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COMMENTS

Comment on "Beyond the Benzene Dimer: An Investigation of the Additivity of $\pi-\pi$ Interactions"

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In ref 1, Tauer and Sherrill presented nonadditive three-body energies for selected configurations of the benzene trimer using the supermolecular second-order Møller−Plesset (MP2) method with a small basis set. The justification for this approach is based on the idea sometimes used for the benzene dimer, that the application of small basis sets underestimate binding, whereas MP2 overestimates it. The authors compared this approach with the coupled cluster method with singles, doubles, and noniterative triples [CCSD(T)] for a single cyclic configuration representing the global minimum of the benzene trimer and for three stacked-trimer configurations. In all cases, the results of the MP2 approach were fairly accurate.

It has already been pointed out in ref 2 that this approach "may prove to be incorrect if a broader range of configurations is considered" since the supermolecular MP2 method does not include the nonadditive dispersion energy and the first nonadditive dispersion contribution is present only in the third order of the Møller−Plesset perturbation theory.[3] However, for the cyclic configuration considered in ref 1, the contributions from orders higher than the third partially cancel out against the third-order dispersion contributions,[2] which explains the good performance of the MP2 method for this particular geometry. Moreover, for the stacked trimers, the nonadditive dispersion energy is significantly smaller than the other nonadditive contributions since the leading nonadditive dispersion term depends on all three intermolecular distances, whereas for other terms, two of them enter the energy expressions.[4] Therefore, testing MP2 on such configurations would not lead to large differences with CCSD(T). On the other hand, in a recent study of the benzene crystal,[5] using the nonadditive approach of ref 2, it has been found that the total nonadditive energy of the crystal is dominated by the positive dispersion contribution and the total nonadditive MP2 energy is only mildly positive since the MP2 contributions from individual trimers cancel out almost completely whereas majority of the dispersion contributions are of the same sign. The total nonadditive energy constitutes more than 10% of the total cohesion energy of the crystal, i.e. nonadditive effects are more important for the crystal (and are of opposite sign) than for the minimum cyclic trimer considered in ref 1. Even taking into account that the method of ref 2 leads to a small overestimation of the nonadditive energy, such results contradict that of ref 6, where the approach of ref 1 was used for the benzene crystal resulting in a negligible three-body contribution.

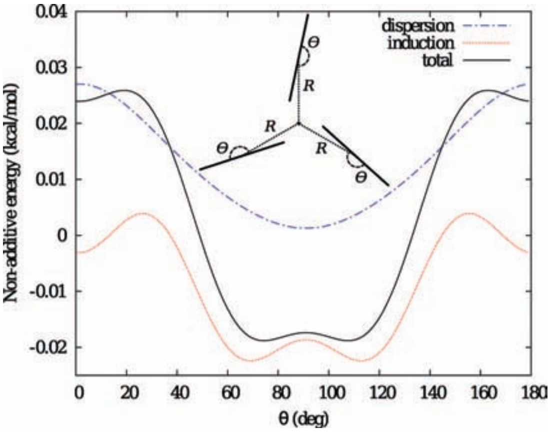

Figure 1. Asymptotic nonadditive three-body contributions for the benzene trimer in the cyclic C_{3h} configuration for $R = 3.695$ Å.

TABLE 1: Nonadditive Three-Body Energies (in kilocalories per mole) of the Benzene Trimer Structure from Figure 1 for $\theta = 168°$ and the cc-pVDZ+ Basis Set of Reference 1[a]

SCF	MP2	MP3	CCSD(T)	MP2 + disp[3]
−0.029	−0.030	0.051	0.035	0.056

[a] "disp[3]" corresponds to the three-body SAPT(DFT) dispersion. The MP2 + disp[3] was denoted MP2 + SDFT in ref 2.

Moreover, it can be shown numerically that, for some configurations of the trimer, the approach suggested by Tauer and Sherrill leads to results of opposite sign to that of the CCSD(T). To look for such possible configurations, the asymptotic dispersion and induction three-body energies[4] (with multipole moments and polarizabilities taken from ref 7) were calculated for the cyclic configuration, varying the angle between the center of the mass of the trimer and the benzene planes. The results and the picture of the configuration are presented in Figure 1. One can see that some configurations are (asymptotically) dominated by the induction whereas for different θ, the nonadditive energy is dominated by the dispersion. For a sample configuration from the latter regime, we calculated nonadditive energies by supermolecular methods and three-body dispersion from symmetry-adapted perturbation theory based on the Kohn−Sham description of the monomers [SAPT-(DFT)].[2] The energies are presented in Table 1. The results clearly show that the MP2 approach fails in this case whereas MP2 + disp[3] or MP3 give reasonable accuracy. Due to the deficiencies of the supermolecular MP2 method for the bulk phase[5] and qualitative disagreements for certain configurations of the benzene trimer, the approach of ref 1 should not be used for the benzene trimer and for similar systems dominated by dispersion.

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