that is reversed from that observed for the reduction of free substrate in solution. The same holds true for the enzyme-catalyzed reduction of methenyl-H_4F with NADH or NADPH as coenzyme. In both cases we can conclude from NMR spectroscopic data that the reactive conformation in the enzyme-catalyzed reaction does not match that in solution. In addition, in the enzyme-catalyzed reaction the product is formed in an energetically unfavorable conformation. This could possibly prevent product inhibition.

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Modeling the Supramolecular Properties of Aliphatic-Aromatic Hydrocarbons with Convex–Concave Topology[**]

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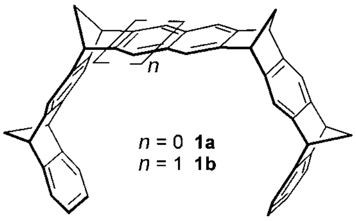
and François Diederich

Dedicated to Professor Emanuel Vogel
on the occasion of his 70th birthday

In supramolecular and biological chemistry, for example in the case of molecular recognition, arenes make an important contribution to the formation of superstructures.[1] Their interactions with other arenes (π–π or arene–arene interactions)[2] and with positively charged ions (cation–π interactions)[3] are particularly common and are used in the design of synthetic receptors. The properties of selective complexation[4] discovered for molecular tweezers of the type **1** and the results known from other receptors with concave–convex topology stimulated the theoretical model studies introduced here.



$n = 0$ **1a**
$n = 1$ **1b**

The molecular tweezers **1a** and **1b** serve as receptors for acceptor-substituted and cationic arenes as well as corresponding aliphatic substrates, whereas electron-rich arenes or anionic compounds are not complexed by them.[4] These experimental results, together with the established solvent dependence, indicate a substantial contribution of electrostatic interaction, as was already described in the electrostatic model for the attractive arene–arene interaction.[2] To find out the extent of electrostatic interaction in the molecular tweezers **1a** and **1b**, we calculated their electrostatic potential surfaces (EPSs) with the semiempirical AM1 method.[5] We thus found a potential which was surprisingly negative for pure hydrocarbons on the concave side of each molecule (most negative potentials: **1a**: -35.48, **1b**: -33.30 kcal mol^{-1}). In contrast, the potentials on the convex sides almost correspond to that of a tetraalkyl benzene such as durene (most negative potential: -25.60 kcal mol^{-1}; Figure 1, Table 1). When analogous calculations are performed for the potential substrates **2**–**6**, the complementary nature of their electrostatic potential surfaces to those of the cavity of the receptors **1a** and **1b** becomes evident.

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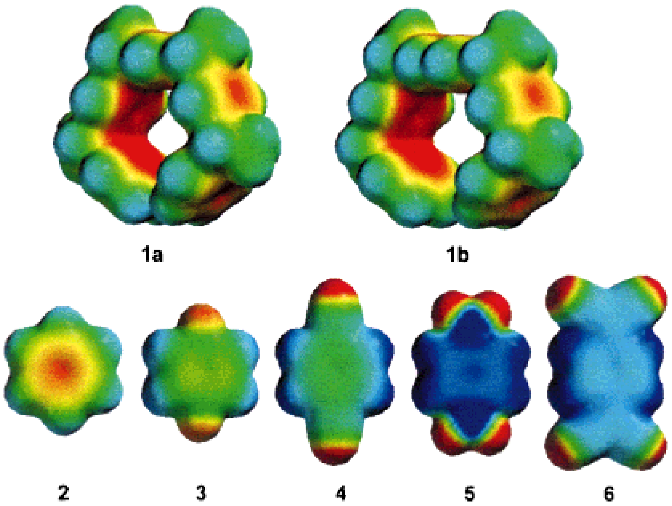


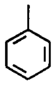
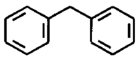
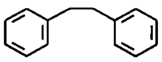
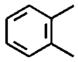
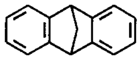
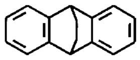
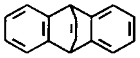
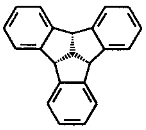
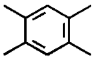
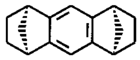
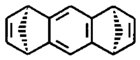
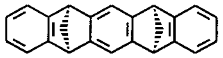
Figure 1. Semiempirically calculated (AM1) electrostatic potential surfaces of the molecular tweezers **1a** and **1b** (top) and the potential guest molecules benzene (**2**), *p*-difluorobenzene (**3**), *p*-dicyanobenzene (**4**), *p*-dinitrobenzene (**5**), and 7,7,8,8-tetracyanoquinodimethane (TCNQ, **6**). The color code spans from −25 (red) to 25 kcal mol^{-1} (blue).

Based on the semiempirically calculated EPSs of the potential guest molecules, a qualitative prediction of their binding affinity towards the receptor **1a** and **1b** also becomes possible:[6] Whereas benzene (**2**) and *p*-difluorobenzene (**3**) do not form detectable complexes with **1a** and **1b** in $CDCl_3$, the compounds with a more positive electrostatic potential, **4**–**6**, are suitable substrates (Figure 1).[4, 7] To establish whether this is a specific property of the molecular tweezers **1a** and **1b** or a universal principle for nonconjugated π-electron systems with concave–convex topology, corresponding calculations were performed on fragments of the molecular tweezers as well as on other molecular units used in synthetic receptors.

Table 1 lists, for some selected compounds, the AM1 values of the most negative electrostatic potentials on the electron density surfaces, which without exception are localized on the concave face of these molecules. The AM1 potentials on the convex sides of these molecules estimated by comparing the color scales are always less negative except in the case of **8**. It is important to note that absolute values are only comparable for molecules with identical substitution patterns, as each additional alkyl substituent decreases the electrostatic potential of the arene. Calculations with the semiempirical PM3 method[5] show the same trend as the AM1 calculations; the absolute values computed with PM3 are, however, smaller than the corresponding AM1 values. To test the semiempirical methods we also carried out ab initio calculations (RHF 6-31G**),[5] which are much more time-consuming, for the example of 9,10-dihydro-9,10-methanoanthracene (**7**), a fragment of **1**, as well as for model systems (Table 1, Figure 2). The results obtained with the different methods follow the same trend; therefore, the semiempirical methods are the methods of choice for EPS calculations, especially for the treatment of larger systems.

Compound **7** already shows a much more negative electrostatic potential on the concave side than on the convex face. The influence of neighboring π-electron systems on the EPS

Table 1. Semiempirically and ab initio calculated values [kcal mol^{-1}] of the most negative electrostatic potentials on the electron density surfaces.[a]

		AM1		PM3	(RHF 6-31G**)
		concave	convex	concave	concave
2		−20.65	–	−16.50	−20.21
		−22.11	–	−17.53	−21.63
11		−25.42	−22.1	−20.58	–
		−22.14	−22.1	−16.58	–
		−23.32	–	−18.77	−22.75
7		−29.70	−22.0	−24.60	−24.16
13		−29.24	−22.5	−24.05	–
12		−27.60	−24.5	−22.56	–
		−33.53	−22.0	−27.13	–
		−25.60	–	−21.11	−23.30
8		−26.51	−26.5	−22.05	−23.74
9		−29.42	−25.0	−24.32	−26.00
10		−31.07	−22.0	−26.64	–
1a		−35.48	−22.0	−29.70	–
1b		−33.30	−24.0	−27.76	–

[a] In all cases these potentials are localized on the concave side of the molecule. The potentials on the convex sides calculated with AM1 were estimated after comparison of the color scales.

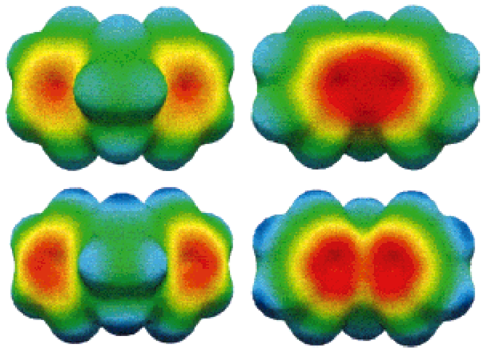


Figure 2. The semiempirically (AM1; top) and ab initio calculated (RHF 6-31G**; bottom) EPSs of 9,10-dihydro-9,10-methanoanthracene (**7**). The convex side of the molecule is shown on the left, and the concave side on the right. The color code spans from −25 (red) to 25 kcal mol^{-1} (blue).

1433-7851/98/3723-3304 $ 17.50+.50/0

of the concave side of the molecule becomes evident in the comparison of **8**–**10** (Figure 3): Whereas the electrostatic potentials on the convex and concave sides of the molecule hardly differ in **8** and are similar to that of durene (Table 1), the negative potential on the concave side increases at the central benzene ring due to the two additional nonconjugated double bonds in **9** and is due to the two additional terminal benzene rings in **10**. On the other hand, the values of the negative potentials on the convex sides of **8**–**10** decrease.

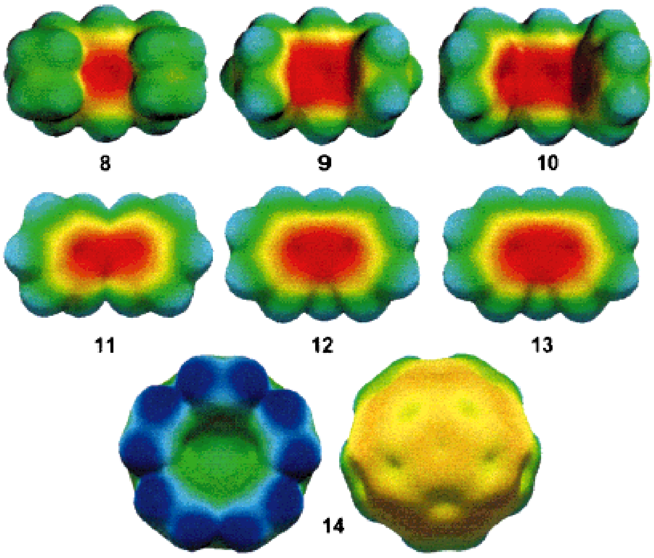


Figure 3. Semiempirically calculated EPSs (AM1) of the concave hydrocarbons **8**–**13** (see Table 1) and of $C_{30}H_{10}$ **14** (left: concave side, right: convex side). The color code spans from -25 (red) to 25 kcal mol^{-1} (blue).

Also in the substructures **11**–**13**, which are present in many cyclophanes and other macrocyclic receptors[1] employed for the complexation of neutral and cationic substrates, a more negative electrostatic potential can be calculated for the concave side of the molecule (Figure 3). This also explains the "edge in angle" interaction[8] between guest molecules and the diphenylmethane units of the receptor often encountered in cyclophanes. The comparison of **12** and **13** is interesting: As **13** (most negative potential: -29.24 kcal mol^{-1}) has a more negative potential than **12** (most negative potential: -27.60 kcal mol^{-1}), the binding properties of the known receptors with the dibenzobarrelene unit[9] towards electron-deficient and positively charged substrates should improve upon hydrogenation of the C=C bond.[10]

The electrostatic potential at a certain site corresponds to the energy of interaction of a positive test charge with the nuclei and the wave functions of all the electrons of the investigated molecule and behaves inversely proportional to the distance from this test charge.[11] The observations made here can be illustrated with the "idealized" π atom of Hunter and Sanders,[2a] which assigns the negative charge (-0.5 on each side) to the π-electron system of an sp^2 C atom and the positive charge to the σ framework (Figure 4). If two "idealized" C atoms are in one plane and the distance between them is large enough, a positive test charge will 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, the two π-electron systems approach on the concave side, and the potential will become more negative on this side at the same distance from the first π-electron system. The participating π molecular orbitals do not have to become significantly unsymmetrical with respect to the plane between the concave and convex sides of the molecule and do not have to undergo rehybridization.

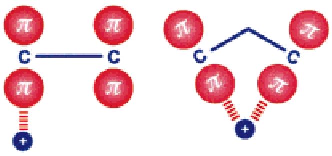


Figure 4. Schematic representation of the interaction of a positive test charge with nonconjugated "idealized" sp^2 C atoms[2] with linear (left) and concave geometry (right). The π-electron systems contain the negative, the σ framework the positive charges. The electrostatic potential is more negative in the concave case.

The theoretical investigations presented here are in excellent agreement with experimental results and provide the reason for the new and surprising properties of the hydrocarbon tweezers **1a** and **1b** as synthetic receptors which selectively bind only acceptor-substituted and cationic substrates. In contrast to the nonconjugated aromatic systems examined here, the more negative potential lies on the convex side of bent conjugated molecules such as fullerene C_{60}[12a, b] as well as the fullerene fragments $C_{30}H_{10}$ (**14**) and corannulene.[12c] The reason for this is the rehybridization of the C atoms due to the nonplanarity of these concave–convex molecules.[12]

With quite simple semiempirical calculation methods the supramolecular properties of molecules based on electrostatic interactions can be visualized. The investigations described here make clear that, apart from the electronic structure, the topology of receptor molecules is of vital importance for the binding properties. The exact knowledge of cooperative effects of spatially separated molecule parts is necessary for the design and construction of new and efficient receptors as well as the self-organization of natural and nonnatural systems,[13] template-controlled syntheses,[14] crystal engineering,[15] and the production of new supramolecular materials.

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Chemical Recycling of Plastics to Useful Organic Compounds by Oxidative Degradation[**]

Anne Pifer and Ayusman Sen[*]

With the production of polymeric materials on the rise and landfill space at a premium, it becomes increasingly important to develop new techniques for reducing the amount of material lost to the landfill. Approximately 20% of landfill volume in the USA is consumed by plastics, and their lack of compatibility with the environment has generated much interest in increasing the amount of polymeric material that is reclaimed as structural material or chemically degraded to fuel or useful organic compounds.[1]

Chemical recycling, which has been increasingly applied in recent years, is defined as the breakdown of polymeric waste into materials that are reusable as fuel or chemicals, including monomers.[1a,c,d, 2] Most chemical recycling being done today focuses on the use of refinery technology and equipment to convert polymers into hydrocarbon feedstocks. Additionally, the depolymerization of condensation polymers, such as poly(ethylene terephthalate), to reusable monomeric material is currently practiced.[3] Of the 27 million tons of plastic material produced in the USA each year, 25% is condensation polymers, while addition polymers constitute 75% of this weight.[4] Addition polymers may be chemically recycled in refineries; however, the price of crude oil and hydrocarbon mixtures produced must compete with oil prices to be economically viable, and the risk to refinery equipment is high when postconsumer mixed plastics are used.[5, 2] Dufaud and Basset have reported a mild new procedure for the catalytic hydrogenolysis of polyolefins.[6] Here we describe a new oxidative degradation procedure that converts the most widely used (addition) polymers—such as polystyrene, polyethylene, and polypropylene—into useful organic compounds, including monomers for other polymerizations. The recycling of these polymers is currently problematical owing to the high costs of collection and sorting, the small difference in prices for virgin and recycled resins, and the reduction in polymer properties caused by the incompatibility of different plastics components.[7] These economic barriers could be overcome if the products generated from these polymers were more valuable and if mixed plastics could be processed together, eliminating sorting costs.

The oxidative degradation of the polymers involved reaction with nitrogen oxides and dioxygen at 170 °C. The results obtained are summarized in Table 1.

Polystyrene with average relative molecular weight of 280000 was converted into a mixture of benzoic acid, 4- and 3-nitrobenzoic acids, and gaseous oxides of carbon under the standard reaction conditions (170 °C, 16 h; partial pressures: 275 kPa NO, 690 kPa O_2, 3170 kPa N_2). No unchanged polymer was detected by ^{1}H NMR spectroscopy. The ratio of benzoic acid to nitrobenzoic acids varied significantly with NO and O_2 content in the reaction mixture; no reaction occurred without the presence of both gases. At a high partial pressure of NO (690 kPa), no benzoic acid was formed, 4-nitrobenzoic acid was the major product, and other nitro species were detected in trace amounts. On the other hand, at a low partial pressure of NO (175 kPa), benzoic acid and unchanged polystyrene predominated, and only trace amounts of nitrobenzoic acids were detected. In reactions where the partial pressure of NO was reduced (140 kPa) and that of O_2 increased (1035 kPa), all the polymer was converted, and the molar ratios of benzoic acid, 4-nitrobenzoic acid, and 3-nitrobenzoic acids were 7:1:1. In general, a O_2 partial pressure of 690 kPa or more was necessary for the reaction to proceed to completion. Benzoic acid, 4-nitrobenzoic acid, and 3-nitrobenzoic acid are easily separated by

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