



Quantum Mechanical Calculations for Benzene Dimer Energies: Present Problems and Future Challenges

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Abstract: Factors influencing quantum mechanical calculations of nonbonded interactions between organic molecules are still imperfectly understood. Much effort has gone into efforts to calculate the structures and binding energies of stable benzene dimers. However, little experimental evidence is available for comparison with theoretical results. As a benchmark for assessing the reliability and accuracy of such calculations, the benzene crystal structure seems a more suitable target than the elusive dimer structures.

For some time now, quantum mechanical calculations have been providing reliable answers to many questions about the binding energies, atomic arrangements, electron density distributions, electrical moments, and vibrational frequencies of small- to medium-sized molecules. Computer programs for carrying out the necessary computations at several theoretical levels are readily available, and many of the calculations can now be carried out with a desktop computer. During the past 10 years or so, attempts have been made to extend such calculations to questions of intermolecular binding. Since intermolecular interaction energies are only a small fraction of intramolecular bond energies, reliable answers to such questions are much more difficult to obtain.

As an example, take benzene. Although several quantum mechanical studies of the preferred structures and binding energies of benzene dimers^{1–9} have been made, there are still serious outstanding problems. Concerning the preferred structures, calculations agree that the T-shaped and parallel-displaced (PD) dimers are the most stable, with approximately equal energies, and that the energy hypersurface is rather flat with a low interconversion barrier. There is less agreement about the binding energies of the dimers. Since the intermolecular attractions are largely due to London dispersion effects, they cannot be adequately handled by Kohn–Sham density functional theory.¹⁰ Additionally, dis-

persion energies are not taken into account at the Hartree–Fock level, which treats the interaction of each electron with the averaged distribution of the other electrons. Thus, at the Hartree–Fock level, enlarging the basis set does not have much influence on the binding energies of dimers, but it has a very big effect on MP2 energies, which tend to overestimate the stabilization of the dimer because of the so-called basis-set superposition error (BSSE), as judged from results of higher-level calculations.

According to one recent study,⁶ high-level calculations with different basis sets and different methods of allowance for electron correlation and basis-set superposition error yield binding energies for the T-shaped dimer ranging from 1.40 to 3.63 kcal mol^{−1}, with 2.7 kcal mol^{−1} as the preferred value. Corresponding energies for the PD dimer range from 2.02 to 4.95 kcal mol^{−1}, with 2.8 kcal mol^{−1} as the preferred value. Even though the preferred values are probably close to the correct binding energies (by an elaborate procedure, Tsuzuki et al.⁴ obtain similar binding energies—2.46 and 2.48 kcal mol^{−1}, respectively, for the two benzene dimers), this is a discouraging result. An uncertainty on the order of a kcal mol^{−1} is too large to provide reliable answers to the problems of interest. Experimental evidence about the structures and binding energies of benzene dimers and small clusters is scarce and difficult to interpret.² Diverse studies using different techniques for preparing and analyzing gas-phase clusters have not yielded consistent structures or energies for benzene dimers. Neutron diffraction shows that there are

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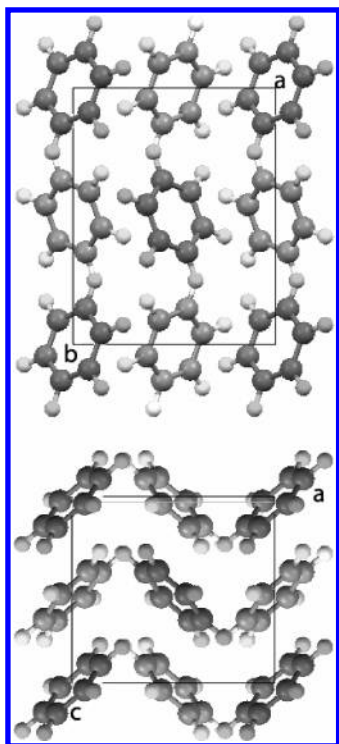


Figure 1. Crystal structure of benzene, viewed down the *b* and *c* axes of the unit cell.

no preferred orientations of neighboring molecules in liquid benzene.¹¹ Thus, there are really no reliable experimental data by which to assess and compare the results of the various computational studies. In place of the benzene dimers, a more suitable target would seem to be the calculation of the lattice energy of crystalline benzene. This is an experimental quantity whose value is known within reasonable limits. A calculation of the energy of the benzene crystal by quantum mechanical methods might first appear to be a much more formidable task than that of calculating the binding energies of benzene dimers, but with a few obvious simplifications and approximations, it should be perfectly feasible. It is, at least, a challenge.

The crystal structure of benzene has been the subject of countless experimental and theoretical studies. At normal pressures, benzene crystallizes in the space group *Pbca* with unit cell dimensions $a = 7.39$, $b = 9.42$, and $c = 6.81$ Å at 138 K.¹² The atomic arrangement is shown in Figure 1. The heat of sublimation of benzene has been variously measured as between 40 and 45 kJ mol⁻¹,¹³ with a preferred value of 44.4 kJ mol⁻¹. The switch from kcal mol⁻¹ to kJ mol⁻¹ energy units should be noted here. The lattice energy of a crystal can be derived as the sum of interaction energies between a central reference molecule and all the other molecules (divided by 2 as result of the counting method).¹⁴ Since the interaction energy falls off rapidly with increasing intermolecular separation, the sum is essentially limited to the contributions of the 12 or 14 first neighbors of the reference molecule, the first coordination shell. Expansion of the shell to include contributions from more distant partners usually adds only a few percent to the sum. For molecular crystals, the error introduced by ignoring many-

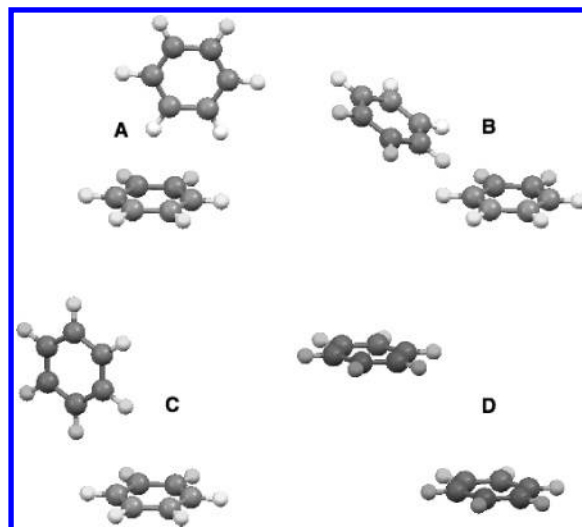


Figure 2. Molecular pairs A, B, C, and D involved in the first coordination shell of a given molecule in the crystal structure of benzene. The pairs A, B, and C are produced by the glide-reflection symmetry operations of the space group, the pair D by the *c* translation (see Table 1).

body effects in such a straightforward summation is not serious. For the benzene crystal structure, with its high symmetry, we need to consider only four types of molecular neighbor pairs, illustrated in Figure 2, with approximate interaction energies in Table 1. These pairs are *not* minimum energy pairs. They are compromises, subject to the pulls and pushes of neighboring molecules in the repeating crystal pattern, but they are, so to say, the building blocks of the crystal. Their energies were estimated by the semiclassical density sums or Pixel method^{15–18} and at two ab initio computational levels using 6-31+g(d) and 6-31++g(d,p) basis sets of orbitals, including second-order Møller–Plesset correlation energy (MP2 treatment), both with and without counterpoise corrections (Gaussian 03).¹⁹ The calculations were based on the experimental atomic coordinates and unit cell dimensions^{12,20} without any energy minimization, so that the benzene molecules in the computational scheme deviate slightly from their ideal D_{6h} symmetry. These small deviations from ideality should not have a serious effect on the pattern of pair energies.

As seen from Figure 2, a given reference molecule is engaged in four pairs of each type A, B, and C (glide reflections) and in two pairs of type D ($\pm c$ axis translation). Taking the sum of the calculated interaction energies with the appropriate multiplicities and dividing by 2, we obtain a value of 43.8 kJ mol⁻¹ for the estimated lattice energy with the Pixel values, as good an agreement with the experimental value as we could possibly hope for. The results of the corresponding ab initio calculations are not so clear. In concordance with earlier experience,^{3,6} the MP2 calculations greatly overestimate intermolecular binding and give estimated lattice energies of 89 and 111 kJ mol⁻¹, which are at least double the experimental value. Counterpoise corrections indeed reduce these energies to less than half of the uncorrected values, but the results still miss the mark. Compared with the experimental value, the smaller basis set yields too low a lattice energy (34 kJ mol⁻¹), the larger basis

Table 1. Interaction Energies (kJ mol^{-1}) of Molecular Pairs A–D (Figure 2) in the *Pbca* Crystal Structure of Benzene, as Calculated by the Pixel Method [E_{PIX} , Electron Density Calculated with MP2/6-31++g(d,p)] and by ab Initio Calculations with Two Orbital Basis Sets [6-31+g(d) and 6-31++g(d,p)] at the MP2 Level without (E_{MP2^+} and $E_{\text{MP2}^{++}}$) and with Counterpoise Correction (E_{CP^+} and $E_{\text{CP}^{++}}$)^a

pair	symmetry operation	<i>N</i>	E_{PIX}	E_{MP2^+}	E_{CP^+}	$E_{\text{MP2}^{++}}$	$E_{\text{CP}^{++}}$	<i>D</i> (Å)
A	<i>a/c</i> glide reflection	4	−9.0	−19.6	−7.9	−23.0	−10.5	5.02
B	<i>c/b</i> glide reflection	4	−6.1	−12.1	−4.8	−15.5	−7.3	5.81
C	<i>b/a</i> glide reflection	4	−5.1	−10.6	−3.5	−13.7	−6.1	5.99
D	$\pm c$ translation	2	−1.7	−4.5	−2.0	−6.9	−4.0	6.81
	lattice energy estimate		−43.8	−89.1	−34.4	−111.3	−51.8	

^a The distances *D* are between centers of mass of the two molecules in the pair. Column *N* gives the number of symmetry-related pairs involving a given reference molecule.

Table 2. Pixel Energies (kJ mol^{-1}) for the Molecular Pairs A–D (Figure 2) Based on Charge Densities Calculated at Different Theoretical Levels^a

pair	symmetry operation	<i>N</i>	HF/3-21G	MP2/6-31G**	MP2/6-31+G(d)	MP2/6-31++G(d,p)
A	<i>a/c</i> glide reflection	4	−14.9	−11.2	−9.3	−9.0
B	<i>c/b</i> glide reflection	4	−10.2	−7.7	−7.7	−6.1
C	<i>b/a</i> glide reflection	4	−7.8	−6.2	−5.1	−5.1
D	$\pm c$ translation	2	−2.0	−1.6	−1.8	−1.7
	lattice energy estimate		−69.8	−53.4	−47.8	−43.8

^a Column *N* gives the number of symmetry-related pairs involving a given reference molecule.

set too large an energy (52 kJ mol^{-1}). The simple Pixel calculation gives the best result, and it is interesting that the individual pair energies quite closely parallel those from the MP2/6-31++g(d,p) calculation with counterpoise correction ($E_{\text{CP}^{++}}$).

The experimental estimate of the lattice energy of benzene ($40\text{--}45 \text{ kJ mol}^{-1}$) can be regarded as a kind of benchmark for assessing the reliability of high-quality quantum mechanical calculations for benzene dimers. The Pixel calculation comes close to the mark, but its partitioning of the energy into Coulombic, polarization, dispersion, and repulsion contributions is to some extent arbitrary and parameter-dependent.^{15–17} The MP2 calculations give more than double the correct value and are clearly not very useful. The counterpoise-corrected values yield erratic values for the lattice energy, and it is not obvious how any larger basis set or improved BSSE correction would influence the result. In contrast to the behavior of the quantum mechanical pair energies, Pixel energies show a steady decrease as the quality of the theoretical level of the calculation improves (Table 2).²⁰ The low-level Hartree–Fock 3-21g charge density is wide of the mark, while the final value (MP2/6-31++g(d,p)) is within the experimental range.

In principle, interaction energies of the molecular pairs A–D are no more difficult to calculate than those of the T-shaped and PD dimers—easier, in fact, since no energy minimization procedures are needed—but with a present uncertainty on the order of 1 kcal mol^{-1} ($\sim 4 \text{ kJ mol}^{-1}$) in the estimated interaction energy of each benzene molecular pair, as might be inferred from the range of results for the benzene dimers, the goal of calculating an unconditionally reliable ab initio value for the lattice energy of benzene may still seem remote, but it is on the horizon and should be attainable.

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- (14) Why divide by two? This question may occur to readers unfamiliar with the bookkeeping of lattice energy. For simplicity, consider a cluster of *N* monatomic molecules. Each molecule interacts with all the others, so there are $N(N-1)/2$ separate interactions, each of which contributes to the total cohesive energy of the cluster. If this energy is to be expressed in molar units, e.g., kJ mol^{-1} , then the sum

over the cluster has to be divided by N , the number of molecules in the cluster. For an extended crystal, where all molecules can be regarded as equivalent, the same result is obtained by choosing an arbitrary reference molecule, summing over the $N - 1$ interactions with the remaining molecules, and then dividing by 2. If the molecules in the crystal are not equivalent, e.g., if $Z' > 1$ or in a cocrystal, then the matter becomes more complicated.

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- (20) This information can be conveniently recovered from the Cambridge Structural Database (CSD), distributed by the Cambridge Crystallographic Data Centre, Cambridge, England (www.ccdc.cam.ac.uk), under the refcode BENZEN01.
- (21) In the four Pixel calculations (Table 2), the dispersion contribution to the binding energy is dominant and remains nearly constant. The largest energy changes occur in the repulsion contribution, which increases with the expansion of the basis set.

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