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Prediction of the Dissociation Energy of Hexaphenylethane Using the ONIOM(MO:MO:MO) Method

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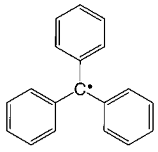
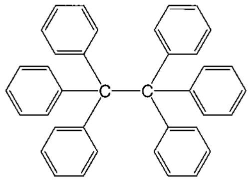
We systematically calibrated a three-level hybrid quantum mechanical ONIOM method that is suitable for the accurate and efficient calculation of bond dissociation energies (BDE's) of phenyl-substituted hydrocarbons. We applied the combination ONIOM(G2MS(R):RMP2/6-31G(d):B3LYP/3-21G)//ONIOM(B3LYP/6-31G:B3LYP/3-21G) to the BDE calculation of hexaphenylethane (HPE). We predict that the BDE of HPE (including the temperature correction) is 16.6 kcal/mol, indicating that synthesis of HPE may be feasible, despite all attempts so far having been unsuccessful.

Introduction

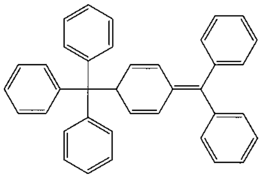
In 1900, Gomberg reported the dimerization of the triphenylmethyl radical (**1**, TPMR),[1] of which the product was thought to be hexaphenylethane (**2**, HPE). Only in 1968, Lankamp, Nauta, and MacLean, showed that the result of the "dimerization" was not **2**, but the asymmetric structure **3**.[2] A historical account of this erroneous assumption being so persistent for such a long time was presented shortly thereafter by McBride.[3] Despite many efforts to synthesize HPE, the most recent being based on the decomposition of crystalline triphenylmethyl iodine,[4] no successful routes have been reported. It has even been suspected that HPE is unstable and dissociates to TMPR, although a close derivative of HPE, hexakis(3,5-di-*tert*-butylphenyl)ethane, was reported synthesized in 1986, with a central bond length of 1.67 Å determined by X-ray crystallography.[5]



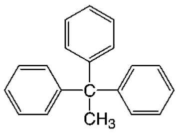
1 (TPMR)



2 (HPE)



3



4 (TPE)

A key question in HPE chemistry is the binding energy of the symmetric dimer, but the size of the molecule makes the accurate calculation by virtue of conventional computational techniques prohibitively expensive. To overcome this problem, one can turn to hybrid computational methods, which can provide a higher accuracy-to-computational-cost ratio than traditional methods. In the current paper we present dissociation energy calculations using our recently developed ONIOM hybrid method.[6−9] In previous studies, we have demonstrated ONIOM to be able to predict bond dissociation energies (BDE's) of large molecular systems accurately for a computational cost highly reduced compared to conventional methods.[10−13] In particular, we have demonstrated that the ONIOM method can reproduce the experimental C−H and C−C bond dissociation energies of a series of 16 hydrocarbons of type $H-CR^1R^2R^3$ and $R^1R^2R^3C-CR^4R^5R^6$ (where R^i = H, Me, and Ph) up to $H-CMePh_2$ and $CH_3-CMePh_2$ with a root-mean-square deviation of 2.4 kcal/mol.[12] Furthermore, the ONIOM method was used to predict the experimentally unavailable C−H BDE of $H-CPh_3$ to be 75.9 kcal/mol and the C−C BDE of H_3C-CPh_3 (**4**, TPE) to be 64.1 kcal/mol.[12] The three-layer ONIOM method was also used successfully to reproduce the experimentally determined energy required to break one CC π bond of the C_{60} fullerene.[11]

The reason that HPE is thought to be unstable, or only just stable, is because of the repulsion of the phenyl groups. If HPE exists, the central bond length is therefore expected to be very large. This was investigated computationally by Mislow and co-workers, who predicted bond lengths of up to 1.64 Å.[14−16] Their methods did not allow for the calculation of dissociation energies, and no further computational studies have been reported.

Computational Methods

Our ONIOM hybrid method has been implemented in the Gaussian package,[17] and can combine any two or three quantum mechanical (QM) and/or molecular mechanical (MM) computational methods. In the present work, we deal with two- and three-layer combinations of QM methods. The ONIOM energy of the system is then obtained from three or five independent calculations, for two- and three-layer ONIOM calculations, respectively.

$$E^{\mathrm{ONIOM2}} = E^{\mathrm{high}}_{\mathrm{model}} - E^{\mathrm{low}}_{\mathrm{model}} + E^{\mathrm{low}}_{\mathrm{real}} \quad (1)$$

$$E^{\mathrm{ONIOM3}} = E^{\mathrm{high}}_{\mathrm{small\ model}} - E^{\mathrm{medium}}_{\mathrm{small\ model}} + E^{\mathrm{medium}}_{\mathrm{intermediate\ model}} - E^{\mathrm{low}}_{\mathrm{intermediate\ model}} + E^{\mathrm{low}}_{\mathrm{real}} \quad (2)$$

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Real denotes the full system, which only needs to be calculated at the lowest computational level. For two-level calculations one additional system is defined, the *model* system, while in three-layer calculations, two additional systems are required, the *small model* and the *intermediate model*. For example, when we would carry out a two-level calculation on HPE with only the two central carbon atoms in the high level layer, the model system would be ethane. From the equations it is clear that ONIOM is an extrapolation scheme; we do not perform separate calculations on the *layers*, but separate calculations on the *systems*. In fact, ONIOM can be extended to any number of layers, although our implementation is currently restricted to three.

When the layers are not covalently bound, the model system is identical to the associated layer, plus all the higher level layers in case of three or more levels. When covalent bonds do exist, the resulting dangling bonds are saturated with *link atoms*, which are chosen so that they best mimic the substituents. Usually hydrogen atoms yield good results when carbon−carbon bonds are broken. The link atom is placed on the line that connects the atom that is substituted and the atom to which it is bound, the distance scaled by the *distance factor*. This ensures that the number of degrees of freedom remains $3N - 6$, so that any method for the investigation of potential energy surfaces for conventional methods can be used with ONIOM as well.

The geometrical derivatives of the ONIOM energy can be obtained in a fashion similar to the energy. If link atoms are present, the Jacobian J must be used to convert the coordinate system for the model systems to that for the real system. The gradients for two- and three-level calculations can be written as

$$\frac{E^{\mathrm{ONIOM2}}}{\partial\lambda} = \frac{E^{\mathrm{high}}_{\mathrm{model}}}{\partial\lambda} J^{\mathrm{real}}_{\mathrm{model}} - \frac{E^{\mathrm{low}}_{\mathrm{model}}}{\partial\lambda} J^{\mathrm{real}}_{\mathrm{model}} + \frac{E^{\mathrm{low}}_{\mathrm{real}}}{\partial\lambda} \tag{3}$$

$$\begin{aligned}\frac{E^{\mathrm{ONIOM3}}}{\partial\lambda} = {} & \frac{E^{\mathrm{high}}_{\mathrm{small\ model}}}{\partial\lambda} J^{\mathrm{real}}_{\mathrm{small\ model}} - \frac{E^{\mathrm{medium}}_{\mathrm{small\ model}}}{\partial\lambda} J^{\mathrm{real}}_{\mathrm{small\ model}} + \\ & \frac{E^{\mathrm{medium}}_{\mathrm{intermediate\ model}}}{\partial\lambda} J^{\mathrm{real}}_{\mathrm{intermediate\ model}} - \\ & \frac{E^{\mathrm{low}}_{\mathrm{intermediate\ model}}}{\partial\lambda} J^{\mathrm{real}}_{\mathrm{intermediate\ model}} + \frac{E^{\mathrm{low}}_{\mathrm{real}}}{\partial\lambda}\end{aligned} \tag{4}$$

Results

In most previous studies that employed the ONIOM method, we used benchmark calculations on small systems to systematically test partitionings and method combinations, rather than testing ONIOM directly against experimental data. The partitionings and combinations that best balance our accuracy and computational expense requirements are subsequently used for the (larger) production calculations, and eventually compared with experiment. In that way we obtained an affordable two-level ONIOM method that reproduced the experimental C−H and C−C bond dissociation energies of a series of 16 hydrocarbons of type $H{-}CR^1R^2R^3$ and $R^1R^2R^3C{-}CR^4R^5R^6$ up to $H{-}CMePh_2$ and $CH_3{-}CMePh_2$ with a root-mean-square deviation of 2.4 kcal/mol. However, that particular ONIOM combination is still too expensive for the calculation of the dissociation energy of HPE. Therefore we will first determine a less expensive three-layer ONIOM combination, using the proven two-layer ONIOM combination as benchmark. This combination will then be used for calculation of the dissociation energy of HPE.

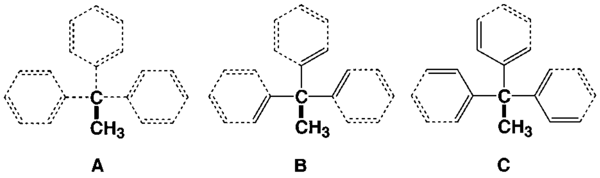

Figure 1. Three-layer partitionings investigated for TPE. The high level, medium level, and low level layers are shown in thick, solid, and broken lines, respectively.

Three-Layer ONIOM Method for Phenyl-Substituted Hydrocarbons. In ref 12 we demonstrated ONIOM(G2MS(R):RMP2/6-31G(d))//B3LYP/6-31G with the *minimal model* (only the dissociating non-H atoms in the high level layer), to predict bond dissociation energies within 2.4 kcal/mol compared to experiment. In this notation G2MS(R) is used for the high level, restricted MP2 for the low level, and B3LYP for the geometry. The latter was also used for the temperature correction. G2MS(R) refers to our own G2-like extrapolation method:[18]

$$\begin{aligned}\mathrm{G2MS(R)} = {} & \mathrm{CCSD(T)/6\text{-}31G(d)} + \\ & \mathrm{RMP2/6\text{-}311{+}G(2df,2p)} - \mathrm{RMP2/6\text{-}31G(d)}\end{aligned} \tag{5}$$

We have used this method for systems up to 20 non-H atoms, but two computational bottlenecks arise for a molecule the size of HPE: the MP2/6-31G(d) energy and the B3LYP frequency calculation, both on the full system. Using the methyl dissociation from triphenylethane (**4**, TPE), we will show that a less expensive alternative for ONIOM(G2MS:MP2)/B3LYP can be found. The reason for using TPE as test is that the previously obtained ONIOM(G2MS:MP2)/B3LYP results can be used as a benchmark, and that the similarity of this molecule with HPE warrants transferability of the ONIOM combination and partitioning.

We will first address the MP2 calculation on the full system. We attempted to divide the MP2 region of the benchmark calculation into a MP2 and a B3LYP/6-31G layer, with the intention of performing an ONIOM(G2MS:MP2:B3LYP)// B3LYP calculation. This is computationally attractive since the B3LYP energy for the full system is calculated already in the geometry optimization. The partitioning schemes we will test are shown in Figure 1. The high level layer, treated with G2MS, always consists of only the two dissociating carbon atoms. Partitioning **A** has no MP2 layer, yielding a two-level ONIOM(G2MS:B3LYP) calculation, which was shown before not to work satisfactorily for systems containing phenyl groups.[12] Partitioning schemes **B** and **C** cut through the aromatic systems. Although this might seem too rigorous at first sight, previous results were quite promising.[10] To assess the performance of these partitioning schemes, we perform the test of *S*-value, or *substituent value*, which is defined as the energy difference between the full system and the (intermediate) model system.

$$S(\mathrm{level}) = \mathrm{BDE(level, real)} - \mathrm{BDE(level, model)} \tag{6}$$

Note that in eq 6, *model* and *real* do not refer to independently optimized structures, but to the systems as defined in ONIOM. Table 1 shows the *S*-values related to partitioning the MP2 region into a MP2 region and a B3LYP region. When the *S*-values of two partitionings are the same, the B3LYP method is a good method to use as the low level when the MP2 method is used as the high level. Since our benchmark level is MP2, we want to use a partitioning where the B3LYP *S*-value is as close as possible to the MP2 *S*-value. Then the difference of

TABLE 1: *S* Values between the Real and Intermediate Model System at the MP2/6-31G(d) and B3LYP/6-31G Levels for the Partitioning Schemes in Figure 1

partitioning	MP2 (au)	B3LYP (au)	ΔS (kcal/mol)
A	−0.03758	−0.05880	13.30
B	0.01786	0.01758	0.17
C	0.01598	0.01842	−1.54

TABLE 2: *S* Values between the Real System and the Intermediate Model System at Various Computational Levels for Partitioning Scheme B

low level	S value (au)	ΔS with B3LYP (kcal/mol)
B3LYP/6-31G	0.01758	0.00
HF/3-21G	0.04148	−14.99
RHF/3-21G	0.00972	4.93
HF/6-31G	0.03447	−10.60
RHF/6-31G	0.00773	6.18
B3LYP/3-21G	0.01960	−1.27

the S-values, ΔS, is the error (relative to the MP2 target) generated if this partition is used. From Table 1 it follows that partitioning **A**, without the MP2 region, introduces an error of 13 kcal/mol. Partitioning schemes **B** and **C** introduces errors less than 2 kcal/mol. The reason partitioning **C** performs worse than the partitioning **B** is most likely due to B3LYP not behaving as systematic as MP2.[12] On the basis of these findings, we chose to continue with partitioning **B**.

The second bottleneck is the B3LYP frequency calculation on the full system, for which we follow a similar strategy as presented in the previous paragraphs. We will now use a two-layer ONIOM optimization and frequency calculation to obtain the geometry and temperature correction. We assume that the B3LYP/6-31G level of theory is required for the geometry of the G2MS and MP2 layers; thus we will search for a method to replace B3LYP/6-31G in the low level layer (the broken lines in Figure 1 **B**). In addition, we will use this method as the low level method in the energy calculation, eliminating the B3LYP/6-31G calculations on the full system. This will affect three components of the final BDE. First the temperature correction, second the energetics associated with the G2MS and MP2 layers (via the geometry), and third the contribution to the BDE from the low level region. Since we will still use B3LYP/6-31G for the geometry of the G2MS and MP2 regions, and the change in the temperature correction should more or less cancel in products and reactant, we expect the energetic change of the low level to be the most significant contribution to the change of the BDE.

In Table 2 we show the S-values for several low level methods that we have tested as alternatives for B3LYP/6-31G. The geometries were optimized at the ONIOM level specifically for each low level method. The S-values in the table represent the effect of the low level region (the broken lines in scheme **B** of Figure 1). It is clear that only the B3LYP method with the 3-21G basis set is able to reproduce the B3LYP/6-31G level; all other methods tested yield errors of at least 5 kcal/mol. However, the S-value test discussed in this paragraph only gives the energetic change of the low level contribution, as in eq 2. Therefore, as a final test, we performed the frequency calculation at the ONIOM(B3LYP/6-31G:B3LYP/3-21G) level and calculated the energetics related to the high and medium levels for the new geometry. The final BDE at the ONIOM(G2MS(R):RMP2/6-31G(d):B3LYP/3-21G)//ONIOM(B3LYP/6-31G:B3LYP/3-21G) level is 65.1 kcal/mol. This differs only by 1 kcal/mol from the 64.0 kcal/mol value[19] obtained with the much more expensive two-layer ONIOM(G2MS(R):RMP2/6-31G(d))//B3LYP/6-31G method. The cost of the three-layer calculation is roughly two-thirds that of the two-layer calculation.[20]

BDE Calculation of HPE. We carried out the BDE calculation of HPE with the new three-layer ONIOM combination, ONIOM(G2MS(R):RMP2/6-31G(d):B3LYP/3-21G)//ONIOM(B3LYP/6-31G:B3LYP/3-21G), determined in the previous section. Regular B3LYP calculations show that the S_6 symmetric conformation is more stable than the D_3 conformation, by about 6 and 3 kcal/mol, for the 3-21G and 6-31G basis sets, respectively. This is in contrast with the findings of Mislow,[14−16] who reported the D_3 conformation to be more stable by several kcal/mol. These calculations, however, were carried out at low computational levels, and we will continue our work with the S_6 symmetric conformation. Applying the three-layer ONIOM method to the S_6 symmetric HPE system results in a BDE of 16.6 kcal/mol. The central bond length is 1.72 Å.

Discussion

We need to address several aspects of the methods presented above that may affect the result. First, the energy difference between the S_6 and D_3 conformations is 6 or 3 kcal/mol at the B3LYP/3-21G level and B3LYP/6-31G levels, respectively. The origin of this difference is likely in the interaction of the phenyl groups. In the D_3 conformation they are all parallel, while in the S_6 conformation they are perpendicular when bound to different carbon centers. Since such interaction between phenyl groups does not exist in the TPE benchmark calculation used for the calibration, the three-layer ONIOM method does not necessarily treat it correctly. Second, although the TPE BDE with the new three-layer calculation is only 1 kcal/mol from the benchmark calculation, cancellation of errors is at least partly the reason for the good performance of the three-layer method. The errors related to reducing the cost of the MP2 calculation and reducing the cost of the frequency calculation are of different sign (+0.17 and −1.27 kcal/mol, respectively; see Tables 1 and 2). In addition, the ΔS-value of −1.54 kcal/mol between B3LYP and MP2 in Table 1 for partitioning **C** suggests that there might be some error due to the unsystematic B3LYP components. However, the "component errors" and "conformation errors" are relatively small compared to the final BDE of 16.6 kcal/mol, and it is very unlikely that our results would be qualitatively different at more accurate levels of theory.

It is not fully clear why the central bond length of 1.72 Å in our computations is so much larger than the 1.67 Å reported for hexakis(3,5-di-*tert*-butyl-phenyl)ethane.[5] It is not likely an artifact from our hybrid method, since both computational levels are B3LYP with fairly similar basis sets. In fact, the C−Me bond length in TPE is 1.56, 1.57, and 1.56 Å at the ONIOM(B3LYP/6-31G:B3LYP/3-21G), B3LYP/6-31G, and B3LYP/3-21G levels, respectively, indicating that the integration scheme behaves correctly. However, the vibrational frequency corresponding to the dissociation mode of HPE is 230 cm^{-1} at the ONIOM level, which is very small compared to the "standard" ethane dissociation mode of 1011 cm^{-1} at the same computational level. Because of this mode being so soft, relatively small differences in the substituents, or aspects such as crystal packing, can strongly affect the resulting bond length.

Conclusions

Our calculations predict HPE to be stable, i.e., the BDE is positive, although this C−C bond is indeed very weak. Therefore, synthesis of the compound might be feasible. The present calculations do not predict the thermodynamic stability of the compound, nor the competition with other compounds, or the effects of the environment. Studies to address a number of these issues are currently in progress.

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(19) This value differs slightly from that in reference 12 because we recalculated it with the current distance factor.

(20) This ratio only reflects the energy calculations; the geometry optimizations have not been taken into account.