Calculation of Quadrupole Moments of Polycyclic Aromatic Hydrocarbons: Applications to Chromatography

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The interactions between polycyclic aromatic hydrocarbons (with up to four rings) and dinitrobenzene have been calculated using semiempirical methods and shown to give poor correlation with experimental stability constants. Quadrupole moments for these molecules have been calculated at the HF/6-31G(d,p) and BLYP/6-31G(d,p) levels of theory. The interaction between polycyclic aromatic hydrocarbons and nitrated benzenes is found to be dependent on the quadrupole moment. Dispersion interactions are estimated to be considerably smaller than quadrupole interactions and not a significant influence on the binding energy. The two methods used show the same trends in the calculated quadrupole moment, and it is shown that a method involving electron correlation may not be necessary for prediction of stability constants.

Introduction

The interaction between a polycyclic aromatic hydrocarbon (PAH) and either a charged center, or an electron acceptor (such as another aromatic system surrounded by electron-withdrawing groups) is considered to be an important noncovalent bond in biological processes such as enzyme−substrate binding and antigen−antibody recognition. Quantum chemical calculations on this interaction, however, have been limited due to the size of the species involved. In separating a large number of polycyclic aromatic hydrocarbons, columns doped with an electron-deficient phenyl group, such as *m*-dinitrobenzene derivatives, have been found to be particularly useful.[1] The interaction between the aromatic group and the dinitrobenzene has been considered to be face-to-face; however no solid proof has been put forward.

In this paper, an attempt is made to correlate stability constants calculated from chromatography with calculated molecular properties of polycyclic aromatic hydrocarbons, with the aim of providing a predictive tool for assisting further study of the separation of polycyclic aromatic hydrocarbons and the detection of unknown species.

Two primary approaches have been used to investigate the interaction between aromatic hydrocarbons and electron acceptors: electrostatics and charge transfer. The two aims of previous electrostatics calculations have been to compute a complete potential energy surface (or to calculate an electronic potential at single points of a surface corresponding to likely binding sites) and to calculate multipole moments. In the case of many PAHs the dipole moment vanishes, and hence quadrupole interactions are the primary source of electrostatic forces. Calculating a charge-transfer interaction involves a supermolecule approach, where both the donor and acceptor are described by a single wave function, and the position of one relative to the other is optimized, leading to a wave function in which the HOMO and LUMO are a combination of the HOMO of the donor molecule and the LUMO of the acceptor.

Clare[2] has made use of the latter method to correlate energies and other quantum chemically defined properties with stability constants for several electron acceptors with methylbenzenes. His calculation of supermolecules at the PM3 level showed sometimes good and sometimes poor correlation with experiment and also showed a range of favored geometries, including some mutually perpendicular geometries. Dougherty and coworkers[3,4] have reported potential surfaces for a series of small aromatic molecules, calculated at both semiempirical and *ab initio* levels, and used these to correlate binding energies with cations. They found that a high-level *ab initio* calculation was required to give an accurate description of the potential energy surface and that there were both qualitative and quantitative differences between *ab initio* and semiempirical surfaces. They also attempted to approximate the surface by calculating a single point near where the cation is expected to reside[5] and found this to give reasonable results in many cases.

The calculation of quadrupole moments has not received much attention in the literature, possibly because of the difficulty of measuring a quadrupole moment experimentally. Most reported work has been on benzene, in particular with regard to its possible dimer structure. In the case of benzene, extensive calculations have been performed to determine the effect on the calculated quadrupole moment of the size of the basis set[6] and the number of configurations in a CI calculation.[7] One density functional study has compared quadrupole moments calculated using the local density approximation with various exchange−correlation terms.[8] One study has calculated interactions for various complexes of benzenes and halogenated benzenes for which the quadrupole moment has been determined experimentally[9] and showed that face-to-face interactions have a higher binding energy than mutually perpendicular orientations.

We report the results of calculations for the interaction of a range of PAHs (up to four rings in size) with dinitrobenzene and some derivatives both by using the supermolecular approach and by calculating quadrupole moments with *ab initio* and density functional methods. These calculated properties are compared with recently determined stability constants in an attempt to rationalize the interaction between dinitrobenzene and various PAHs and to explain the trends in stability constants.

Methods

Standard *ab initio*, semiempirical, and density functional calculations have been performed using the GAUSSIAN 92,[10] MOPAC,[11] and GAMESS[12] platforms running on a RISC 6000. The basis set used was 6-31G(d,p)[13] (which has been shown to accurately reproduce quadrupole moments for benzene and

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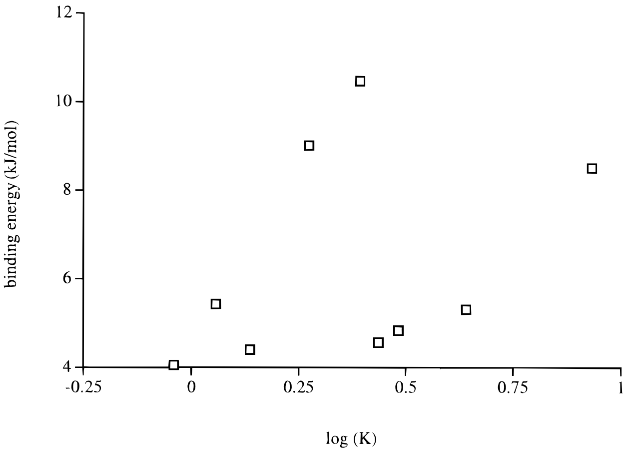


Figure 1. Plot of calculated PM3 binding energy against stability constant for the lowest energy conformation of complexes of *m*-dinitrobenzene and PAH.

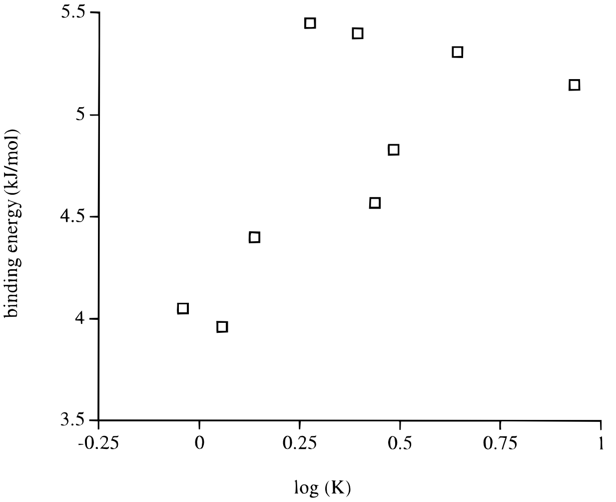


Figure 2. Plot of calculated PM3 binding energy against stability constant for lowest energy face-to-face complexes of *m*-dinitrobenzene and PAH.

naphthalene[6]), all DFT calculations were performed with BLYP,[14] and the semiempirical calculations used the AM1[15] and PM3[16] Hamiltonians.

Binding energies of optimized complexes are presented in Table 1 and plotted in Figures 1−3, quadrupole moments of polycyclic aromatic hydrocarbons in Table 2 and Figures 4 and 5, and quadrupole moments of nitro-substituted benzenes in Table 3. In most cases, the single-point calculations using a method such as BLYP have been performed at a geometry optimized at a semiempirical level of theory such as PM3. This is referred to in the text as BLYP//PM3.

Results and Discussion

Geometries of PAHs containing one to four rings have been optimized using the AM1 and PM3 Hamiltonians. Both methods produce geometries that are close to the experimental results and to each other. Geometries of *m*-dinitrobenzene and several derivatives of nitrobenzenes have been optimized by use of the AM1 and PM3 methods.

The position of a *m*-dinitrobenzene molecule relative to each of the PAHs was optimized using the PM3 Hamiltonian, and then every molecular parameter was relaxed for a complete energy minimization. In no case was there any significant change in molecular geometry between the partially optimized and fully optimized structures. Starting geometries were chosen to incorporate every possible face-to-face interaction, with the distance between the two rings set at 3.5 Å (close to the crystallographic value reported for the hexamethylbenzene−chloranil complex[17]). For most molecules, local minima were found at both parallel and perpendicular orientations; however for naphthalene and phenanthrene, only face-to-face minima were found. Since there are two different types of interaction possible, the lowest energy configuration of each type will be considered. In the case of parallel interactions, the distances between the rings were between 4.0 and 4.5 Å, which is slightly longer than in previously reported studies.[2]

The binding energy for the lowest energy minimum of each complex is given in Table 1 and plotted against the log of the retention factor, which is proportional to the binding energy, in Figure 1. It is clear from this graph that there is no real correlation between the lowest energy conformation and the retention factor. Since PM3 is known to overestimate hydrogen bonding (which would be facilitated by a perpendicular ar-

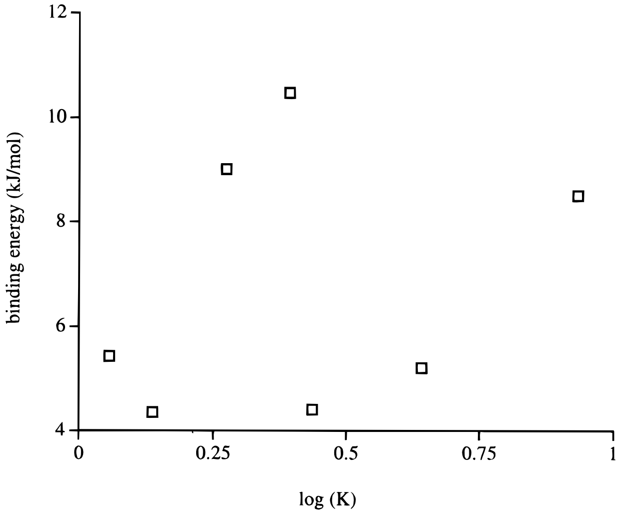


Figure 3. Plot of calculated PM3 binding energy against stability constant for the lowest energy perpendicular complex of *m*-dinitrobenzene and PAH.

TABLE 1: Calculated PM3 Binding Energy (in kJ mol^{-1}) for Complexes with *m*-Dinitrobenzene of Polycyclic Aromatic Hydrocarbons

	E(maximum)	*E*(perpendicular)	*E*(parallel)
naphthalene	4.05		4.05
biphenyl	5.43	5.43	3.96
biphenylene	4.40	4.36	4.40
fluorene	9.01	9.01	5.45
9,10-dihydroanthracene	10.47	10.47	5.40
anthracene	4.57	4.41	4.57
phenanthrene	4.83		4.83
pyrene	5.31	5.21	5.31
tetracene	8.51	8.51	5.15

TABLE 2: Quadrupole Moments (in buckinghams) for Planar (and Near-Planar) Polycyclic Aromatics Calculated Using the 6-31G(d,p) Basis Set

	HF//AM1	HF//PM3	B-LYP//AM1	B-LYP//PM3	previous
benzene	−8.55	−8.45	−6.36	−6.28	−8.48[a]
naphthalene	−13.56	−13.42	−9.86	−9.75	−13.49[b]
biphenylene	−15.79	−15.59	−11.55	−11.39	
fluorene	−14.94	−14.84	−10.53	−10.45	
anthracene	−18.61	−18.43	−13.43	−13.47	−16.59[c]
phenanthrene	−18.74	−18.48	−13.51	−13.28	−16.78[c]
pyrene	−20.82	−20.63	−14.80	−14.65	−17.7[c]
tetracene	−23.85	−23.60	−17.11	−16.87	

[a] Experimental from ref 22. [b] Experimental from ref 23. [c] Previous theoretical (HF/3-21G) from ref 24.

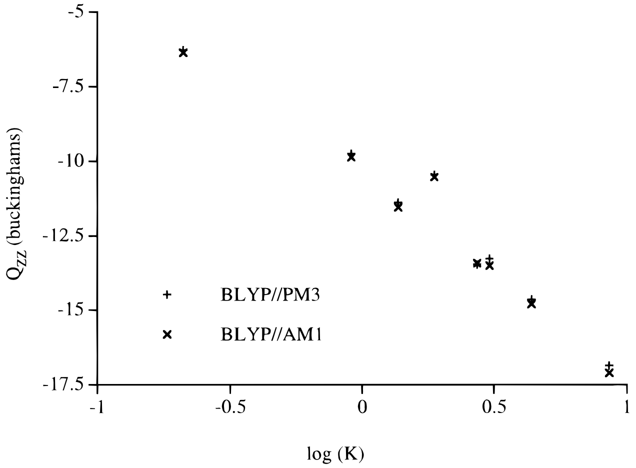


Figure 4. Plot of calculated BLYP/6-31G(d,p) quadrupole moment (in buckinghams) against stability constant for polycyclic aromatic hydrocarbons.

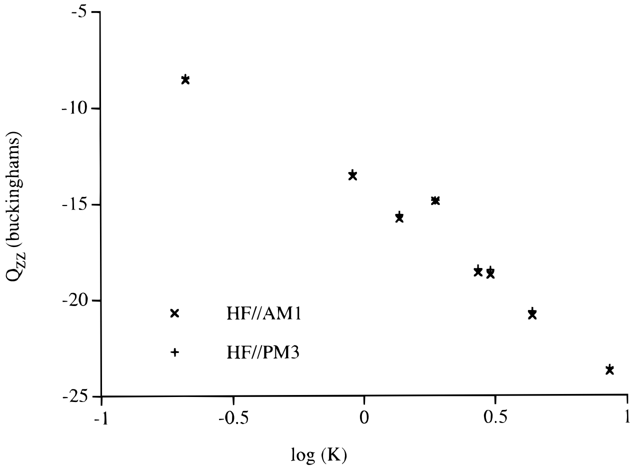


Figure 5. Plot of calculated HF/6-31G(d,p) quadrupole moment (in buckinghams) against stability constant for polycyclic aromatic hydrocarbons.

TABLE 3: Calculated Q_{zz} for Substituted Benzenes Calculated Using the 6-31G(d,p) Basis Set

	HF//AM1	HF//PM3	B-LYP//AM1	B-LYP//PM3
$C_6H_5(NO_2)$	−1.84	−1.66	−0.75	−0.64
m-$C_6H_4(NO_2)_2$	+11.77	+12.23	+10.23	+10.51
p-$C_6H_4(NO_2)_2$	+15.76	+16.41	+13.54	+13.95
$C_6H_3(NO_2)_3$	+27.53	+26.84	+22.35	+22.06

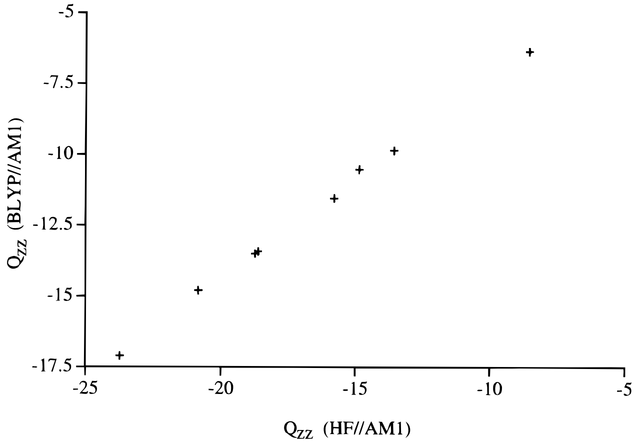
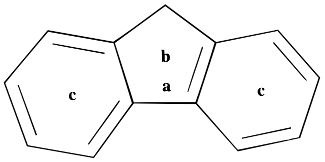


Figure 6. Quadrupole moments (in buckinghams) for PAHs calculated using the 6-31g(d,p) basis set at the BLYP and HF levels of theory.

SCHEME 1: Origins Considered for Calculation of Q_{zz} of Fluorene (a is the center of charge, b and c are the centers of rings)



rangement) and to underestimate $\pi-\pi^*$ type interactions,[18] the lowest energy conformation of each type has been separated and is plotted against the stability constant in Figures 2 and 3. It is clear from these graphs that there is no correlation in the perpendicular arrangement; however for parallel conformations there is some sort of correlation apparent for a number of the points. Some points, however, lie quite far from the line. This is the sort of graph that was suggested by Clare to give the best correlation with experiment.

The calculated quadrupole moments (component Q_{zz} perpendicular to the ring) for planar and some near-planar PAHs are presented in Table 2. It can be seen that for the two semiempirical geometries there is very little change in the quadrupole moment, and hence the semiempirical geometries can be considered to be adequate for the calculations. The quadrupole moments calculated at the HF/6-31G(d,p) level are within experimental error, but this is believed to be due to fortuitous cancellation, since a larger basis set increases the quadrupole moment, and electron correlation has been demonstrated to lower the calculated quadrupole moment. Quadrupole moments calculated using BLYP are consistently lower than those calculated at the Hartree−Fock level, and the two methods are compared in Figure 6. The plot of BLYP against HF is very close to a straight line, indicating that while electron correlation is necessary to obtain the true value of a quadrupole moment, the trends in a series of molecules are well-characterized at the HF level.

The calculated quadrupole moments are plotted against the log of the retention factor in Figures 4 and 5. It can be seen from these that there is a very good correlation for most of the points calculated. This would suggest that the interaction is governed by electrostatics, for which we would expect a linear relationship. The calculated quadrupole moments Q_{zz} for some nitrobenzenes are listed in Table 3. It can be seen that for disubstituted benzenes the quadrupole moment is positive, and hence the preferred orientation for the two molecules (based on the quadrupole−quadrupole interaction) is a parallel conformation of the two rings.

One drawback of describing these interactions by the quadrupole moment is that an experimentally measurable unique quadrupole moment exists only for planar PAHs with a high degree of symmetry. The reported quadrupole moments for phenanthrene and fluorene have been calculated at the center of charge. The calculated Q_{zz} for fluorene is −14.84 B (buckinghams) (1 B = 1.602×10^{-39} C m^2) at the center of charge, −14.55 B at the geometric center of the five-membered ring, and −14.93 B at the center of either aromatic ring (marked a, b, c in Scheme 1). In both plots, fluorene is the only molecule that is not very close to the line. It is probable that the dipole of the molecule plays some role in the interaction; however the proximity of the point to the line suggests there may well be an interaction with the quadrupole.

In large organic systems, dispersion has been considered to be a significant contribution to the binding energy. The PM3 calculations discussed earlier do not describe dispersion interactions well, and a perturbative treatment to obtain the dispersion energy is unfeasible for molecules of this size. The dispersion

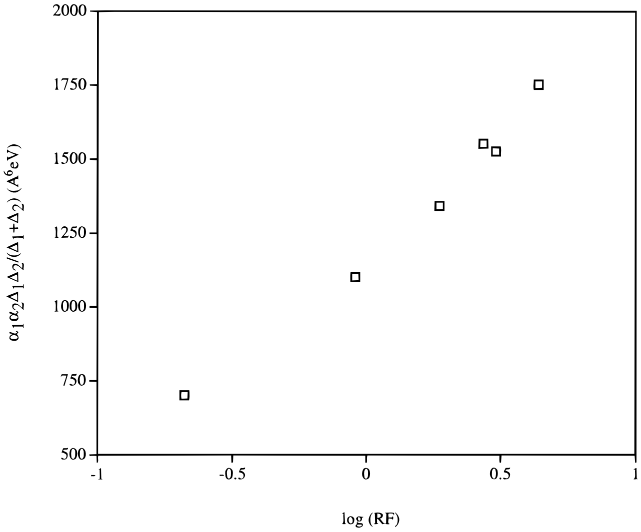


Figure 7. Plot of dispersion coefficient against stability constant for polycyclic aromatic hydrocarbons.

energy of two molecules can be estimated using the London expression $W_d = -3\alpha_1\alpha_2\Delta_1\Delta_2/(\Delta_1 + \Delta_2)32\pi^2\epsilon_0^2r^6$, where α_1 and α_2 are the molecular polarizabilities, Δ_1 and Δ_2 are the ionization potentials of molecule 1 and 2, and r is the intermolecular distance. Figure 7 plots the value of $3\alpha_1\alpha_2\Delta_1\Delta_2/(\Delta_1 + \Delta_2)$ against the stability constant for polycyclic aromatics for which experimental polarizabilities[19] and ionization potentials[20] are available (the polarizability of dinitrobenzene is estimated to be 13.78 Å^3 using the empirical method of Miller[21]). There seems to be a good linear correlation, with the positions of the isomers anthracene and phenanthrene being in the wrong order. However, if dispersion energy were the dominant contribution to the binding energy, then one would expect both *n*-hexane and cyclohexane to have a higher stability constant than benzene, but no alkyl compounds were retained strongly in the experimental study. The dispersion energy is thus considered to be a relatively minor contribution to the binding energy of polycyclic aromatic hydrocarbons to *m*-dinitrobenzene.

Conclusions

PM3 and AM1 Hamiltonians provide molecular geometries for polycyclic aromatic hydrocarbons and for nitrated benzenes that are close to the experimental results and are sufficient for calculating quadrupole moments. Optimization of complexes shows that there do exist face-to-face as well as perpendicular conformations that are local minima on the potential energy surface at the PM3 level, but a comparison of the energy with the stability constant gives no reasonable correlation. Contrary to previous work in this area, PM3 is inadequate for the calculation of binding energies of these systems.

At the HF/6-31G(d,p) level the quadrupole moments for benzene and naphthalene are within experimental error, probably due to fortuitous cancellation of errors. A plot of the quadrupole moment against the stability constant gives a good correlation, and it is suggested that this is an indication that the interaction is electrostatically controlled, and the dominant interaction is the quadrupoles of the two aromatic groups. This makes prediction of stability constants difficult, as for most species, the quadrupole moment is origin-dependent and hence cannot be uniquely determined. However, we have correlated retention behavior reasonably well with a one-electron property that can be readily determined theoretically, and this could be used as a predictive tool for larger aromatic systems for which there is little previous experimental data. A comparison of quadrupole moments calculated at the HF and DFT levels of theory shows that the two methods produce quadrupole moments that are effectively proportional to each other, and so a high-level treatment is not necessary to correlate the theory with the experiment, which makes it computationally efficient to use this method for prediction.

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