

Effects of Intramolecular Basis Set Superposition Error on Conformational Energy Difference of 1,2-Difluoroethane and 1,2-Dimethoxyethane[†]

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The conformation dependences of basis set superposition errors (BSSE) for 1,2-difluoroethane (DFE) and 1,2-dimethoxyethane (DME) molecules have been estimated using counterpoise method at the Möller-Plesset second order perturbation (MP2) level of theory with various basis sets, assuming that all BSSE dependences on conformations are due to the change in CC bond. The BSSE on the energy differences between eclipsed and gauche forms of DFE are in the range of 0.2-1.2 kcal/mol and those between local minima, gauche and anti forms, are less than 0.2 kcal/mol. For the larger DME molecule, the BSSE differences between local minima are still less than 0.4 kcal/mol, but may not be ignored compared to the energy differences of 0.2-3.0 kcal/mol between conformers.

Key Words : Intramolecular BSSE, Counterpoise correction, MP2 calculations, 1,2-Difluoroethane, 1,2-Dimethoxyethane

Introduction

Theoretical studies on conformations imply that using extended basis sets with diffuse and multiple polarization functions is more important than the high-level treatment of electron correlations.¹⁻⁴ An acceptable procedure for estimating the relative energies between conformers in a molecule is to optimize geometry at the MP2 (or HF) level of theory using double zeta polarized basis set and perform single point calculations at MP4 (or MP2) using triple zeta multiple polarized basis set augmented with one diffuse sp set.^{4,5} The variation of the basis set superposition error (BSSE) is seldom considered in the calculations of conformational energy differences although it is not difficult to recognize the existence of BSSE which varies with conformation.⁴ There are many studies investigating the BSSE in intermolecular interaction between two closed-shell molecules, but no systematic studies for the intramolecular BSSE effects on conformations have, to the best of our knowledge, been reported. We suggest a method of estimating BSSE differences among different conformations and apply the method to study the BSSE for 1,2-difluoroethane (DFE) and 1,2-dimethoxyethane (DME). Those molecules are selected for their gauche effect where polar substituents cause the preferred conformation about a C-C bond to switch from a trans to a gauche form.

Method and Calculations

One can eliminate BSSE by increasing the basis set until conformation energy differences converge to the desired accuracy, but such an approach is slowly convergent and

viable only for small systems. The usual practice is to estimate BSSE for the given basis sets using the counterpoise (CP) method.^{6,7} Although the CP method can be applied separately to every atom in a molecule for all conformations, the resulting calculation will not be practical for most molecules of interest. In this work, we evaluate BSSE associated with the one C-C bond in order to obtain corrections for the conformational energy differences under the assumption that this C-C bond contains the major differential BSSE for differing conformers. Since conformation energy is concerned with the rotation of a single bond in a molecule, the C-C bond in this case, it is meaningful to estimate BSSE contained in the interaction energy (or dissociation energy) of the C-C bond.

The BSSE present in the interaction energy of the C-C bond can be calculated as

$$BSSE = E_{AB}^{\alpha}(A) + E_{AB}^{\beta}(B) - E_{AB}^{\alpha\cup\beta}(A) - E_{AB}^{\alpha\cup\beta}(B) \quad (1)$$

where the electronic energy of a molecular system M at geometry G computed with basis set σ is defined as $E_G^{\sigma}(M)$.⁸ Eq. (1) is exact within the CP scheme where fragments A and B have constant geometries. Since geometries of fragments are usually quite similar among conformers, a reasonable correction of BSSE for conformational energies can be obtained by comparing BSSEs calculated by Eq. (1) for various conformers. The main quantity of interest here is the variation of BSSE among many conformers and not the BSSE itself of Eq. (1). When the geometry relaxations of the fragments are substantial, BSSE and geometry relaxation should be considered simultaneously. One extreme case is that of the bonding dissociation energy (BDE). In such cases, the BDE corrected for BSSE by the CP method (BDE_CP) can be expressed as^{8,9}

$$BDE_CP =$$

$$E_{AB}^{\alpha\cup\beta}(AB) - E_{AB}^{\alpha\cup\beta}(A) - E_{AB}^{\alpha\cup\beta}(B) + E_{rel}^{\alpha}(A) + E_{rel}^{\beta}(B) \quad (2)$$

[†]Dedicated to the late Professor Sang Chul Shim in memory of his great contribution to photochemistry and organic chemistry

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where $E_{rel}^{\alpha}(A) = E_{AB}^{\alpha}(A) - E_A^{\alpha}(A)$ and $E_{rel}^{\alpha}(B) = E_{AB}^{\alpha}(B) - E_B^{\alpha}(B)$ are the fragment relaxation energies corresponding to the energy penalty for distorting the fragments from their isolated geometries to the ones in the complex. While there can be many debates about the utility of Eq. (2) as a better estimate of BDE in general due to the presence of BSSE in the relaxation process of each fragment, BDE_CP is used here to serve as a convenient reference point in comparing many different conformations. Bond dissociation is a convenient reference point since the relaxed fragments A and B are almost identical for all conformers. The validity of the present scheme of using BDE_CP of Eq. (2) as the reference strongly relies on the observation that fragments A and B differ very little among conformers, *i.e.* relaxed geometries of a given fragment are almost identical among conformers under consideration although they may differ substantially from the geometry of minimum energy.

The CP correction provides neither upper nor lower bounds for BSSE.^{7,10-12} We expect that our approach of employing the CP method to estimate BSSE on the conformational energy difference is rather reliable since no bond breaking is involved. We have estimated the intramolecular BSSE effects on the energy differences among the fluorine-fluorine gauche, anti, and eclipsed conformations of DFE and energy differences among nine conformers of DME. Both for DFE and DME, only the fragmentation and thus the BDE of the central C-C bond is treated by the CP method.

Electronic energies of DFE have been calculated at the MP2 level of theory using 6-311G, 6-311++G, 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p), 6-311++G(2d,2p), 6-311G(3d,3p), 6-311++G(3d,3p), 6-311G(3df,3pd), and 6-311++G(3df,3pd) basis sets. These basis sets are selected to show the role of sp diffuse set denoted by ++ and the polarization (additional functions in parentheses) sets explicitly. The outermost d exponent of 0.4375 for the fluorine atom and the outermost p exponent of 0.1875 for the hydrogen atom have significant diffuse character in the basis sets, 6-311G(3d,3p), 6-311++G(3d,3p), 6-311G(3df,3pd), and 6-311++G(3df,3pd).

Density functional theory (DFT) calculations with B3LYP functionals were performed with 6-311G and 6-311++G (3df,3pd) basis sets. We optimized geometries of the DME molecule at the MP2 level of theory using D95** basis sets, followed by a series of MP2 single-point calculations using extended D95+(2df,p) basis sets. All calculations have been performed with the GAUSSIAN94 suite of programs.¹³

Results and Discussion

A. 1,2-Difluoroethane (DFE). Table 1 shows BDE_CPs corresponding to the fission of DFE into two CFH₂ fragments for anti, eclipsed, and gauche forms of the DFE conformers with the BSSE correction. The differences of BDEs between conformers without BSSE correction are equivalent to the energy differences between the conformers of DFE. The BSSEs in three conformers for the various basis sets are plotted in Figure 1 where the abscissa roughly reflects total number of basis functions in the basis set. While the absolute values of BSSEs contain many errors mainly from relaxation process, the relative values or trends are useful. The same relative values can also be obtained by employing Eq. (1) without any reference to BDE_CP. The intramolecular BSSE decreases, as the size of basis set increases, from about 9-10 kcal/mol to about 3 kcal/mol. The decrease of BSSE is not monotonous since the contribution of the sp diffuse sets is larger than that of the additional polarization sets. The BSSE of fluorine-fluorine eclipsed structure is smaller than that of gauche or anti form due to the fact that the distance between CFH₂ fragments in the eclipsed form is longer than those of other forms as shown in Table 1, reflecting larger repulsions between two F atoms in the eclipsed structure. The BSSE differences between two local minima cannot be explained by the C-C bond lengths, implying the presence of subtle ligand effects.

The calculated BSSEs in the internal rotation barrier of DFE (E(eclipsed)-E(gauche)) are in the range of 0.2-1.2 kcal/mol for the various basis sets. As shown in Figure 2, the

Table 1. The C-C bond lengths (R_{CC}) and the bonding dissociation energies with BSSE correction (BDE_CP)^a between the two CFH₂ fragments for anti, eclipsed, and gauche forms of 1,2-difluoroethane. Bond lengths are in Å and energies are in kcal/mol

Basis set	Anti			Eclipsed			Gauche		
	R_{CC}	BSSE	BDE_CP	R_{CC}	BSSE	BDE_CP	R_{CC}	BSSE	BDE_CP
6-311G (B3LYP) ^b	1.517	10.0 (4.3)	84.5 (91.3)	1.546	8.8 (3.6)	76.0 (83.0)	1.506	10.0 (4.2)	84.1 (91.3)
6-311++G	1.518	8.2	86.4	1.547	7.6	77.6	1.505	8.4	86.3
6-311G(d,p)	1.515	6.8	91.6	1.547	5.9	84.6	1.505	6.6	92.0
6-311++G(d,p)	1.516	4.8	92.8	1.548	4.3	85.7	1.504	4.9	93.4
6-311G(2d,2p)	1.510	5.7	93.2	1.543	5.3	86.3	1.499	5.6	93.7
6-311++G(2d,2p)	1.510	4.1	94.2	1.543	3.8	87.0	1.498	4.1	94.8
6-311G(3d,3p)	1.512	4.4	94.8	1.545	4.1	88.1	1.501	4.5	95.6
6-311++G(3d,3p)	1.513	3.8	95.4	1.545	3.7	88.3	1.501	3.9	96.1
6-311G(3df,3pd)	1.510	3.3	96.6	1.543	3.1	90.0	1.500	3.4	97.5
6-311++G(3df,3pd) (B3LYP) ^b	1.511	2.7 (0.8)	97.3 (91.2)	1.544	2.6 (0.8)	90.4 (84.6)	1.499	2.7 (0.8)	98.1 (92.2)

^aAll BDE_CP values are absolute values. ^bValues from DFT calculations with B3LYP functionals with the basis set above are in parenthesis.

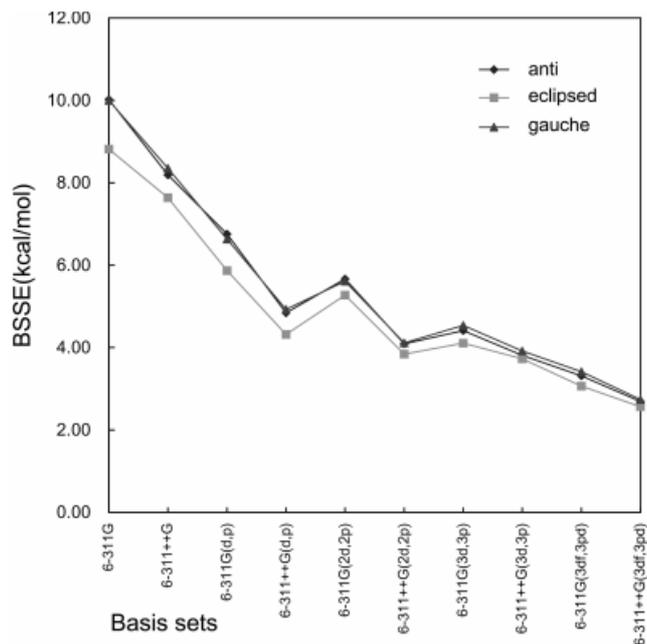


Figure 1. BSSEs in the anti, gauche, and eclipsed structures of the 1,2-difluoroethane (DFE) for various basis sets.

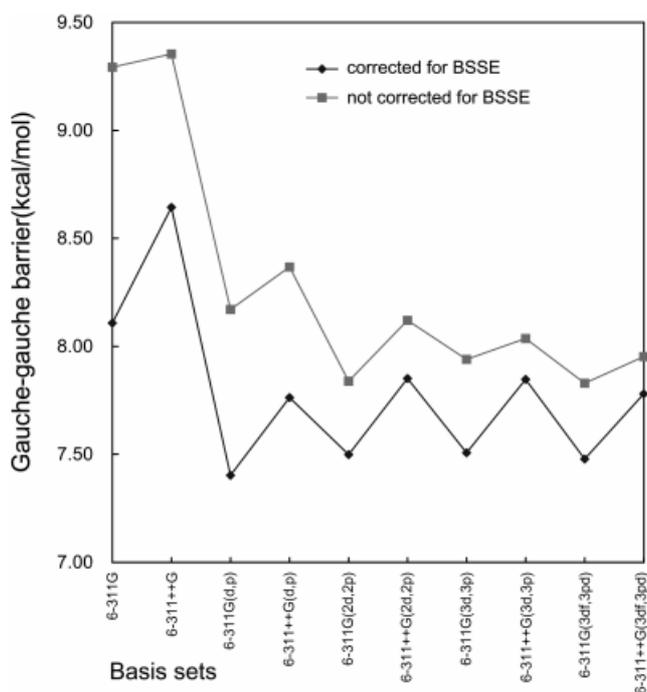


Figure 2. The barrier height for the internal rotation, $E(\text{eclipsed})-E(\text{gauche})$, of DFE at the MP2 level of theory using various basis sets.

BSSE corrections always decrease the barrier since the BSSE is smallest in the eclipsed form. The *sp* diffuse sets also decrease BSSE significantly and increase the barrier by about 0.3 kcal/mol uniformly. However, the BSSE effects on the energy difference between two local minima, gauche and anti structures, are relatively small, being less than 0.2 kcal/mol. The BSSE effects on the energy differences, $E(\text{gauche})-E(\text{anti})$, plotted in Figure 3 suggest an interesting feature

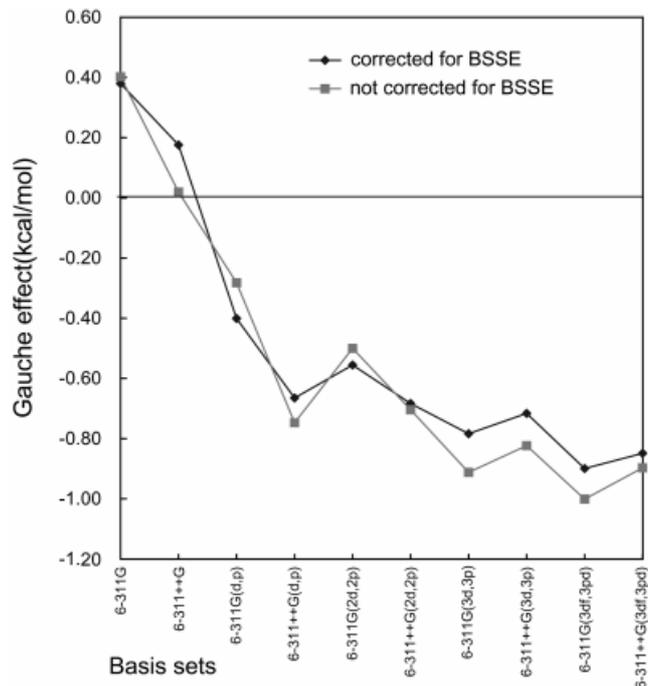


Figure 3. The gauche effect, $E(\text{gauche})-E(\text{anti})$, of DFE at the MP2 level of theory using various basis sets.

about the role of *sp* diffuse sets. Previous theoretical studies for the DFE molecule indicate that the *sp* diffuse functions are crucial for the accurate estimate of the $\Delta E(E(\text{gauche})-E(\text{anti}))$ value,^{2,14} which is certainly true for the basis sets of moderate size in popular use. The change of ΔE from 6-311G(d,p) to 6-311++G(d,p) is -0.50 kcal/mol, which is larger in magnitude than the change of ΔE , -0.20 kcal/mol, from 6-311G(d,p) to 6-311G(2d,2p) basis set. However, the BSSE corrected value for the former case is -0.25 kcal/mol and that for the latter case is -0.20 kcal/mol. It appears that the *sp* diffuse function plays a major role in the limited region of basis set size due to the intramolecular BSSE.

The CP corrected results for the DFE in the case of using pure *sp* basis sets are not consistent with large basis set results, which implies that there are remaining basis set incompleteness errors in the CP corrected results. Most of those basis set incompleteness errors disappear after adding one polarization function.

In the DFT calculations, the magnitude of BSSE is smaller than that of MP2 ones especially for the small basis. The effects of BSSE on relative energies are also smaller in DFT than in MP2.

B. 1,2-Dimethoxyethane (DME). We have performed the calculations for the DME molecule using the same procedure as the DFE case. The DME molecule can be formed by substituting $-\text{OCH}_3$ for the F atom of DFE. The ground state structures of *t*t*t* and *t*g*g*2 conformers (*t* for *trans*- and *g* for *gauche*- form) are shown in Figure 4. In DME, the energy differences among conformers are obtained from the BDE_CP of two $\text{CH}_2(\text{OCH}_3)$ fragments. The same energy differences can also be obtained by correcting the total energies of conformer with the corresponding BSSE calcu-

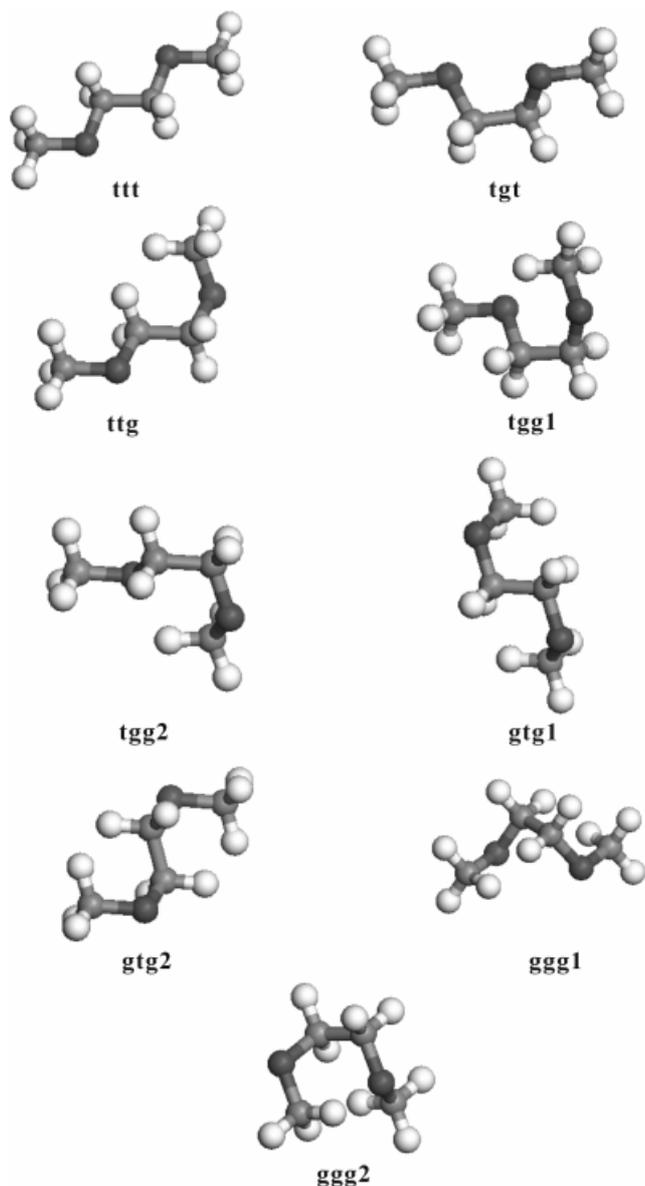


Figure 4. The ttt, tgt, ttg, tgg1, tgg2, gtg1, gtg2, ggg1, and ggg2 structures of 1,2-dimethoxyethane (DME).

lated by Eq. (1) for each conformer. Jaffe *et al.*⁴ calculated the conformational properties of DME using *ab initio* approaches by optimizing the molecule at the HF level of theory using D95** basis set and performing the single-point energy calculations at the MP2 level of theory using the larger D95+(2df,p) basis set. In order to estimate the pure BSSE effect, we reoptimized the molecule at the MP2/D95** level and calculated MP2/D95+(2df,p) energies at the optimized geometries.

Table 2 summarizes the relative energies of various conformers compared to that of the ttt form. The MP2 energy differences between conformers are only slightly affected by the geometries employed. The MP2 energy differences calculated at the HF geometries from those at the MP2 ones by less than 0.18 kcal/mol, as shown in Table 2. The estimated error originating from the intramolecular BSSE

Table 2. Calculated relative energies for various conformers of the DME molecule. Units are in kcal/mol

Conformation	MP2/ D95+(2df,p)	MP2/ D95+(2df,p)	BSSE	MP2/ D95+(2df,p)(CP) ^a
	//HF/D95**	//MP2/D95**		//MP2/D95**
ttt	0.00	0.00	0.00	0.00
tgt	0.15	0.21	0.11	0.32
ttg	1.43	1.47	0.10	1.57
tgg1	1.51	1.46	0.35	1.81
tgg2	0.23	0.29	0.40	0.69
gtg1	3.31	3.07	0.13	3.20
gtg2	3.08	2.94	0.13	3.07
ggg1	1.64	1.46	0.31	1.77
ggg2	1.86	1.82	0.19	2.01

^aThe BSSE corrected relative values employing the CP procedure explained in the text.

becomes as large as 0.40 kcal/mol, even for the D95+(2df,p) basis set. Since the energy differences among conformers are in the range of 0.2–3.1 kcal/mol, BSSE cannot be ignored in all cases. The magnitude of BSSE for the C–C bond of the conformers with the gauche conformations in the middle are generally larger than those with the trans ones, partly because the distances between –OCH₃ fragments are shorter in the former cases. The BSSE correction by the CP method increases the relative energies in all cases, indicating that the intramolecular BSSE is minimum for the ground ttt structure among the conformers.

The relative populations of conformers from the simple Boltzmann distribution equation at 273.15 K are listed in

Table 3. Relative populations of DME conformers at 0 °C

Conformation (degeneracy)	MP2/ D95+(2df,p)	MP2/ D95+(2df,p)	MP2/ D95+(2df,p)(CP) ^a
	//HF/D95**	//MP2/D95**	//MP2/D95**
ttt(1)	1.00	1.00	1.00
tgt(2)	1.55	1.36	1.11
ttg(4)	0.29	0.27	0.22
tgg1(4)	0.25	0.27	0.14
tgg2(4)	2.62	2.34	1.12
gtg1(2)	0.01	0.01	0.01
gtg2(2)	0.01	0.01	0.01
ggg1(2)	0.10	0.14	0.08
ggg2(4)	0.13	0.14	0.10

^aThe BSSE corrected relative values employing the CP procedure explained in the text.

Table 4. The relative energies of the tgt and tgg2 forms to the ttt conformer for the DME molecule using various basis sets at the MP2/D95** geometries. Units are kcal/mol

Conformation	D95+ (2d,p)	D95+ (2d,2p)	D95++ (2d,p)	6-311+G (2d,p)
	ttt	0.000	0.000	0.000
tgt	0.297	0.376	0.272	0.281
tgg2	0.235	0.235	0.241	0.534

Table 3 using energies with and without BSSE corrections. The population changes are remarkable in two tgg forms. In particular, the tgg2 population calculated as the most popular conformer without BSSE corrections^{4,15} is reduced by a factor of about 2, and becomes similar to tgt or ttt populations.

To the best of our knowledge, the appropriate correction procedure for the intramolecular BSSE has not been presented at the correlated levels of theory. Although there are limitations and arbitrariness in the present approach of treating only the central C-C bond to be regarded as a general method of estimating the intramolecular BSSE, we have demonstrated that the systematic studies on the one-particle basis set effects on conformational energy difference are possible and could be important.

The previous study of DME by Jaffe *et al.*⁴ tested the basis set performance only for the relative energies of the tgt form to the ttt one. We have also included the tgg2 form as well as the tgt conformer in the basis set study as summarized in Table 4. Although the relative energies of the tgt conformer do not vary substantially with the change of the basis sets, which is in line with Jaffe *et al.*'s results, the enlargement of the basis set to triple-zeta quality increases the relative energy of the tgg2 conformer from 0.229 kcal/mol to 0.534 kcal/mol.

Conclusions

We have investigated the effect of the intramolecular BSSE in the conformational energy differences for the DFE and the DME molecules. The BSSE effects on the energy difference between two local minima, gauche and anti structures, of DFE are small, less than 0.2 kcal/mol, for the the basis sets of various sizes. The estimated BSSE becomes as large as 0.40 kcal/mol in the DME case, even for the extended basis set of D95+(2df,p). According to the present estimate, the intramolecular BSSE can become a source of error in the evaluation of the conformational energy differences even for the molecules of the moderate size such as DME. Whenever there are many conformations in the same energy range, a careful estimate of BSSE is highly desirable.

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