

HIGH LEVEL *ab initio* CALCULATIONS ON ACETYLENE DIMER — A PROTOTYPE FOR ESTIMATION OF THE ACCURACY OF THE BENZENE DIMER STABILIZATION ENERGY

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High level *ab initio* calculations (up to MP4/DZ + (2*df*, 2*p*)) on acetylene dimer permit the evaluation of a highly accurate stabilization energy of the dimer (5.9 kJ/mol) and hence serves as a test case for the error limit for lower level calculations. This error limit was employed to estimate the stabilization energy and enthalpy in the benzene dimer calculation. From this the theoretical value of formation enthalpy at 0 K (11.3 kJ/mol) is obtained which is larger than the corresponding experimental value (6.7 ± 2.1 kJ/mol).

As the measurements on large van der Waals molecules become feasible it is important to compare such measurements with accurate *ab initio* calculations, of tested precision. The bonding between two benzene molecules has been intensively studied theoretically and experimentally in the recent years¹⁻⁴. Whereas the theoretically determined structure and dipole moment are consistent with experimental findings, the theoretical stabilization energy of the dimer differs from the experimental value¹.

The stabilization energy of the benzene dimer was determined¹ using second order Møller-Plesset perturbation theory (MP2) with basis set of DZ quality augmented by diffuse *s*, *p* and *d* functions. While the SCF interaction energy is believed to be accurate enough, the correlation interaction energy may suffer from two reasons: (i) Lack of higher polarization functions, (ii) truncation of perturbation theory at the second order. Inclusion of higher polarization functions usually leads to larger stabilization^{5,6}. The effect of inclusion of higher-order correlation contributions, however, is not as straightforward; with some complexes it leads to larger stabilization, with other ones to smaller stabilization^{5,6}. The size of the benzene dimer prevents one from the studying both effects more carefully and thus determine the stabilization more accurately. In fact calculations of the dimer with 252 orbitals were on the limit of performance of the computer used (CRAY-YMP). The only way how to estimate effects mentioned is to perform the high-level calculations for smaller van der Waals molecule. We are aware of problems of the choice of such

a model system. The model system should be structurally and electronically similar to the pattern van der Waals molecule, further, the overall stabilization should originate from the same energy contributions. As a model for the benzene dimer we have chosen the acetylene dimer. The optimal structure of this dimer is the same as that of the benzene dimer, i.e. the T-shape structure^{7,8}. Further, the overall stabilization comes from the same contributions as in the case of benzene dimer: 1) quadrupole-quadrupole electrostatic contribution; 2) H-bond contribution between H of one subsystem and π -electrons of the second subsystem; 3) dispersion contribution. The size of the acetylene dimer allows us to study the role of higher order correlation contributions as well as to use an extended basis sets. In this way we can evaluate the energy difference when passing from low (MP2/6-31 + G*) to high (MP4/extended basis set) level. We believe that because of the similarity between both dimers we can use the difference found for acetylene dimer for the estimation of the high level stabilization energy of the benzene dimer. The high level refers to MP4 calculations with an extended basis set; it is clear, however, that stabilization energy evaluated even at this level is still not saturated. The respective difference could only be estimated from a few published data on very small van der Waals molecules.

The aim of the present paper is following:

- 1) to calculate the acetylene dimer stabilization energy at low and high levels and to determine the respective difference;
- 2) to use this difference for evaluation of the high level stabilization energy of the benzene dimer (from the known¹ low value stabilization energy);
- 3) to estimate the true stabilization energy of the benzene dimer on the basis of published data on small van der Waals molecules;
- 4) to determine the zero-point energy of the benzene dimer and thus the respective stabilization enthalpy.

THEORETICAL

The interaction energy (ΔE) was determined with second- (MP2) and fourth-order (MP4) Møller-Plesset theory (MP4 means SDTQ-MP4). The ΔE term consists of SCF and correlation energy (COR) contributions.

$$\Delta E = \Delta E^{\text{SCF}} + \Delta E^{\text{COR}}(\text{MP}_n) \quad n = 2, 4 \quad (1)$$

The basis set superposition at SCF and post-SCF levels was eliminated by the counterpoise method of Boys and Bernardi⁹; all the orbitals of the "ghost" system were included.

Three different basis sets were used. The first one (A), is the basis used for benzene dimer¹. It is the 6-31 + G* basis set; exponents of diffuse *sp*-shell and of diffuse *d*-shell are 0.056 and 0.25, respectively. The second basis set is DZ basis set¹⁰ aug-

mented by the same diffuse *sp*-shell as basis A; further two sets of *d*-functions ($a(d_1) = 0.8$; $a(d_2) = 0.15$) on the carbon atoms and two sets of *p*-functions ($a(p_1) = 1.1$; $a(p_2) = 0.1$) on the hydrogen atoms were added. Finally, basis set C is basically basis B with addition of *f*-functions on the carbon atoms. These *f*-functions were dispersion optimized, and the resulting exponent is 0.12.

RESULTS AND DISCUSSION

Acetylene Dimer

The intrasystem geometry of the acetylene monomer was kept rigid during all the calculations and originates from MP2 optimization with the TZ2P basis set of ref.⁷ (C—C 120.8 pm, C—H 106.0 pm).

First, the T-shape structure of the acetylene dimer was optimized at MP2 level with basis set A. The minimum (5.23 kJ/mol) was found at 449.3 pm (distance of mass centers). The distance is larger than that found in ref.⁷ (430.9 pm (MP2/DZP); 434.1 pm (MP2/TZ2P)); it must be kept in mind, however, that the potential energy surface is extremely shallow. Our stabilization energy agrees very well with results of ref.⁷ obtained with a larger (TZ2P) basis set (5.27 kJ/mol). The nice agreement gives support for the quality of the basis set A containing only one set of *d*-functions (contrary to two sets used in TZ2P basis set of ref.⁷). It clearly demonstrates the importance of the diffuse *d*- as well as *sp*-shells¹¹.

At the minimum found we have further calculated the fourth-order correlation energy with basis set A. The resulting stabilization energy decreases from 5.23 kJ/mol (MP2) to 4.85 kJ/mol, i.e. by about 7%. A similar decrease was found^{5,6} for other van der Waals molecules. The third order correlation contribution for acetylene dimer is of a repulsive nature and in absolute value it is larger than the fourth-order term. It is important to note that pilot calculations with minimal basis set for the benzene dimer¹ have shown that the sum of MP3 and MP4 contributions is slightly repulsive (+0.4 kJ/mol).

In the next step the MP2 stabilization energy was evaluated with a larger basis sets B and C. Enlarging the basis set resulted, as expected, in an increase of stabilization: basis set B gives 5.48 kJ/mol; basis set C gives 5.69 kJ/mol (both calculations were done at $r = 449.3$ pm). The addition of the second set of *d*-functions on the carbon atoms and of two sets of *p*-functions on the hydrogen atoms increased the stabilization by about 5%; additional extension by *f*-functions is surprisingly important and leads to a stabilization increase of about 4%. Basis set B gives larger stabilization than the TZ2P basis set of ref.⁷ what is again due to the presence of diffuse functions in the basis set B. With basis sets B and C we were not able to perform the MP4 calculations; the respective values were estimated as follows.

Passing from MP2 to MP4 brings reduction of stabilization by a factor 0.928. Applying the factor to the MP2/basis set C stabilization energy we estimate that the MP4/basis set C stabilization energy amounts to 5.27 kJ/mol. This value differs only negligibly from the MP2/basis set A stabilization energy (5.23 kJ/mol). It does not mean that higher correlation contributions as well as the extension of the basis set do not play a role but rather that these effects compensate. (Similar compensation occurs in the calculation of molecular interactions very frequently).

Estimation of High Level Stabilization Energy and Enthalpy (at 0 K) of the Benzene Dimer

The MP2 stabilization energy of the benzene dimer (T-shape) calculated with the basis set A (ref.¹) amounts to 11.17 kJ/mol. On the basis of conclusion from the previous paragraph we can expect that this value will not change when passing to extended basis set and MP4 level. Estimation of the true stabilization energy is based on published results on two small van der Waals molecules, (He)₂ (ref.¹²) and (Ar)₂ (ref.¹³). The stabilization energy for both complexes was determined at the MP4 level using an extended basis set. It was further found^{12,13} that the MP4 stabilization energy underestimate the true stabilization energy by about 20%. We expect that this underestimation will be for benzene dimer lower, because the dispersion energy for benzene dimer is less dominant than that for (He)₂ and (Ar)₂; quadrupole–quadrupole electrostatic interaction contributes in case of T-shape benzene dimer to the overall stabilization too. Taking the 10% underestimation into account we estimate that the true stabilization energy of the benzene dimer amounts to 12.30 kJ/mol. In experiments one is not determining the interaction energy but rather the interaction enthalpy, i.e. the zero-point energy has to be included.

The intermolecular vibrations of the benzene dimer were evaluated using the QCFF/PI force field¹⁴; the parameters of the pairwise 6–12 potential were taken from ref.¹⁵. The respective vibrations are calculated to be 86 cm⁻¹, 36 cm⁻¹, 24 cm⁻¹, 17 cm⁻¹, 8 cm⁻¹, and 3 cm⁻¹. Using other empirical or semiempirical potential would lead to similar values. Correcting the estimated stabilization energy of the benzene dimer for the zero-point energy we obtain a stabilization enthalpy of 11.3 kJ/mol (0 K). The respective experiemntal value¹⁶ of 6.7 ± 2.1 kJ/mol therefore seems to be too small.

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