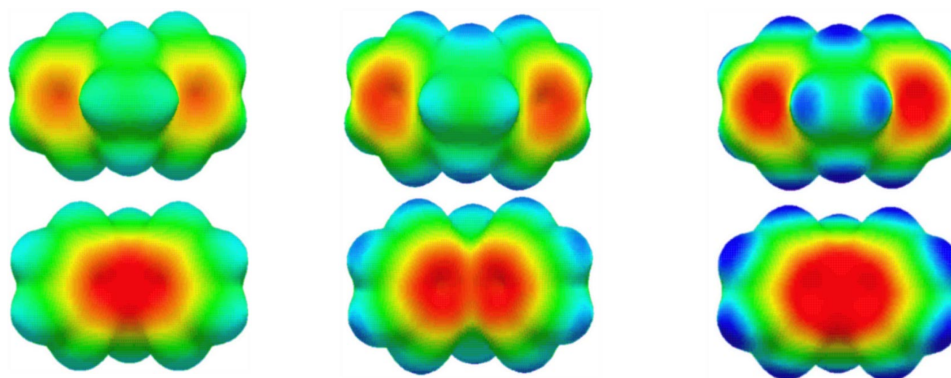
Table 4 *A comparison between the most negative molecular potentials (MEPs) on the* con*cave and* con*vex side of conjugated arene (molecular bowls)* **17-22** *calculated with the semiempirical AM1,* ab initio *HF/6-31G*, and DFT pBP/DN***

| Compound | MEP [kcal·mol⁻¹] | | | | | |
| | AM1 | | HF/6-31G* | | pBP/DN** | |
	concave	*convex*	*concave*	*convex*	*concave*	*convex*
17	-16.94	-27.41	-17.98	-17.00	-35.64	-30.64
18[a]	-16.52	-23.73	-18.30	-16.52	-35.04	-32.15
19	-8.45	-20.60	-14.67	-16.55	-34.11	-26.28
20[a]	-12.09	-22.63	-17.43	-16.67	-35.32	-30.35
21[a]	-12.21	-23.89	-17.12	-16.30	-35.85	-28.69
22	-8.28	-20.38	-15.39	-14.36	-34.52	-26.79

*[a] single-point calculations with geometries optimized by AM1 calculations*

bowls **17-22**, each of which represents a fully-conjugated, bent polyarene, give conflicting results depending on the method used for the calculation. The semiempirical AM1 calculations invariably predict that the more negative MEP lies on the convex side of the molecule, whereas the DFT calculations give precisely the opposite result, i.e., that in these systems the MEP is more negative on the concave side of the molecule, (Table 4) as in the nonconjugated systems shown in Table 2 and 3. The *ab initio* calculations at the HF/6-31G* level do not show a strong preference of the MEP for one side over the other but generally agree more with the DFT results than with AM1. It is interesting to note that as one goes to smaller atomic orbital basis sets, e.g., the omission of polarization and Gaussian functions on carbon, the difference between the most negative MEP on the convex and concave surfaces [DMEP = MEP(convex) - MEP(concave)] of these molecular bowls drops almost to zero at both the *ab initio* and the DFT levels of theory. In the case of corannulene (**17**), for example, with a constant AM1 geometry, we see (DMEP in parentheses): HF/3-21G$^{(*)}$ (0.93), HF/STO3G (0.34), and pBP/DN (0.32), which are insignificant relative to the large DMEP calculated by AM1 (-10.47) and pBP/DN** (5.00).

The degree of curvature in the geodesic polyarenes **17-22** roughly follows the order of their molecular size, and as this curvature increases, the MEP on both faces becomes less negative according to AM1 calculations (see Table 4). When calculated by HF/6-31G* and DFT, however, they remain more nearly constant (also Table 4). This represents another discrepancy among the theories. Surprisingly, none of the theoretical methods predicts any significant correlation between DMEP and the degree of curvature within the family of continuously conjugated molecular bowls studied here.

An even more extreme case of molecular curvature in a continuous system can of course be found in C_{60}. At the AM1 level of theory, the most negative MEP is just barely negative (only -0.06) on the outside/convex surface, whereas it is actually predicted to be quite positive (+29.43) on the inside/concave surface! At the DFT level of theory, both surfaces are likewise less negative than those of the open geodesic polyarenes **17-22**; however, as with the molecular clips and tweezers, it is the inside/concave surface that is now more negative than the outside/convex surface, i.e., just the reverse again of what AM1 predicts. Owing to computer limitations, our DFT calculations on C_{60} were performed without polarization functions (which underestimates DMEP, *vida supra*), but the EPS trends are easily seen by comparing these results with those obtained for corannulene (**17**) calculated at the same level of theory (pBP/DN//AM1). Thus, we see (MEP in parentheses): C_{60} inside/concave (-13.38), C_{60} outside/convex (-5.45), **17** concave (-37.95), **17** convex (-37.63).

Figure 5 *The EPS of molecular clip* **14a** *calculated by AM1 (left) and HF/6-31G* (geometry optimized by pBP/DN**) (right). The color code spans from –25 (red) to +25 kcal·mol⁻¹ (blue)*
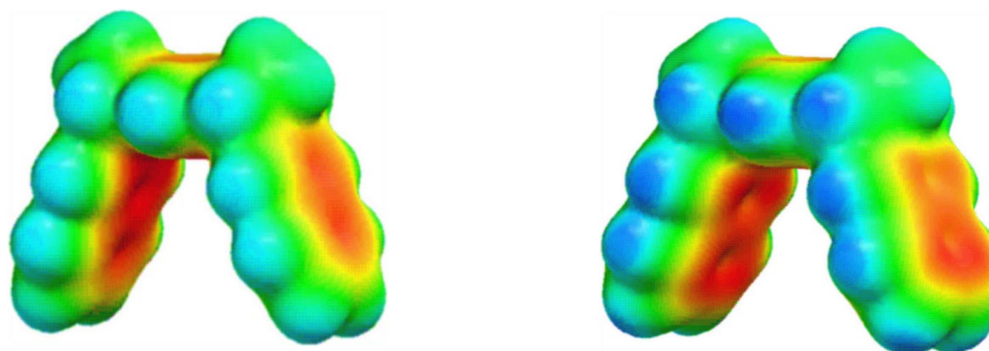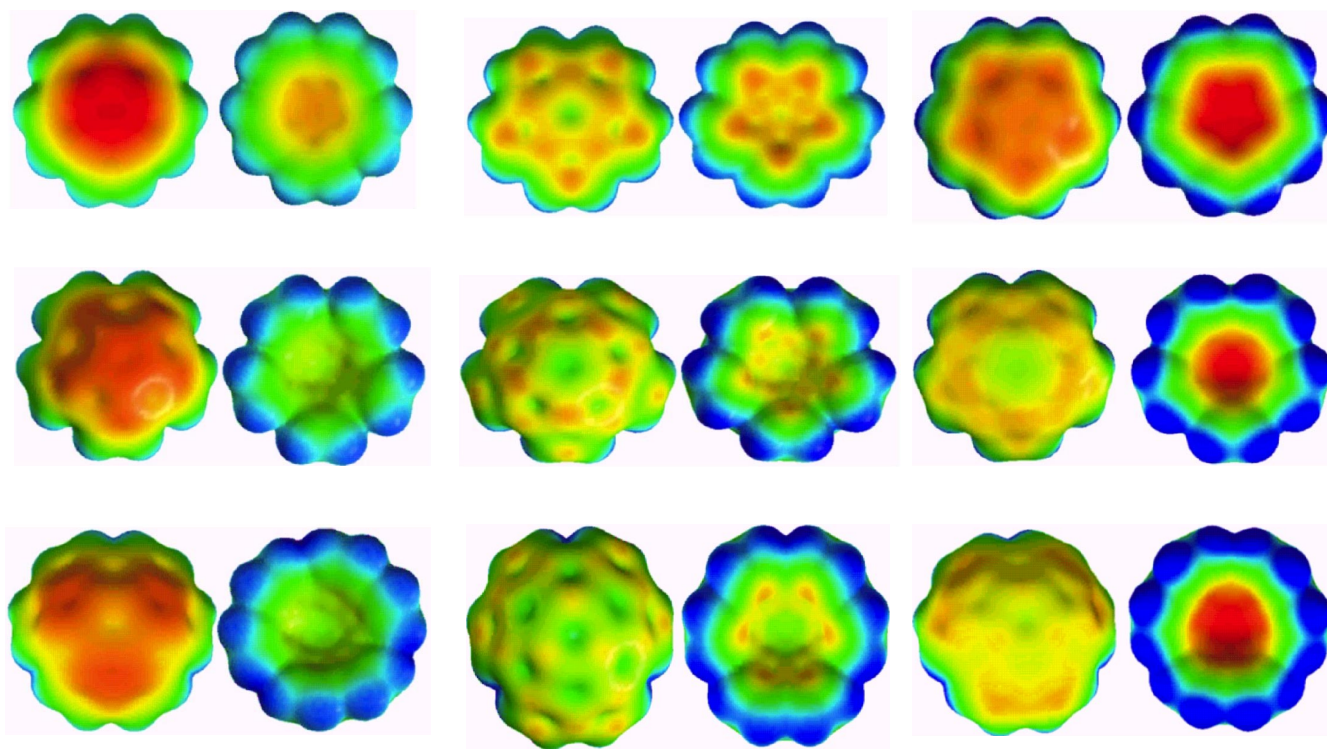
Figure 6 *The EPS of the molecular bowls* **17** *(top),* **19** *(middle), and* **22** *(bottom) calculated by AM1 (left), HF/6-31G* (middle), and pBP/DN** (right). The color code spans from –25 (red) to +25 kcal mol^{-1} (blue) for the AM1 and HF/6-31G* calculations and from -35 (red) to +10 kcal·mol^{-1} (blue) for the pBP/DN** calculations. Within each pair the convex surface is shown on the left and the concave on the right*

Why does the satisfying agreement among the results obtained for compounds **1**-**16** by the semiempirical, *ab initio*, and DFT methods collapse when the same methods are used to calculate the electrostatic potential surfaces of the fully conjugated bowls **17**-**22**? Surely the proximity effect illustrated in Figure 3, which puts the positive point charge closer to more p orbitals on the concave face than on the convex face, must still operate in the open geodesic polyarenes. There are, however, additional factors to consider in curved systems. Most important is the fact that the "interior" carbon atoms in compounds **17**-**22** (*i.e.*, those atoms that belong to *three* rings) are all pyramidalized and are therefore no longer purely sp^2 hybridized. The "p" orbitals at these carbon atoms all have some degree of s-character mixed in, which inflates the lobes of the "p" orbitals on the convex surface and deflates the lobes on the concave surface. By contrast, the individual systems in compounds **1**-**16** are all locally planar and comprised entirely of carbon atoms that are essentially purely sp^2 hybridized. Since semiempirical molecular orbital methods are critically dependent on parameterization against the properties of "representative" compounds in a basis set, and no compounds with pyramidalized carbon atoms were used to parameterize the AM1 method, one must be cautious about the AM1 predictions for compounds **17**-**22**.

Neither the *ab initio* nor the DFT methods should suffer from this shortcoming. It is well established, however, that electron correlation takes on special importance for the satisfactory electronic description of molecules that are characterized by extensive electron delocalization. In this connection, the Hartree-Fock *ab initio* HF/6-31G* method may be adequate for compounds such as **1**-**16**, in which conjugation is interrupted, but large, continuous systems of the sort found in compounds **17**-**22** will probably be best described by molecular orbital methods that include electron correlation, *e.g.*, DFT methods.

In light of these considerations, it is probably prudent to trust the DFT calculations more than either the semiempirical or *ab initio* methods for predictions concerning the electrostatic potential surfaces of bowl shaped polyarenes such as compounds **17**-**22**. According to the DFT calculations, these molecular bowls should form supramolecular complexes inside the cavity preferentially with electron deficient guests, as the molecular tweezers and clips do.

Conclusions

According to EPS calculations at different levels of theory (semiempirical AM1, *ab initio* HF/6-31G* and DFT pBP/DN**) the MEP on the concave side of the molecular tweezers **1**,**2** and clips **14**-**16** is surprisingly negative for hydrocar-

bons. This finding seems to be a general phenomenon in nonconjugated π electron systems with concave-convex topology, and it explains the receptor properties of these systems. Analogous calculations were performed for the conjugated aromatic molecular bowls **17**-**22**. The DFT calculations predict that also in these systems the more negative MEP lies on the concave side of the molecule, analogously to the findings for the nonconjugated systems, whereas the AM1 calculations lead to the opposite result, that the MEP is more negative on the convex side of **17**-**22**. Since, thus far, no experimental data for the molecular bowls as potential receptors are available, the question concerning the electrostatic properties of these systems remains open.

References and notes

1. (a) Hunter, C. A. *Chem. Soc. Rev.*, **1994**, 101-109. (b) Adams, H.; Carver, F. J.; Hunter, C. A.; Morales, J. C.; Seward, E. M. *Angew. Chem.* **1996**, *108*, 1628-1631; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1542-1544. (c) Kim, E.; Paliwal, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 11192-11193. (d) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768-4774. (e) Chipot, C.; Jaffe, R.; Maigret, B.; Pearlman, D. A.; Kollman, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 11217-11224.

2. (a) Dougherty, D. A. *Science* **1996**, *271*, 163-168. (b) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303-1324 and references cited therein. (c) Ngola, S. M.; Dougherty, D. A. *J. Org. Chem.* **1998**, *63*, 4566-4567. (d) Ngoly, S. M.; Kearney, P. C.; Mecozzi, S.; Russell, K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 1192-1201.

3. Reviews: (a) Lehn, J.-M. *Supramolecular Chemistry. Concepts and Perspectives*; VCH: Weinheim, 1995. (b) Diederich, F. *Cyclophanes*; The Royal Society of Chemistry: Cambridge, 1991. (c) Cram, D. J. *Container Molecules and their Guests*; The Royal Society of Chemistry: Cambridge, 1994. (d) Vögtle, F. *Supramoleculare Chemie*; Teubner: Stuttgart, 1989.

4. (a) Klärner, F.-G.; Burkert, U.; Kamieth, M.; Boese, R.; Benet-Buchholz, J. *Chem. Eur. J.* **1999**, *5*, 1700-1707. (b) Kamieth, M.; Klärner, F.-G. *J. Prakt. Chem.* **1999**, *341*, 245-251. (c) Kamieth, M.; Burkert, U.; Corbin, P. S.; Dell, S. J.; Zimmerman, S. C.; Klärner, F.-G. *Eur. J. Org. Chem.* **1999**, 2741-2749. (d) Klärner, F.-G.; Burkert, U.; Kamieth, M.; Boese, R., manuscript submitted to *J. Phys. Org. Chem.*

5. Kamieth, M.; Klärner, F.-G.; Diederich, F. *Angew. Chem.* **1998**, *110*, 3497-3500; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3303-3306.

6. (a) Chirlian, L. E.; Franck, M. M. *J. Comput. Chem.* **1987**, *8*, 894-905. (b) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361-373.

7. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525-5534.

8. (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082-7084. (b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920-1921. (c) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291-300 and references cited therein. (d) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743-8744. (e) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406-408. (f) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963-10968. (g) Scott, L. T. *Pure Appl. Chem.* **1999**, *71*, in press and references cited therein.(h) Ansems, R. B. M.; Scott, L. T. *J. Am. Chem. Soc.,* in press.

9. (a) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921-1923. (b) Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycyclic Aromat. Compd.* **1995**, *4*, 209-217. (c) Rabideau, P. W.; Sygula, A. in *Adv. Theor. Interesting Mol.*; Thummel, R. P., Ed.; JAI Press: Greenwich, 1995; Vol. 3, pp 1-36 and references cited therein. (d) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235-42 and references cited therein. (e) Mehta, G.; Rao, H. S. P. *Adv. Strain Org. Chem* **1997**, *6*, 139-187 and references cited therein. (f) Schulman, J. M.; Disch, R. L. *J. Comput. Chem.* **1998**, *19*, 189-194. (g) Seiders, T. J.; Elliott, E. L., Grube, G. H., Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804-7813.

10. More recent DFT calculations on bowl-shaped hydrocarbons $C_{30}H_{12}$ were reported by Ferrer, S. M.; Molina, J. N. *J. Comput. Chem.* **1999**, *20*, 1412-1421.

11. (a) All methods of calculation used here are implemented in the program package SPARTAN 5.1.3, Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612, USA. (b) Review of these methods: Hehre, W. J.; Yu, J.; Klunzinger, P. E.; Lou, L. *A Brief Guide to Molecular Mechanics and Quantum Mechanical Calculations*; Wavefunction, Inc.: Irvine, CA, 1998.

12. (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902-3909. (b) Reviews of semiempirical methods: Clark, T., *A Handbook of Computational Chemistry*; Wiley & Sons: New York, 1986. (c) Stewart, J. J. P. *Comput. Aided Mol. Design* **1990**, *4*, 1.

13. Review of Hartree-Fock (HF) and MØller-Plesset (MP) models: Hehre, W. J.; Radon, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

14. (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3089. (b) Perdew, J.P. *Phys. Rev. B* **1986**, *33*, 8822. (c) Review: St-Amant, A. In *Reviews in Computational Chemistry;* Lipkowitz, K. B.; Boyd, D. B, Eds.; VCH: New York 1996; Vol 7, pp 217-239.

15. Hehre, W. J.; Yu, J.; Klunzinger, P. E.; Lou, L. *A Brief Guide to Molecular Mechanics and Quantum Mechanical Calculations*; Wavefunction, Inc.: Irvine, CA, 1998, pp 90-94.

16. Luque, F. J.; Orozco, M.; Illas, F.; Rubio, J. *J. Am. Chem. Soc.* **1991**, *113*, 5203-5211.

17. Stutmant, A.; Cornell, W. D.; Kollmann, P. A. *J. Comput. Chem.* **1995**, *16*, 1483-1506.

18. Panitzky, J.; Klärner, F.-G., unpublished results.

19. Mecozzi, S.; West, A. P.; Dougherty, D. A. *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 10566-10571.

20. (a) Ibach, S.; Prantzsch, V.; Vögtle, F.; Chartroux, C.; Gloc, K. *Acc. Chem. Res.* **1999**, *32*, 729-740 and cited literature. (b) A most recent application of EPS calculation for the understanding of receptor properties of calixarenes was reported by Schalley, C. A.; Castellano, R. K.; Brody, M. S.; Rudkevich, D. M.; Sinzdak, G.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 4668-4579.

21. (a) Kuck, D.; Lindenthal, T.; Schuster, A. *Chem. Ber.* **1992**, *125*, 1449-1460; (b) Kuck, D.; Neumann, E.; Schuster, A. *Chem. Ber.* **1994**, *127*, 151-164; (c) Review: Kuck, D. *Top. Curr. Chem.* **1998**, *196*, 167-220.