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Potential Energy Surface of the Benzene Dimer: Ab Initio Theoretical Study

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Abstract: The potential energy surface of the benzene dimer was studied by ab initio methods with inclusion of correlation energy. Three minima of importance were localized on the surface and a further one at a higher energy. Surprisingly the most stable structure was found to be the parallel-displaced structure at all theoretical levels followed by two T-shaped structures, one normal and one displaced. The normal T-shaped structure is slightly less stable. The energy barriers among the three most stable minima are very low, so that all are in dynamic equilibrium. The experimental intermolecular distance (4.96 Å) determined for the T-shaped structure agrees nicely with the respective theoretical value of 5.0 Å. The theoretical stabilization enthalpy (2.3 kcal/mol) supports one of the experimental values based on bulk properties of benzene (2.4 kcal/mol). The stabilization enthalpy derived from experimental measurements of appearance potentials (1.6 ± 0.2 kcal/mol) is slightly below the theoretical value here. The structural preponderance of the T-shaped and parallel-displaced forms even for larger systems—and their semiquantitative understanding as quadrupole–quadrupole interactions—also is seen to carry through to complex aromatic–aromatic interactions in solid benzene as well as in the crystalline proteins, showing these interactions to be of generic importance.

Introduction

Why is the benzene–benzene interaction so important? The answer is simple: it is the prototype for significant interactions between aromatic π-systems in chemistry, biology, and physics. The interaction of benzene molecules represents without a doubt an archetypal system for the interaction of aromatic molecules. Understanding the nature of interaction in the benzene dimer will elucidate the nature of such diverse phenomena as vertical base–base interaction in DNA, intercalation of drugs into DNA, packing of homogeneous and heterogeneous aromatic molecules in crystals, tertiary structures of proteins, and porphyrin aggregation.

A short survey of the most important experimental and theoretical studies contributing to the description of the dimer is as follows. The benzene dimer was believed to have a parallel-sandwich structure, but the experimental results[1] showed a dipole moment for the dimer which clearly excludes this structure. It was later suggested[2] on this basis that the molecules are located in perpendicular planes forming the T-shaped structure, but really only their inequivalence could be stated. Even this conclusion, however, does not prove that only a single T-shaped structure exists; in the respective experiments, only the structures with a dipole moment are active, and hence only these are observed. The dimer was studied in this laboratory,[3,4] and from the excitation splitting of homoisotopic dimers $(C_6H_6)_2$ and $(C_6D_6)_2$ it was concluded that the dihedral angle between the two planes is not 90° but rather 70–90°. Karlström and coauthors[5] published as early as 1983 a high-quality ab initio configuration interaction study on the dimer and found the T-shaped structure to be more stable than the parallel-sandwich or planar structure.

Calculations by Williams[6] for the conformation of clusters of benzene molecules employing an exponential-6–1 pairwise potential led to a "herring bone" structure for the dimer. Schauer and Bernstein[7] then studied the benzene dimer also with an empirical potential. The simple exponential-6 potential predicted a parallel-sandwich as the only structure; the potential augmented by the electrostatic quadrupole term predicted again only one structure, but now the parallel-displaced C_{2h} one. Replacing the point charge electrostatic term for the quadrupole electrostatic term, one has two energetically similar structures:[7] the "herring bone" and the T-shaped structures. Similar results on the dimer were published by van de Waal[8] in 1986. The author utilized the empirical atom–atom potential with point changes for the electrostatic term. If the point charges were smaller than 0.13 e, a parallel-displaced structure resulted; when the charge was increased to about 0.17 e, a T-shaped structure was also found.

In the row of force-field calculations nine different dimer structures were also investigated,[9] employing the empirical Fraga potential; here the parallel-displaced and T-shaped structures were found to be the most stable. Čársky with coauthors[10] using ab initio SCF with dispersion energy demonstrated that the T-shaped structure is more stable than the parallel-sandwich one. In addition, it was shown[10] that distortion from the T-shaped structure (by wagging of one ring) is associated with only a marginal change in energy. In our first paper on the benzene dimer[11] nine structures were investigated using ab initio calculations with the second-order Møller–Plesset (MP2) theory. Using a small basis set, the T-shaped structure was found to be the most stable, followed by the parallel-displaced one. Further, the distortion from the T-shaped structure was connected with only

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a small energy increase. The larger basis set was applied only to the most stable T-shaped structure.

The experimental determination of the stabilization energy is somewhat involved. The only experimental information on the stabilization of the dimer comes from measurements[12] of the ionization and appearance potentials. The resulting value of 565 cm^{-1} for the binding energy contains the zero-point energy and corresponds therefore to the stabilization enthalpy.

Experimental results obtained[13] with mass-selective, ionization-detected simulated Raman spectroscopy were consistent with a T-shaped structure. The same structure resulted[14] from rotationally resolved spectra of microwave experiments. In the paper[14] some evidence was also mentioned that a still lower state of the dimer could exist.

Surprising new results were obtained[15] in this laboratory by a new way of mass-selected hole-burning experiments in the gas phase. The observed spectra are consistent with the existence of three different ground-state dimer structures. On the basis of these experiments, however, it is not possible to deduce the structure and stabilization energy of single structures. The results mentioned prompted us to reinvestigate the potential energy surface (PES), applying the larger basis set from our previous study.[11] As a result, two structures, the T-shaped and parallel-displaced, were found,[16] the latter being surprisingly more stable (−1230 versus −924 cm^{-1}). Both structures were shown to be an energy minimum. Force-field calculations employing the Fraga potential was used[17] again, and altogether ten benzene dimer structures were studied; the nature of all the stationary points was determined. In the case of a one-center charge model the only minimum on the PES corresponds to the T-shaped structure, but if the three-center charge model was utilized, two minima, parallel-displaced and T-shaped, resulted, the former structure being more stable than the latter one (−860 versus −802 cm^{-1}). The results obtained with any empirical potential should be, however, interpreted with care.

From the above survey it is evident that despite the intensive experimental and theoretical effort, the basic features of the benzene dimer PES are still not explained. We have decided therefore to reinvestigate the dimer at higher theoretical levels with the following aims: (i) to localize all the minima on the PES; (ii) to evaluate reliable stabilization energies of these structures; (iii) to estimate the computation error and hence evaluate the experimental results; (iv) to elucidate the nature of the binding in the dimer; (v) to compare the gas-phase benzene dimer structures with those occurring in the solid-phase benzene as well as with phenyl···phenyl structures found in proteins.

Calculations

Interaction Energy. Interaction energy of the dimer was determined as the sum of SCF interaction energy and correlation (COR) energy.

$$\Delta E = \Delta E^{SCF} + \Delta E^{COR} \qquad (1)$$

ΔE^{COR} was evaluated employing the second-order Møller–Plesset (MP2) theory. All the calculations were performed with the finite basis sets, and therefore, the basis set extension effects should be eliminated. The basis set superposition error (BSSE) was eliminated for ΔE^{SCF} as well as for ΔE^{COR} by using the counterpoise procedure of Boys and Bernardi.[18] All the occupied and virtual orbitals of the "ghost" system were used. We would like to mention here that recent studies[19–21] give convincing evidence that there is not any overcorrection in the original function counterpoise procedure; this conclusion was based on formal as well as numerical results.

The MP2 calculations were performed with the "frozen" core approximation; that is, the 1s electrons of carbon were not considered in the calculation of correlation energy. If not otherwise stated, the benzene geometry was kept rigid during optimization and originates from experiment (R_{CC} = 1.406 Å, R_{CH} = 1.08 Å). Only selected intermolecular degrees of freedom were optimized.

Dimer calculations were performed with the GAUSSIAN 92 set of programs,[22] utilizing the direct SCF as well as MP2 options. The one-electron properties were calculated with the CADPAC set of programs.[23]

Basis Set. Different basis sets were used for different tasks; the use of a particular basis set was dictated by the economy of the calculations. A small basis set of split-valence quality was used for the gradient optimization of the dimer. The DZ + 2P basis set (with polarization functions localized on carbons only) was utilized for a detailed MP2 search on the PES of the dimer. The full DZ + 2P basis set was applied for accurate MP2 calculations on the minima found. Finally, extended basis sets were utilized for calculations of one-electron properties of benzene. A description of all the basis sets used is presented in Table 1.

Results and Discussion

One-Electron Properties. As mentioned above the electrostatic quadrupole–quadrupole and dispersion energies are of special importance for the benzene dimer. This gives us a chance to test the quality of the basis set used already at the level of one-electron properties, by using the quadrupole moment and the dipole polarizability. From Table 1 it is clear that the quadrupole moment is not too sensitive to the quality of the basis set and all the basis sets give the quadrupole moment within experimental error. The only exception is the smallest basis set used, the MIDI-4 one. Quadrupole moments presented in Table 1 were obtained from the SCF density matrix. Passing to the MP2 density matrix, the quadrupole moments are reduced. With basis sets 2, 3, and 4 the following values of Q were obtained: −6.41, −6.40, and −7.11. For the largest basis set, for which we were able to evaluate the correlation energy correction, namely, for basis set 4, the reduction equals about 7%. Similar or smaller reductions can be expected also for larger basis sets.

Contrary to the quadrupole moment, the polarizability is much more sensitive to the quality of the basis set, and if this does not contain the polarization functions, a too small value of the polarizability results. From Table 1 it is further seen that it is especially the vertical component of the polarizability which is influenced by the quality of the basis set. Addition of two sets

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Table 1. Calculated Properties of Benzene (*E*, Total Energy; *Q*, Quadrupole Moment; α, Dipole Polarizability) (All Values in Hartrees)

no.	basis set	exponents of diffuse and polarization functions	$-E$	$-Q_{zz}$	α_{xx}	α_{zz}	α
1	MIDI-4[a]		230.158 31	8.57	72.9	21.7	55.9
2	6-31+G° [b]	sp: 0.056. D: 0.25	230.652 74	7.21	78.2	43.8	66.7
3	DZ[c]		230.640 65	7.39	69.7	24.1	54.5
4	DZ+2P[d]	C: 1.6, 0.4	230.727 03	7.59	72.3	32.8	59.1
5	DZ+2P	C: 1.6, 0.4. H: 2.0, 0.5	230.745 60	7.38	73.0	33.5	59.8
6	DZ+2P;2f	X[e]: 1.6, 0.4	230.748 88	7.27	73.9	33.6	60.5
7	DZ+2P+s(C)+s(H);2f	C: 0.0511. H: 0.0592	230.749 93	7.07	76.2	41.6	64.7
8	DZ+2P+s(C)+p(C)+2(H);2f	C: 0.0382	230.750 83	7.18	78.3	44.2	66.9
9	DZ+2P+s(C)+p(C)+s(H);3f	X[e]: 2.4, 0.8, 0.267	230.752 74	7.12	78.9	44.4	67.4
10	DZ+2P+s(C)+p(C)+s(H);4f	X[e]: 3.2, 1.6, 0.4, 0.2	230.753 01	7.08	79.2	44.5	67.7
11	DZ+2P+s(C)+p(C)+f(C)+s(H)[f]	C: 0.8	230.761 79	7.13	77.7	43.6	66.3
	exponential			7.4 ± 0.5[g]			69.6[h]

[a] Reference 24. [b] References 25, 26, 27. [c] Reference 28. [d] Polarization functions on C only. [e] Dummy atom at the center of mass. [f] Only one set of p-polarization functions on H with exponent equal to 1.0. [g] Reference 29. [h] Reference 30.

of *f*-functions to basis set 5 brings almost no improvement. On the other hand, if diffuse *s*- and *p*-functions were added (basis sets 7 and 8), a significant improvement of polarizability resulted. It is seen, however, that only extended basis sets provide polarizability within a 10% limit of the experimental value. Values presented in Table 1 were obtained again on the SCF level. From Table 1 it is clear that the polarizability is less sensitive to the inclusion of the correlation energy than the quadrupole moment. The following MP2 polarizabilities were obtained with basis sets 2, 3, and 4: 67.8, 58.9, and 58.6.

Worth mentioning is the polarizability evaluated with the medium basis set, 2, which is rather close to that evaluated with the much larger extended basis set, 8. From the values given in Table 1 as well as from values presented in Table 1 of ref 11 it is possible to conclude that it is the presence of diffuse sp-shell (exp 0.056) and diffuse d-polarization functions (exp 0.25) which is responsible for the surprisingly good value of the polarizability calculated with basis set 2. The total benzene energy calculated with basis set 2, however, is much higher than that determined with basis set 8. It must be therefore concluded that the reasonable value of the polarizability evaluated with basis set 2 is either artificial or that this basis set is well suited only for the evaluation of the polarizability. Other characteristics evaluated with this basis set, however, could be of lower quality.

For the MP2 calculations of the benzene dimer, basis sets 4 and 5 were selected. The smaller basis set, 4, was used for the detailed investigation of the dimer PES. The larger basis set, 5, was utilized for accurate calculations of the minima found. Basis sets 4 and 5 possess 288 and 360 orbitals, respectively, for the dimer.

Structure, Stabilization Energies, and Dipole Moments of Various Structures of the Benzene Dimer. Among various perturbation contributions to the interaction energy between two benzene molecules the electrostatic quadrupole–quadrupole term has a special status. This is because of its R^{-5} dependence, where *R* is the distance between centers of mass. The dispersion energy decreases more rapidly (as R^{-6}), and the last important term, the exchange–repulsion, decreases fastest (as R^{-12}). The electrostatic energy is further known[31] to be more structure dependent than the other attractive contribution, the dispersion energy. It is therefore useful to investigate the PES of the electrostatic quadrupole–quadrupole interaction. Using the expression for linear quadrupoles,[31] only two stable structures were found. In the first one the linear quadrupoles are perpendicular, while in the second one they are parallel but mutually displaced. For other structures (like parallel or linear) the quadrupole–quadrupole electrostatic term is positive, i.e. repulsive.

In our previous paper[11] nine different structures of the dimer were studied at the MP2 level utilizing small basis set. Among these structures the T-shaped and parallel-displaced structures were found[11] to be the most stable, with the former one being the global minimum. Only for this global minimum the higher level calculations (MP2/6-31+G*) were performed. Due to uncertainties with the 6-31+G* basis set (see above), the larger and more reliable basis set, 4, was used for a brief screening of the benzene dimer PES. Structures studied are presented in Figure 1. We would like to mention here that perpendicular quadrupoles are realized not only in the well-known T-shaped structure a but also in structures b and c.

Table 2 summarizes the values of the interaction energy for structures a, b, c, e, f, and g. Results obtained at the MP2/basis set 4 level will be discussed first. The most stable structure found is surprisingly the parallel-displaced structure e, followed by the displaced T-shaped structure g, and the T-shaped structures a and b. The parallel-sandwich structure f is considerably less stable, but it is still more stable than the T-shaped structure c.

One now has to raise the question whether all these structures represent energy minima. To answer this question unambiguously, it would be necessary to calculate the second derivatives of the energy with respect to all the intermolecular coordinates at the same theoretical level as it was used for the optimization. Unfortunately such a calculation at the MP2 level with basis set 4 is far beyond the capabilities of present computers. The character of the structures found was therefore determined in the following way. The geometrical structure at any stationary point is determined completely by six intermolecular degrees of freedom. If a change of any of them leads to an energy increase, the stationary point in question corresponds to a minimum. If, on the other hand, a change of any of them leads to an energy decrease, then this point does not correspond to a minimum. The choice of intermolecular degrees is arbitrary; we have taken the three translations (Δx, Δy, Δz) and three rotations (around local axes *x*, *y*, and *z*). The intermolecular distances were changed in these calculations by ±0.2 Å; all the angular coordinates were changed by ±10°. Applying this procedure, it was shown that structure a is a minimum, the rotation of one subsystem being however free. Rotation of the upper molecule in structure b around the axis coinciding with its C_6 axis leads to an energy decrease; hence, structure b could not be a minimum, and it is seen that this motion converts structure b into minimum a. Changing all six intermolecular coordinates in structure c leads to an energy increase; the same is true for structures e and g. The parallel-sandwich structure (f) clearly does not fulfill the conditions for being a minimum; displacing or rotating of one subsystem results in an energy decrease. The motions convert structure f to either d or a. Earlier, at the MP2/6-31+G$^+$ level, we have shown that the rotation of the upper subsystem in structure d around its C_6 axis leads to an energy decrease. This indicates that structure d cannot be a minimum. The motion mentioned converts structure d to e. On the basis of these results as well as of previous ones[11] we can conclude that there exists at least four stable minima on the PES of the benzene dimer.

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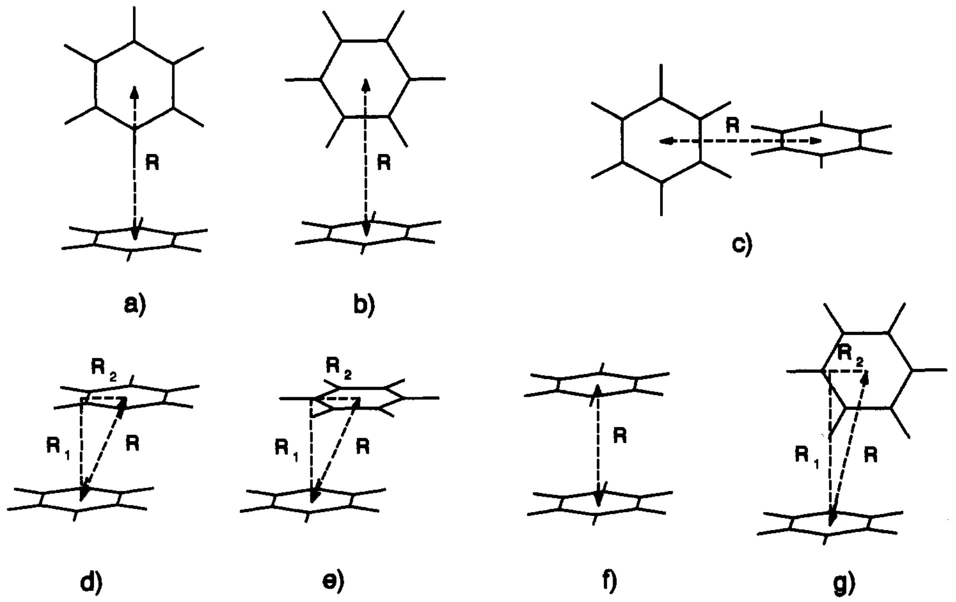

Figure 1. Structures for the benzene dimer: (a, b, and c) T-shaped; (d and e) parallel-displaced; (f) planar-sandwich; (g) displaced T-shaped.

Table 2. Interaction Energies (in kcal/mol) for Different Structures[a] of the Benzene Dimer Calculated in Basis Set 4[b] (Values in Parentheses Correspond to Interaction Energies Determined in Larger Basis Set 5[b])

	structure[a]					
R (Å)[a]	a	b	c	e	f	g
3.60					−0.360	
3.75				−1.893 (−2.225)[c]		
3.80					−0.824	
3.85				−1.978 (−2.276)[d]		
3.90					−0.853	
3.95				−1.945 (−2.211)[e]		
4.00					−0.806	
4.90	−1.792 (−2.078)					
4.96						−1.892[f]
5.00	−1.893 (−2.107)	−1.614				
5.05						−1.921 (−2.101)[g]
5.10	−1.889 (−2.049)	−1.658				
5.15						−1.862[h]
5.20		−1.618				
5.25						−1.754[i]
6.12			−0.638 (−0.888)			
6.22			−0.682 (−0.890)			
6.32			−0.666 (−0.841)			
6.42			−0.613			

[a] See Figure 1. [b] Cf. Table 1. [c] $R_1 = 3.41$ Å, $R_2 = 1.56$ Å. [d] $R_1 = 3.5$ Å, $R_2 = 1.6$ Å. [e] $R_1 = 3.59$ Å, $R_2 = 1.64$ Å. [f] $R_1 = 4.8$ Å, $R_2 = 1.2445$ Å. [g] $R_1 = 4.9$ Å, $R_2 = 1.2$ Å. [h] $R_1 = 5.0$ Å, $R_2 = 1.2445$ Å. [i] $R_1 = 5.1$ Å, $R_2 = 1.2445$ Å.

To verify the relative stabilities of the four minima found, the larger basis set, 5, was used. At that level not only were interaction energies at optimal geometries (found at the lower level) calculated but the optimization was also performed. From Table 2 it is evident that the geometry of the minima is not changed. This is not surprising because the geometry of molecular clusters is not too sensitive to the theoretical level applied. This conclusion is supported by the fact that the same geometry for T-shaped a and parallel-displaced e structures was found already at the MP2/6-31+G* level.[16] Further, the absolute value of the stabilization energy for all the minima increased when passing to basis set 5. It is important that also at that level the relative order of stabilities is unchanged; that is, the parallel-displaced structure e is more stable than the displaced T-shaped structure g and the T-shaped structure a. The respective energy differences are now 0.18 and 0.17 kcal/mol, which should be compared with the values of 0.06 and 0.09 kcal/mol, respectively, obtained at the lower level.

From the four minima found the T-shaped a, T-shaped displaced g, and parallel-displaced e structures possess a dipole moment. For the former two structures it is considerably higher than for the latter one (0.537, 0.443, and 0.004 D; HF/6-31+G* level). The T-shaped structure c has a center of inversion and, therefore, does not have a dipole moment.

Energy Barriers among the Most Stable Minima. It was shown in the previous paragraph that there exist four minima on the PES; three of them, T-shaped a, displaced T-shaped g, and parallel-displaced e, are very close in stabilization energy. To be able to distinguish these structures, the energy barriers among them should be high enough. Let us first consider the T-shaped structure a and the displaced T-shaped structure g. The wagging motion around the lowest hydrogen (i.e. pointing to the center of the second benzene molecule) converts the former structure to the latter one. Due to the symmetry, there are in fact two displaced T-shaped structures separated by the T-shaped structure a. The wagging motion described is connected with the stabilization energy decrease. The respective energy barrier was estimated from the energy of the "transition" structure, defined as the structure between both structures considered. Preliminary calculations at the MP2 level with the basis set 4 lead to the very low barrier of about 20 cm^{-1}. The two structures differ not only by their stabilization energy but also (and this is more important) by symmetry. The T-shaped structure possesses a symmetry axis given by the 6-fold rotation axis of the benzene molecule on the top. No barrier for the motion around this axis of the benzene molecule of the system was found in the calculations, which allows a free internal rotation of this dimer. This free internal rotation is unique for the perfect T-shaped structure, and the low rotational constants increase the density of energetically available states at low temperatures.

The wagging motion converting the T-shaped structure to the displaced T-shaped one is basically one-dimensional, whereas the respective motion converting the T-shaped structure to the parallel-displaced one is more-dimensional. Besides the wagging motion the displacement of the upper molecule and its approach toward the lower molecule must be considered. The more-dimensional problem brings clearly the difficulties with optimization of the transition structure. The pilot calculations have also shown that this barrier is rather low. This displaced sandwich structure also lacks the possibility of a free internal rotation, which reduces the energetically available states at low temperatures compared to the T-shaped structure.

Accuracy of Calculated Stabilization Energy. (i) The effect of truncation of the basis set has to be considered first. Basis sets larger than basis set 5 could not be used for reasons of economy for the evaluation of stabilization energies of the benzene dimer. These basis sets could be used, however, for the calculation of the quadrupole moment and the polarizability. The accuracy of the calculated stabilization energy will then be deduced from the accuracy of the these one-electron properties. From Table 1 it is clear that basis set 5 gives a rather accurate value of the quadrupole moment which agrees fairly well with that calculated using larger basis sets. On the other hand basis set 5 is still not satisfactory with respect to the calculation of the polarizability. Passing to the larger basis sets, the dipole polarizability increases by about 10%. Because the dispersion energy is proportional to the square of the polarizabilities, we may expect that by utilizing basis set 5, the stabilization energy of the benzene dimer will be underestimated by about 20%.

(ii) The role of higher correlation energy contributions has to be further taken into consideration. From the literature it is known[32] that for smaller complexes the MP3 and MP4 contributions compensate. The question arises whether a similar compensation exists also in the case of larger complexes and in particular in the case of the benzene dimer. An unambiguous answer could only be found by performing the MP4 calculation for various structures of the dimer with at least basis set 4. Such calculations are again beyond the possibilities of present computers. Smaller basis sets could not be used because they give incorrect values of absolute as well as relative stabilization energies for various structures of the dimer. The only change to estimate the higher correlation energy contributions is to use results obtained for the other benzene-containing clusters. Here we refer to our previous results on the benzene···He complex.[33] MP4 and MP2 stabilization energies, evaluated with the 6-31+G*/7s4p2d basis set, were almost identical (64.2 and 63.7 cm^{-1}), which confirms the MP3–MP4 compensation.

(iii) Finally, the effect of the subsystem geometry optimization is considered. Keeping the subsystem geometry frozen, the relaxation of the subsystem geometry upon formation of the dimer is neglected. This relaxation is known to be rather important in the case of formation of H-bonded complexes, and it is the prolongation of the X–H bond (X = O or N) in the X–H···Y H-bond which brings about the most important part of the H-bond relaxation energy. A similar effect could be expected in the case of the T-shaped benzene dimer, where the H-bond of the type C–H···π-electrons may be formed.

For the gradient optimization of the dimer the MIDI-4 basis set was selected (cf. Table 1). First, the MP2 optimization of the subsystem was performed; the following geometry parameters resulted: r(C–C) = 1.4166 Å, r(C–H) – 1.0959 Å, α = 120°. Next, the T-shaped dimer with frozen subsystem geometries was optimized. The MP2 gradient optimization of all the intermolecular degrees of freedom led to a stabilization energy of 2.80 kcal/mol and an intermolecular distance R of 4.96 Å (cf. Table 2). Finally, all the C–C and C–H bond lengths were relaxed. As a result, the geometry of the dimer changed only negligibly (no prolongation of the C–H bond was found; C–C bonds in the lower benzene increased to 1.4170 Å) and the stabilization energy increased only marginally (by 0.01 kcal/mol). Clearly the results mentioned do not support the formation of an H-bond of a C–H···π-electron type.

Evaluating the three above-mentioned effects, we can conclude that the real stabilization energy of various benzene dimer structures will be about 20% larger than the calculated one; the relative stabilization of these structures remains unchanged.

The Zero-Point Energy. In the previous paragraph it was concluded that even reaching the limit of real stabilization energies, the parallel-displaced structure remains slightly more stable than the displaced T-shaped and the T-shaped structures. Experimentally, however, it is the interaction enthalpy or change in Gibbs free energy only which can be measured. It means the zero-point energy (ZPE) as well as the entropy should be included. The intermolecular frequencies in all three structures considered are expected to be very similar. In our previous paper[34] they were estimated for the T-shaped structure using the QCFF/PI force field;[35] the respective ZPE was evaluated to be about 90 cm^{-1}, i.e. less than 0.25 kcal/mol.

Comparison with Experiment. Experimental geometry is available only for the T-shaped structure[14] with a distance of centers of mass of 4.96 Å. It was further shown[13] that in the T-shaped dimer the benzene rotates freely about its C_6 axis. The optimal theoretical distance for the T-shaped structure equals 5.0 Å; the internal rotation was found to be free. The experiments in this laboratory with mass-selected hole-burning spectroscopy[15] showed the existence of three stable conformational isomers of the benzene dimer, and the most prominent feature in the spectrum could be assigned to the T-shaped structure. The other two structures are found to increase in intensity only at strong cooling conditions, i.e. at very low temperatures, and represent most probably the displaced sandwich and displaced T-shaped structures. The weaker signal relative to the T-shaped structure can be explained by the lower symmetry and the absence of a free internal rotation, which reduces the energetically available states. For vibrational temperatures which lead to excitation above the barriers for interconversion between the different conformational isomers, the structure is no longer different and is described as T-shaped with large amplitude wagging vibrations. Therefore the displaced structures are only found at very low temperatures where they cannot cross the barriers and thus represent stable isomers.

The experimentally determined stabilization enthalpy[12] of the dimer is 1.6 ± 0.2 kcal/mol. The optimal theoretical stabilization energy amounts to 2.3 kcal/mol. This value was shown to be underestimated by about 20%. The real stabilization energy is therefore expected to be about 2.7 kcal/mol. Adding the estimated value of the ZPE (0.3 kcal/mol[34]), we obtain a value for the stabilization enthalpy of about 2.4 kcal/mol. The experimental value determined from ionization and appearance potentials seems to be too low. On the other hand our value agrees nicely with the stabilization enthalpy of 2.3 kcal/mol[36] obtained by evaluating different bulk properties of benzene.

The Role of the BSSE. All the energies discussed so far were

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Table 3. SCF, MP2, and Total (TOT) Interaction Energies and Basis Set Superposition Errors (BSSE) for the T-Shaped and Parallel-Displaced Structures of the Benzene Dimer (Values in Parentheses Correspond to the Interaction Energy Not Corrected for the BSSE)

		SCF		MP2		TOT	
structure[a]	basis set	ΔE	BSSE	ΔE	BSSE	ΔE	BSSE
T-shaped	6-31G+G*	1.005 (0.469)	0.536	−3.647 (−5.688)	2.041	−2.642 (−5.219)	2.577
	DZ+2P[b]	0.877 (0.532)	0.345	−2.771 (−4.778)	2.007	−1.893 (−4.245)	2.352
	DZ+2P	0.837 (0.508)	0.346	−2.944 (−4.945)	2.001	−2.107 (−4.289)	2.330
parallel-displaced	6-31+G*	4.248 (3.493)	0.755	−7.765 (−4.520)	3.517	−3.517 (−7.517)	4.000
	DZ+2P[b]	4.429 (3.929)	0.503	−6.407 (−3.500)	2.907	−1.978 (−5.385)	3.407
	DZ+2P	4.476 (4.049)	0.427	−6.752 (−4.184)	2.568	−2.276 (−5.271)	2.995

[a] Cf. Figure 1. [b] Polarization function only on carbons.

Table 4. Various Contributions to the Total Interaction Energy Evaluated with Basis Set 5 for Optimal Distances of the T-Shaped a and Parallel-Displaced e Structures (Energies in kcal/mol)

structure[a]	R (Å)	ΔE^{SCF} [b]	E^{QQ} [c]	ΔE^{MP2} [d]	E^{D} [e]	ΔE
T-shaped	5.0	0.837	−1.361	−2.944	−0.803	−2.107
parallel-displaced	3.85	4.476	−1.476	−6.752	−3.856	−2.276

[a] Cf. Figure 1. [b] SCF interaction energy. [c] Electrostatic quadrupole–quadrupole energy. [d] MP2 interaction energy. [e] London dispersion energy.

corrected for the BSSE. As mentioned before, there are now no doubts about the correctness of this procedure. To demonstrate this and also to shed more light on this question, we present in Table 3 values for the interaction energies which were and were not corrected for the BSSE. Clearly, the BSSE(SCF) is considerably smaller then the BSSE(MP2). Increasing the size of the basis set leads to the BSSE decreasing but only very slowly. Extending the basis set even further, the BSSE and especially the BSSE(MP2) will remain large. This is due to the presence of diffuse polarization functions in the calculation. These functions are, however, inevitable for the proper description of the correlation interaction energy. Hence, the idea that the BSSE should converge to a negligible value upon extending the basis set is not correct. The values of the uncorrected interaction energies represent a further argument supporting the inclusion of the BSSE. From Table 3 at first sight it is evident that these energies are too large for the T-shaped and especially for the parallel-displaced structure, exceeding several times the experimental value. Inclusion of the BSSE is appropriate for obtaining reasonable values not only for the stabilization energies but also for the intermolecular distances. As shown above, the theoretical intermolecular distance found for the T-shaped structure agrees nicely with the respective experimental value. Not taking the BSSE into account resulted in shorter intermolecular distances. At the MP2/basis set 3 level this gives 4.90 and 3.65 Å for the T-shaped and parallel-displaced structures, respectively.

Analysis of Stabilization Energy at the Energy Minima. Various contributions to the interaction energy at the energy minimum of the T-shaped a and parallel-displaced e structures are presented in Table 4. The perturbation electrostatic quadrupole–quadrupole moment and the London dispersion energies were calculated along the known expressions[31] using the quadrupole moment and dipole polarizability evaluated at the HF level with basis set 5 (cf. Table 1). Let us recall that ΔE^{SCF} contains besides the electrostatic quadrupole–quadrupole term other contributions such as exchange–repulsion, penetration, or induction. Similarly, the ΔE^{MP2} contains besides the London dispersion energy other contributions such as intrasystem correlation energy or higher contributions to the dispersion energy. From Table 4 it is evident that despite the fact that the electrostatic term stabilizes both structures, the ΔE^{SCF} term destabilizes them. This clearly demonstrates the importance of the exchange–repulsion term. Further, the ΔE^{MP2} is for both structures more stabilizing than the electrostatic energy. On the other hand the absolute as well as the relative values of the quadrupole–quadrupole term are similar to those of ΔE. From the above discussion, however, it is evident that this is only due to the compensation of different energy contributions which can be larger in absolute value than the electrostatic quadrupole–quadrupole term. Further, it must be considered that this conclusion was made for the intermolecular distances found by ab initio calculations.

We can conclude this section by stating that the bonding in both structures is governed by the correlation interaction energy and that the electrostatic quadrupole–quadrupole energy is smaller. The latter term is in the region of the energy minima comparable to the London dispersion energy. Due to its distance dependence, the electrostatic energy is structure determining.

Comparison of the Calculated Benzene–Benzene Interactions with Phenylalanine–Phenylalanine Interactions in Proteins and with Benzene–Benzene Interactions in the Solid Phase. Geometries of aromatic residues in proteins of 200 kD were analyzed[37] using high-resolution crystal structures. It was found[37] that a specific geometric aromatic–aromatic interaction dominates and occurs most frequently. These interactions appeared with a significantly higher frequency than was expected from the random distribution.[37] Two hundred and twenty phenylalanine–phenylalanine interactions found in crystal structures of proteins exhibit high occurrence of T-shaped and parallel-displaced structures and almost no occurrence of sandwich and planar structures. This points to definitive long-range interactions within protein molecules via the aromatic rings and led Hunter and Sanders[38] to formulate empirical rules explaining the interaction of aromatic π-systems. The first three rules are as follows: (i) Face-to-face orientations are unfavorable and are not observed. (ii) Edge-to-face interactions are favorable and are observed. (iii) Offset stacked interactions are favorable and are observed.

Evidently, these rules are a summary of the observed structures but can be seen here to directly result from the interaction of two quadrupoles. To describe the interaction of π-systems, the authors[38] have introduced the simple electrostatic model. To be able to explain stabilization of both the T-shaped and parallel-displaced structures, the π-charges above and below the benzene plane were introduced. This is without a doubt the correct idea. The position of these charges as well as determination of π-σ charge splitting in their work is, however, almost arbitrary. With another choice of these "parameters" different optimal structures result. For example, increasing the original charge separation of ±0.05 e (ref 38) to the more realistic value of ±0.1 e or ±0.15 e results in no stabilization for the parallel-displaced structure! The solution to this arbitrary mode is straightforward. It is only necessary to recognize the role of molecular quadrupoles; it is the interaction of these quadrupoles which is responsible for the structure of aromatic π-systems. When analyzing the simple expression for the quadrupole–quadrupole electrostatic interaction (see above), one finds the parallel-displaced and T-shaped structures to be the only ones favorable, and the sandwich and planar structures to be unfavorable. With this simple model all the Hunter–Sanders rules (not only the first three mentioned above) follow in a straightforward way.

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From neutron diffraction experiments[39] on the solid benzene it is found that the solid is formed from parallel-displaced and T-shaped orientations of aromatic rings.

This section should be concluded by noting that the most stable structures predicted by theoretical calculations are also those found to be predominant in solid benzene or in crystalline proteins, and in fact explain long-range interactions in these proteins.

Conclusion

(i) Four minima were localized on the PES of the benzene dimer. The parallel-displaced structure was found to be slightly more stable than the displaced T-shaped and the T-shaped ones; the fourth minimum was considerably less stable.

(ii) The energy barriers among the three most stable minima found were shown to be very low. These structures are found only at very low temperatures in the jet where the benzene dimer is trapped in one of the minima of the PES. If the temperature of the intermolecular vibrational moiety is increased, the dimer can be vibrationally excited above the barriers separating the minima, and the vibrational motion can be best described as a wagging motion of the T-shaped structure with a large amplitude. During this motion all three structures will be visited. The extra stability of the normal T-shape can be caused by an increased entropy contribution from the nearly free rotation of the T-shaped structure. This increased stability would then explain the three structures observed in the experiment.

(iii) The geometry calculated for the T-shaped structure ($R = 5.0$ Å) agrees nicely with the experiments available ($R = 4.96$ Å). The calculated stabilization enthalpy of the dimer (2.4 kcal/mol) is higher than that derived from ionization and appearance potentials (1.6 ± 0.2 kcal/mol) but agrees closely with that found from bulk properties of benzene (2.3 kcal/mol).

(iv) The quadrupole–quadrupole electrostatic energies (absolute as well as relative values) are similar to the total interaction energies. This is due to the compensation of various terms, some of them being in absolute value larger than the quadrupole–quadrupole electrostatic term. Due to its distance dependence, the quadrupole–quadrupole electrostatic term determines the structure.

(v) Two of the most stable structures of the dimer, the parallel-displaced and T-shaped, were the only structures found in the solid benzene and in crystalline proteins. This surprising result sheds new light on the nature of stabilization in the solid phase as well as in crystals of biomolecules and displays an interesting generalization from the results found here.

(vi) The preferable orientation of aromatic rings of phenylalanines in protein crystals was interpreted using Hunter–Sanders rules. We have pointed out that it was not necessary to introduce these empirical rules if the role of molecular quadrupole moments of aromatic π-systems would be recognized. The same conclusions obtained by applying all the rules could be gained by a simple analysis of the quadrupole–quadrupole electrostatic term as the structurally important term which also will contribute to long-range interactions in protein structure and dynamics.

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