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Benzene Dimer: Dynamic Structure and Thermodynamics Derived from On-the-Fly ab initio DFT-D Molecular Dynamic Simulations

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Abstract: The dynamic nature of the benzene dimer was explored by on-the-fly molecular dynamics simulations based on the DFT-D method covering the dispersion energy. An all-electron DFT was performed at the BLYP/TZVP level. The parameters in the dispersion correction term were fitted to mimic the benchmark CCSD(T)/complete basis set limit potential energy curves for both the parallel-displaced (PD) and T-shaped (TS) structures of the dimer exactly. A dynamic description is important at temperatures above 10 K, where interconversion between the TS and PD structures is possible and a mixture of these two species exists. The higher the temperature, the more dominant the TS structure because of a favorable entropic contribution to the free energy. An analysis of the TS structures revealed that the symmetric c_{2v} structure, a low-lying transition state, is practically not populated and that the tilted c_s TS structure is prevalent. This finding is in perfect agreement with infrared spectroscopy.

Introduction

A key role in biomacromolecules, organic and biomolecular crystals and nanomaterials is played by aromatic $\pi-\pi$ interactions,[1] a prototype of which is the benzene dimer. The potential energy surface (PES) of the benzene dimer contains two energy minima, the tilted T-shaped (TS) and parallel-displaced (PD) structures (see Figure 1 in our previous article[5]), which are separated by several transition structures. The relative stability between these minima has been the subject of dozens of experimental and theoretical papers, and its accurate determination requires an extremely high level of quantum mechanical description. Unfortunately, this information cannot be provided by experiments. The recent studies where the stabilization energies were determined at the CCSD(T)/complete basis set (CBS) level[2–6] or the DFT-SAPT/CBS level[7] have convincingly shown that both structures are practically isoenergetic. On the other hand, high temperature favors the T-shaped structure, as it is more flexible (with both the rotation and especially the tilting motions of the axial benzene) and therefore would be more stabilized than the stacked structure at nonzero temperatures owing to entropic effects.[4]

Yet another important fact is that the energy barriers separating the TS and PD energy minima, as well as the two TS minima, are very low, of the order of magnitude of 0.1 kcal/mol.[4,7,8] These extremely low barriers indicate that the concept of equilibrium structure is misleading and should be replaced by a dynamic average structure. This is even truer for nonzero temperatures, where in addition to the enthalpy term the entropy term becomes important. Since the vast majority of experiments are performed at nonzero temperatures, passing from the PES to the free energy surface (FES) is imperative. From the above-mentioned description of the PES of the benzene dimer, it is evident that a harmonic approach (like the rigid rotor−harmonic oscillator−ideal gas approximation) has several drawbacks. One possible solution is the application of molecular dynamics (MD) simulations. It is, however, evident that empirical potentials cannot describe the fine features of the PES and more accurate, quantum mechanical procedures are required. The choice of a suitable method is limited, since the dominant stabilization energy term in all benzene dimer structures is the London

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dispersion energy. It is now well-known that all standard DFT procedures fail to describe the dispersion energy[9,10] and only correlated methods like the MP2 or CCSD(T) can be utilized. These methods are expensive and cannot be applied in the on-the-fly MD simulations of such a large complex as the benzene dimer. However, the recently introduced DFT method augmented by the empirical dipsersion energy[11,12] (DFT-D) is a good approach to solving this problem.

Very recently, Pavone et al.[13] have studied the benzene dimer using atom-centered density matrix propagation ab initio molecular dynamics by means of the DFT-D method in the original Grimme's parametrization.[11] The authors presented 4 ps simulations at relatively high temperature (65 K) and found that the average structure converged rapidly to the T-shaped structure with the distance of the centers of mass being about 4.9 Å. However, several issues remain unresolved. First, Grimme's DFT-D underestimates the PD structure by about 0.6 kcal/mol as compared to the TS structure, whereas the most accurate QM methods (see above) show that the structures are practically isoenergetic. The "artificial" preference for the TS structure definitely affects the results of the presented simulations. Second, the system should be studied at temperatures ranging from very low to higher so that the temperature dependence of its behavior could be investigated. This dependence is also important for a comparison between the calculations and experiment, because the experimental conditions are not clearly defined. Finally, longer simulations, started from different minima, will bring more reliable statistics.

The goal of this paper is to investigate the PES and FES of the benzene dimer with the aim of describing the dynamic structure of the dimer at various temperatures. To this end, we carried out on-the-fly MD simulations based on the DFT-D procedure covering the dispersion energy, which exactly mimics the benchmark CCSD(T)/CBS for the PD and TS potential energy curves.

The determination of the dynamic structure of the benzene dimer is also topical in terms of an explanation of the nature of the C−H stretching mode shift observed in the infrared spectrum upon dimerization. It should be mentioned that the benzene dimer (T-shaped c_{2v} structure) was the first system where we predicted[14] the improper blue-shifting hydrogen bond. While various examples of the blue-shifting bond were later detected experimentally,[15] the C−H⋯π blue-shifting bond in the benzene dimer was not confirmed. On the other hand, von Helden et al.[16] have recently found a small red shift (of ∼3 cm^{-1}) of the C−H stretch in the benzene dimer and shown that the two benzenes in the dimer are symmetrically inequivalent, which indicates a T-shape configuration. Very recently, we have suggested[17] that this may be explained by the fact that the c_{2v} T-shaped structure, where we confirmed the existence of the blue shift, is a transition state. In an energy minimum, which is the tilted T-shaped (c_s symmetry) structure, our anharmonic calculations suggest a red shift. However, the transition state is energetically very close to the minimum and may be accessible at higher temperatures.

Methods

DFT-D Calculations. A description of the delicate balance between the conformations of benzene dimer requires an extremely accurate method. However, accurate methods tend to be computational expensive and thus unsuitable for MD simulations. The DFT-D method,[11,12] which uses transferable parameters applicable to a wide range of molecular complexes, can yield chemical accuracy but is still not accurate enough for a description of the benzene dimer. The next logical step is a parametrization of the DFT-D just on the benzene dimer, sacrificing the transferability of the parameters in order to reach the desired accuracy. Such parameters, derived in the preceding paper,[5] provide both the desired accuracy and efficiency and have been adopted for this study.

To maximize efficiency, this DFT-D procedure is based on the B-LYP[18,19] functional. Since a reasonably large basis set must be used to achieve the required precision, we selected the triple-ζ TZVP basis set.[20]

On-the-Fly Molecular Dynamics. On-the-fly molecular dynamics is also known as Born−Oppenheimer molecular dynamics, because it obeys the Born−Oppenheimer approximation. The electronic and nuclear motions are separated; the electronic structure is treated quantum mechanically, creating a potential for classical dynamics of the nuclei. In practice, this involves calculating the energy and gradients using the ab initio quantum mechanical (QM) method in each step of classical molecular dynamics.

We have developed our own molecular dynamics code that employs external programs to perform the QM calculations. The advantage of this design is that the MD algorithms and interfaces to external programs can be written in a high-level programming language, in this case Ruby, while the most time-consuming step, the QM calculation, is performed in software optimized for that task. As a result, the code is easy to extend and modify, yet very efficient. Modular design allows the use of various software packages for the actual calculation, but in this study, we consistently used Turbomole 5.9,[21] because it offers an extremely efficient implementation of the resolution of identity (RI) approximation with an optimized auxiliary basis set[22] within the DFT procedure. The interface to the QM packages includes the implementation of the empirical dispersion calculation within the DFT-D scheme and is thus independent of the actual code used for calculation.

Energy Conservation in On-the-Fly Ab Initio MD. The first and most obvious parameter affecting energy conservation is the time step. We tested several values in simulations at constant energy. In this study, we used a 1 fs step, which had proven to be short enough to conserve total energy well while maximizing the accessible simulation time scale.

On-the-fly MD involve one more problem with energy conservation unknown in molecular mechanics—residual gradients caused by an imperfect convergence of the SCF procedure in the QM calculation. Some error due to the finite convergence limit always occurs, and Pulay and Fogarasi[23]

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have shown that this error accumulates during the simulation if molecular orbitals from the previous step are used as an initial guess for the calculation. This systematic error leads to serious leaks of kinetic energy in the time scale of picoseconds. To avoid this problem, we started the QM calculation from scratch in each step. In this case, the convergence error becomes stochastic and is canceled out during the simulation. The SCF convergence limit is set to the default value of 10^{-6} Hartree. However, such a calculation takes roughly twice as much time as starting from the previous step, but this is the best solution possible within our implementation.

With the described setup, we were able to run 20 ps constant energy simulations of the benzene dimer with a perfect conservation of total energy.

Selection of a Thermostat Algorithm. Since the time scale accessible to a molecular dynamics simulation at this level is relatively short, extra care must be taken to ensure proper sampling of conformational space. We have found that the selection of the thermostat algorithm is the most important choice affecting the results, especially in the gas phase. When a thermostat based on a global scaling of velocities, such as the commonly used Nosé–Hoover algorithm, is utilized, the only path of the redistribution of the kinetic energy in the molecule is an internal energy flow, which is slow. As a result, the conversion between the accessible conformations does not occur or takes a very long time. This effect has not been observed in condensed phase simulations, where the solvent facilitates the energy transfer.

To overcome this problem, an algorithm that does not conserve the direction of momentum should be applied. We use the Andersen thermostat, which simulates random collisions with a thermal bath. During the simulation, the velocity of a randomly selected atom is newly generated from a Maxwell distribution for a desired temperature with a selected average collision frequency. As a result, the average temperature as well as the kinetic energy distribution is conserved, but the momentum direction is randomly modified several times during the simulation. This makes it possible for the system to escape from the local minimum and thus leads to more efficient sampling.

Simulation Protocol. All the simulations presented here were 20 ps long, with a time step of 1 fs. The Verlet propagation algorithm was used in conjunction with the Andersen thermostat.[24] The mean collision frequency of the thermostat was set to 2.5 ps^{-1}.

In this work, we explored temperatures ranging from 10 to 100 K in 10 K increments. This was necessary for proper comparison with experiment. The temperature in the molecular clusters after expansion was definitely very low (~10 K). However, in almost all cases, the pre-expansion (nozzle) temperatures were much higher, which enabled sampling of a greater variety of species. The temperature gradient during the expansion was large enough to freeze the structures populated only at higher temperatures instantaneously.

At each temperature, eight MD simulations were run. Since there are two main minima corresponding to the TS and PD structures, we started half of the simulations from one minimum and half from the other. At low temperatures, we

explored only two structures, whereas at temperatures above the interconversion barrier, this allowed us to check how the trajectory depended on the initial structure. At 80 K, we doubled the number of simulations to check the reliability of the averaging.

The trajectories in one set differed only in the random initial velocities, generated from a Maxwell distribution for the given temperature.

Probability Distribution of Structural Parameters. Raw trajectories were processed to obtain a probability distribution of the structural parameters at a given temperature. First of all, we had to ensure that the collected results were not affected by the initial structure. To assess how long a time scale it would take to lose this correlation, we calculated the autocorrelation function c of the Cartesian displacement coordinates q

$$q_i = x_i - \bar{x}_i \qquad (1)$$

and variance σ^2 of the coordinates in the simulation with N frames

$$\sigma^2 = \frac{1}{N}\sum_{t=1}^{N}(x(t) - \bar{x})\cdot(x(t) - \bar{x}) \qquad (2)$$

where $x(t)$ denoted the geometry in frame t as

$$c(t) = \frac{\langle(x(t) - \bar{x})\cdot(x(0) - \bar{x})\rangle}{\langle\sigma^2\rangle} \qquad (3)$$

where angle brackets denoted the average over multiple trajectories differing in their initial conditions.

To obtain a result independent of the initial geometry, we could take only a part of the trajectory beyond the point where the autocorrelation approaches zero. In practice, we always discarded the first half (10 ps) of each trajectory after we determined that the autocorrelation decayed in approximately 5 ps. We did so because our autocorrelation functions were not perfect as they had been averaged over a small set of trajectories.

In the remaining part of the trajectory, the desired parameter was measured in each frame. A normalized histogram (probability distribution) of these values was built and averaged over the trajectories in the set.

Results and Discussion

A total of 88 trajectories were calculated, which took a total CPU time of 3.4 CPU years. All the trajectories were processed using the above-described protocol to reduce the data to probability distributions (histograms) of the structural parameters for each combination of temperature and initial structure.

First of all, we looked at populations of the T-shaped and parallel-displaced minima. The histogram of the angle between the benzene plane rings (α, see Figure 1), a coordinate best distinguishing these two structures, is plotted in Figure 2. Degrees of 0 and 90 correspond to the PD and TS structures, respectively. In this coordinate, the peak at 90° covers all the possible T-shaped structures, which may differ in the tilt angle (see the discussion below). Separate analyses were conducted for simulations starting from the
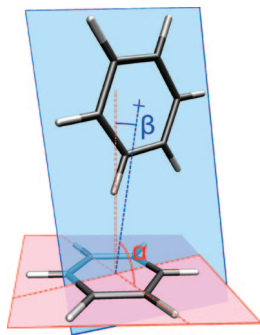
Figure 1. Definition of the angle between the ring planes α and the tilt angle β.

(a)

(b)
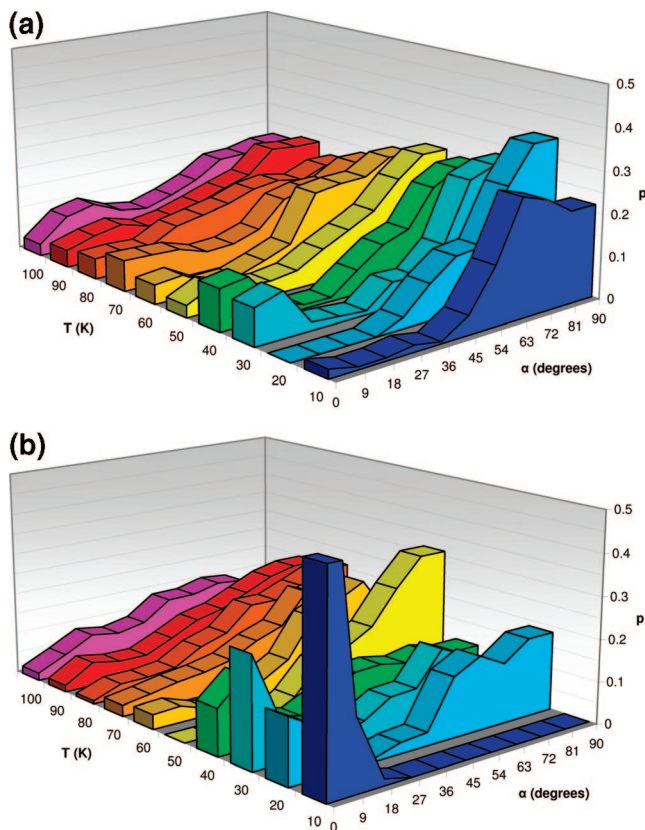
Figure 2. Probability distribution (histogram) of angle α between the benzene rings in the dimer, plotted for various temperatures. Degrees of 0 and 90 correspond to the PD and T-shaped structures, respectively. The simulations were started from the TS (a) and PD (b) minima.

T-shaped structure (a) and the parallel-displaced structure (b). Due to the short length of the trajectories, the histograms are not always smooth and there are some outlying points, yet the trends are well resolved.

Before we begin an analysis of the simulations, we should look at the benzene dimer at 0 K. The interaction energy suggests that the tilted T-shape is slightly more stable (by 0.08 kcal/mol in the DFT-D potential used in our simulations) or practically isoenergetic, as discussed above. When we add the zero-point vibration energy (ZPVE) and compare the resulting enthalpy at 0 K, these two structures become isoenergetic (see ref 4 for further details) or the PD structure is slightly favored (by 0.15 kcal/mol in our potential). On the other hand, experiment at temperatures close to 0 K
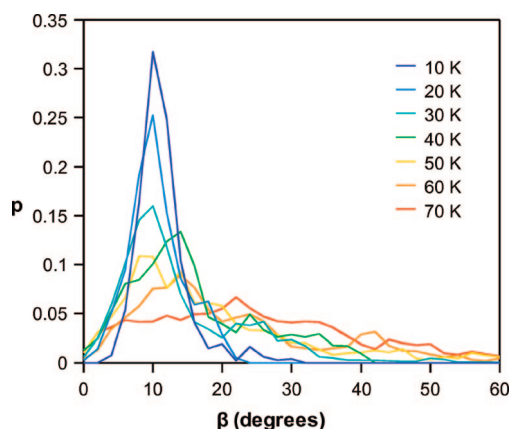
(achieved by jet cooling) records the T-shaped structure of benzene dimer. The question remains whether the vibrational temperature is really so low (see above). An accurate theoretical description of the benzene dimer at 0 K is yet to be achieved, mainly through a more accurate calculation of the lowest vibrational modes.

It must be noted that the harmonic calculation of the lowest vibrational frequencies is only a crude approximation, because these vibrations are anharmonic or nonharmonic (the anharmonic treatment is still an approximation, although of a higher order; the nonharmonic calculation would pose no limitations on the potential form). These limitations are absent in molecular dynamics: True nonharmonic potential is explored in the simulation. We also attempted to go beyond the harmonic approximation in the static description by using perturbation theory[25] as implemented in Gaussian 03,[26] but these calculations failed.

At the lowest simulated temperature of 10 K, the barrier between the TS and PD structure cannot be overcome, and the dimer stays in the minimum from which the simulation started. Above this temperature, interconversion between TS and PD is possible. There is an interesting region between 20 and 40 K, where a well-resolved peak at 0° corresponding to the PD structure is observed even in simulations starting from the T-shape. Here, both structures can coexist, although the T-shaped minimum is more populated.

At higher tempereatures (from 50 K and above), however, the results are unambiguous and the T-shaped structures are clearly favored. The question arises what the driving force for this preference is if both structures are practically isoenergetic. The answer is clear—the entropy is what turns the balance toward the T-shaped structure. Although the stacked structures are usually entropically favored when compared to the hydrogen-bonded ones, e.g. in DNA base pairs, the CH$\cdots\pi$ interaction in the benzene dimer is not rigid at all. The entropy gain as compared to the PD structure comes mainly from two sources: an almost free rotation of the horizontal (in the T letter) benzene and a very soft tilting vibrations of the vertical one (causing a very broad distribution of the T-shaped structure in the plane angle histograms even at low temperatures). Both benzene rings do rotate in both structures, but particularly this rotation is observed at the lowest temperature. The stacked arrangement is more rigid because the whole rings are involved in the interaction. As a measure of this rigidity, we have calculated harmonic frequencies of the six intermolecular vibrational modes. For the TS structure, the average value is 80 cm^{-1}, while in PD, the average is 87 cm^{-1}. We believe that this difference will be even more pronounced in an anharmonic calculation.

The entropy can be estimated on the basis of the MD simulations performed. Although the length of the trajectories is not sufficient for an accurate analysis, it is enough to show the trends and provide semiquantitative results. For this analysis, the border between the PD and TS structures should be defined. One possibility is to divide the range into halves and set the threshold for further analysis to 45°. The other possibility is to use the minimum from the plane angle histograms at about 30° (cf. Figure 2). Both values lead to similar results; the calculation presented below is based on

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Figure 3. Population (p) of tilt angle β in simulations of the T-shaped benzene dimer at various temperatures.

Table 1. Average Distance of the Benzene Centers of Mass in the Parallel-Displaced (PD) and T-Shaped (TS) Dimers from MD Simulations at Different Temperatures

T(K)	distance (Å)	
	PD	TS
10	3.95	4.87
20	3.98	4.88
30	4.00	4.87
40	4.03	4.89
50	4.07	4.93
60	a	4.88
70	4.12	4.98
80	4.10	4.99
90	4.13	5.01
100	4.16	4.99

[a] No parallel-displaced structure was observed in the simulation.

the 45° threshold. At each temperature, we calculated the equilibrium constant K as a ratio of the TS and PD structures. From the equilibrium constant, we can readily obtain the free energy difference

$$\Delta G = -RT \ln K \tag{4}$$

From a linear regression of the temperature dependence of ΔG, we can extrapolate to 0 K to obtain ΔH^0. We found the TS structure disfavored by 0.035 ± 0.05 kcal/mol at 0 K. From the slope of the fitted line, we obtained an entropy difference $\Delta S = 0.004 \pm 0.001$ kcal/(mol K). At 100 K, the entropic stabilization of the TS structure thus amounted to −0.4 kcal/mol.

This result is extremely important for the interpretation of the experiments, because it shows that the T-shaped conformation is more populated even at low temperatures and prevalent at high temperatures (which is important even in experiments at low temperature, as discussed above).

However, the measure discussed above does not distinguish between the tilted T-shaped global minimum (c_s) and the symmetrical transition state (c_{2v}). To solve this issue, we measured tilt angle β (0° for the symmetrical structure, 7.4° for the tilted global minimum; cf. Figure 1) in the trajectories starting from the TS structure, where it could be easily defined. The results, summarized in Figure 3, show that there is only a negligible population of the symmetrical structure at higher temperatures and none at 10 K. Passing from 10 K to higher temperatures, the average tilt angle gradually increases above the equilibrium value of 7.4°. At temperatures above 30 K, the trajectories sample both minima, and angle β no longer describes only the TS structure.

This finding makes it possible for us to interpret the experimental results of von Helden et al. (see above). Evidently, the small red shift which they found should be assigned to the prevalent tilted T-shaped structure. This is in agreement with our previous calculations,[17] where we predicted a red shift for this structure; a blue shift was assigned to the c_{2v} structure, which is only negligibly populated in our simulations.

Another parameter studied was the distance of the centers of masses of the benzene monomers. It distinguishes perfectly between the parallel-displaced (3.90 Å in the minimum) and

T-shaped (4.90 Å in the minimum) structures. The value for the T-shaped structure, calculated by our DFT-D method, agrees well with the experimentally measured[27] distance of 4.9 ± 0.01 Å, determined from the rotational spectrum.

From molecular dynamics, we can extract the average distance for each structure at different temperatures. The results, listed in Table 1, show an increase of the distance with temperature. This proves the anharmonic nature of this intermolecular mode, and the rate of this increase (higher in the PD structure) could serve as a measure of anharmonicity.

Conclusions

• The DFT-D method offers a very good accuracy-to-computational-cost ratio. The parameters customized precisely for the benzene dimer made it possible for us to run on-the-fly molecular dynamics simulations with a precision of coupled-cluster calculations.

• The static description of the benzene dimer at a temperature of 0 K based on an accurate energy calculation and a harmonic calculation of the vibrational frequencies suggests that the parallel-displaced structure is slightly more stable, whereas experiment detects the T-shaped structure. This issue is yet to be resolved, namely by an accurate anharmonic calculation of the vibrational frequencies and the zero-point vibrational energy.

• The dynamic description becomes important at temperatures above 10 K, where interconversion between the TS and PD structures becomes accessible. At low temperatures, a mixture of these two configurations exists, but the T-shaped structure becomes dominant as temperature increases, because it is favored by the entropic contribution to the free energy. This finding explains the experimental studies which detected only the TS structure provided that the vibrational temperature of the cluster was above 0 K, which is probable in jet cooling experiments.

• The T-shaped structure is tilted and the fully symmetric c_{2v} T-shaped transition state remains unpopulated even at high temperatures. This is in full agreement with infrared spectroscopy and the calculations that assigned the spectrum to the tilted TS.

• The intramolecular distance measured in our calculations is in perfect agreement with the experimental value; its

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increase with temperature provides evidence of the anharmonicity of the intermolecular potential.

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