

## $\pi$ Interactions Studied with Electronic Structure Methods: The Ethyne Methyl Isocyanide Complex and Thioanisole

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**Abstract:** Two molecular systems for which previous studies had found qualitative differences in the results from calculations with the B3LYP and MP2 methods are investigated with a range of different electronic structure methods, including meta and double hybrid density functionals and DFT-D (DFT augmented with an empirical dispersion term). The performance of the different methods is assessed by comparison to estimated CCSD(T)/CBS (complete basis set) results. The first molecular system studied is the ethyne methyl isocyanide complex ( $\text{CH}_3\text{NC}-\text{C}_2\text{H}_2$ ), which exhibits  $\pi$  hydrogen bonds involving the  $\text{C}\equiv\text{C}$  and  $\text{N}\equiv\text{C}$  triple bonds. Earlier work on this system had shown that B3LYP predicts significantly longer hydrogen-bond distances than MP2. Here, we show that this is likely due to missing dispersion in the B3LYP calculations. On the basis of the CCSD(T) results, the ethyne methyl isocyanide interaction energy is estimated to be  $12 \pm 1$  kJ/mol. B3LYP significantly underestimates the stability of the complex, whereas MP2 slightly overestimates. M05-2X, B3LYP-D, and (CP-corrected) mPW2-PLYP-D give results in close proximity to the CCSD(T) reference values. The second molecule investigated is thioanisole ( $\text{C}_6\text{H}_5\text{SCH}_3$ ), which can adopt two different conformations (thiomethyl group either planar or perpendicular with respect to the benzene ring). Potential energy curves for rotation around the  $\text{C}(\text{sp}^2)-\text{S}$  bond are computed and compared to the estimated CCSD(T)/CBS curve. CCSD(T) predicts the planar conformation to be the global minimum, with a plateau region near the perpendicular conformation ( $\sim 4$  kJ/mol higher in energy than the planar conformation). The shape of the curve, and location of minima and barriers, is very dependent on the method and basis set employed. MP2, B3LYP, M05-2X, mPW2-PLYP, and mPW2-PLYP-D (employing basis sets of double- or triple- $\zeta$  quality) give results in reasonable agreement with the CCSD(T) results, whereas B3LYP-D and M06-L give vastly overestimated barriers at the perpendicular conformation.

### 1. Introduction

Interactions with  $\pi$  systems are important in many areas of chemistry. For example, interactions with the ring systems of the aromatic amino acids tyrosine, phenylalanine, and tryptophan stabilize peptides and proteins,<sup>1</sup> whereas  $\pi$ -stacking interactions between consecutive nucleic acid bases stabilize the structure of the DNA double helix.<sup>2</sup> Interactions with aromatic rings also play key roles in chemical and biological recognition<sup>3</sup> and supramolecular chemistry.<sup>4,5</sup> A

computational description of these interactions is however fraught with difficulties, because  $\pi$  interactions are much weaker than covalent interactions. In addition, London dispersion forces play an important role in  $\pi$  interactions, and these are inherently difficult to describe properly using computational methods. Density functional theory (DFT) has become very popular over the past few decades, due to its greater computational efficiency relative to correlated ab initio methods like second-order Møller–Plesset (MP2) perturbation theory.<sup>6</sup> However, conventional density functionals like B3LYP<sup>7–9</sup> do not describe dispersion<sup>10–22</sup> appropriately and may therefore not give correct results for

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$\pi$  interactions. Examples of the deficiency of the B3LYP functional to correctly describe  $\pi$  interactions include the  $\pi$ -bonded indole–water minimum,<sup>23</sup> and some conformers of the tyrosine–glycine (Tyr–Gly) dipeptide.<sup>24</sup> MP2 does describe dispersion; however, MP2 calculations suffer from larger basis set superposition error (BSSE) values than DFT, particularly when small to medium-sized basis sets are employed, and may therefore also not produce the correct result. For example, we found before that BSSE distorts the MP2/6-31+G(d) potential energy surface of some Tyr–Gly conformers to such an extent that artificial minima are created or real minima are masked.<sup>24,25</sup>

The current study evolved from two recent computational studies in the literature,<sup>26,27</sup> reporting qualitative differences in the results obtained with the MP2 and B3LYP methods. For both molecular systems investigated in these studies,  $\pi$  interactions are likely important. One of these is an intermolecular complex, ethyne methyl isocyanide ( $\text{CH}_3\text{NC}-\text{C}_2\text{H}_2$ ), which exhibits  $\pi$  hydrogen bonds (H bonds) involving the  $\text{C}\equiv\text{C}$  and  $\text{N}\equiv\text{C}$  triple bonds. For this system, MP2 predicts a much closer contact between the two molecules in the complex and yields a stronger interaction than B3LYP.<sup>26</sup> The second molecular system is thioanisole, consisting of a benzene ring and a thiomethyl ( $-\text{SCH}_3$ ) moiety. This molecule may exhibit intramolecular interactions between the thiomethyl group and the  $\pi$ -electron cloud of the benzene ring. Here, B3LYP and MP2 were reported to give different minima.<sup>27</sup> B3LYP/cc-pVTZ yields a planar structure, in which the thiomethyl group and the benzene ring are coplanar, whereas MP2/6-311G(d,p) calculations result in a conformer in which the thiomethyl group is perpendicular with respect to the aromatic ring. MP2/cc-pVTZ finds both structures, with the planar one the most stable of these.

There have been a number of previous computational studies on the structure of thioanisole. Vondrák et al.<sup>28</sup> computed a potential energy curve for rotation around the  $\text{C}(\text{sp}^2)-\text{S}$  bond using Hartree–Fock (HF) and the 6-311G(d,p) basis set and found a single potential energy minimum at the perpendicular conformation. Dal Colle et al.<sup>29</sup> found similar results using HF/6-31G(d,p). Dolgounitcheva et al.<sup>30</sup> optimized the structure of the molecule at the HF and B3LYP levels of theory, using the 6-31G(d) and (for HF) 6-311G(d) basis sets. HF optimizations yielded minima for the perpendicular conformation and transition states for the planar structure. B3LYP optimizations yielded the opposite result. Gellini et al.<sup>31</sup> also located the planar conformer with B3LYP/6-31G(d,p). Bzhezovskii and Kapustin<sup>32,33</sup> computed the potential energy curves using B3LYP/6-31G(d) and MP2/6-31G(d). The B3LYP calculations found two minima at the planar and perpendicular conformations, with the planar one the global minimum. In contrast, MP2 located the minimum near the planar conformation, whereas both the planar and perpendicular structures were characterized as transition states. Bossa et al.<sup>34</sup> computed potential energy curves using HF, MP $n$  ( $n = 2-4$ ), and various density functionals, including B1LYP, B3LYP, mPW1PW, and B&hLYP. The MP $n$  calculations employing a 6-31G(d) basis set found that the perpendicular structure is a minimum whereas the planar

structure is a transition state. The DFT calculations gave different results, yielding the planar structure as the global minimum. Some functionals located a secondary minimum close to the perpendicular conformation. The perpendicular conformation was found to be a transition state for all functionals employed. Apart from the study of Suzuki et al.,<sup>27</sup> which prompted the current work, we are aware of only one study that employed basis sets larger than 6-31G(d) in the MP2 calculations: Shiskov et al.<sup>35</sup> found a single minimum for the perpendicular conformation with MP2/6-31G(d), an additional shallow minimum for the planar conformation with MP2/6-311G(d,p), whereas MP2/cc-pVTZ calculations yield the planar orientation as the global minimum, with an additional shallow minimum at the perpendicular orientation. In agreement with the previous studies, B3LYP/cc-pVTZ predicts a single minimum for the planar orientation.

Numerous experimental studies on thioanisole<sup>28,29,31,35-50</sup> indicate the existence of a single planar or nearly planar structure, or the coexistence of the planar and perpendicular forms. B3LYP calculations indicate that the barrier height for rotation around the  $\text{C}(\text{sp}^2)-\text{S}$  bond is much smaller for thioanisole than for anisole.<sup>31</sup> Solution-phase NMR predicts a barrier height for the thioanisole internal rotation of 6.0 kJ/mol,<sup>44,45,47</sup> whereas various computational studies showed that the barrier (both the height as well as the location) is very dependent on the computational method employed.<sup>27,33-35</sup>

Only a few studies on molecules with the type of  $\pi$  H bonds as occurring in the ethyne methyl isocyanide complex ( $\text{C}\equiv\text{N}$  bond acting as the H-bond acceptor) have been published in the literature. Using the B3LYP and MP2 methods, Bakó et al.<sup>51</sup> found two distinct minima for the acetonitrile–water complex; one of these contains a H bond between one of the water hydrogens and the  $\text{C}\equiv\text{N}$  bond of acetonitrile. The MP2 calculations yielded  $\text{H}\cdots\text{C}$  and  $\text{H}\cdots\text{N}$  distances that are about 0.1 Å shorter than those predicted by B3LYP. Cao et al.<sup>26</sup> studied several of these systems, including  $\text{CH}_3\text{C}\equiv\text{N}\cdots\text{H}_2\text{O}$ ,  $\text{CH}_3\text{N}\equiv\text{C}\cdots\text{H}_2\text{O}$ ,  $\text{CH}_3\text{C}\equiv\text{N}\cdots\text{H}_3\text{N}$ , and  $\text{CH}_3\text{N}\equiv\text{C}\cdots\text{H}_2\text{C}_2$  (ethyne methyl isocyanide). For all of these, MP2 predicts shorter intermolecular distances than B3LYP. The differences are largest in the ethyne methyl isocyanide complex, where the  $(\text{C}=\text{C})\cdots\text{H}(\text{CH}_2)$  distance predicted by MP2 is nearly 0.5 Å shorter than the value obtained with B3LYP. Tschumper et al.<sup>52-54</sup> studied a number of  $\pi-\pi$  systems, including the dimers and trimers of cyanogen ( $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$ ). They showed that an accurate description of the  $\pi$  interactions in these systems requires the application of the CCSD(T) method (or the equivalent thereof). In addition, even the inclusion of quadruple excitations was found to result in non-negligible changes to the binding energy.<sup>53</sup>

In the current paper, calculations using CCSD(T) (coupled cluster including single, double, and perturbative triple excitations), at the estimated CBS (complete basis set) limit, are used to assess the correctness of the B3LYP and MP2 methods to describe the two molecular systems studied in this work. CCSD(T) has been described as the “gold standard” of electronic structure theory, providing very reliable results for basically all single-reference systems. In addition, several other electronic structure methods are

assessed, including the meta and meta hybrid functionals M06-L<sup>55</sup> and M05-2X,<sup>56</sup> the double hybrid functional mPW2-PLYP,<sup>57,58</sup> and DFT-D (DFT augmented with an empirical dispersion term).<sup>59,60</sup> M06-L and M05-2X were developed to provide broad applicability in chemistry and have been shown to yield much improved results for weak intermolecular interactions as compared to B3LYP.<sup>55,61–74</sup> Also, DFT-D generally yields good results for weak interactions,<sup>64,74–78</sup> though it has been shown that B3LYP-D yields overestimated interaction energies for anisole–water and anisole–ammonia.<sup>79</sup> The double hybrid functional mPW2-PLYP was found to give good performance in general,<sup>57,80</sup> though it underestimates the interaction in van der Waals complexes.<sup>81,82</sup> mPW2-PLYP satisfactorily describes the well depth of CO<sub>2</sub>–He and CO<sub>2</sub>–Ne but fails to produce correct interaction energies for CO<sub>2</sub> complexed with heavier rare-gas atoms.<sup>83</sup> To overcome the underestimated dispersion in mPW2-PLYP, we also consider the mPW2-PLYP-D method (mPW2-PLYP augmented with an empirical dispersion term).<sup>81</sup> This method was found to give the best performance for the description of the three minima along the  $\phi_{\text{Gly}}$  rotational profile of one particular Tyr-Gly conformer.<sup>64</sup>

As mentioned above, BSSE may be a possible explanation for the different results obtained with the B3LYP and MP2 methods. It is well recognized that BSSE causes an overestimation of the stability of intermolecular complexes, like the ethyne methyl isocyanide complex. However, intramolecular BSSE can also have effects on the relative conformational energies of single molecules. In thioanisole, close contact between the benzene ring and the –SCH<sub>3</sub> group may induce intramolecular BSSE. For both molecular systems, the effects of BSSE are investigated using the counterpoise (CP) procedure of Boys and Bernardi.<sup>84</sup> The treatment of the *intermolecular* BSSE in the ethyne methyl isocyanide complex is straightforward: the standard procedure is to take the individual monomers, in this case the ethyne and methyl isocyanide molecules, as the isolated fragments. However, correction of the *intramolecular* BSSE in the thioanisole molecule is more ambiguous. In previous work,<sup>24,25,85</sup> the intramolecular BSSE in structures of the tyrosyl–glycine (Tyr-Gly) dipeptide was approximated by the intermolecular BSSE in complexes of phenol and *N*-formylglycine with conformations and spatial arrangements identical to the Tyr-Gly structures. Thus, the Tyr-Gly molecule was split into two fragments by removing the –CH<sub>2</sub>–N(H)(NH<sub>2</sub>)– linkage between the phenol and *N*-formylglycine moieties, after which the dangling bonds were saturated with hydrogens. A similar approach was used by Valdés et al.<sup>86</sup> to compute the intramolecular BSSE in different conformations of the phenylalanine–glycine–phenylalanine tripeptide, which was partitioned into two benzene molecules with the same geometries and spatial arrangements as in the tripeptide. In thioanisole, we want to estimate the magnitude of the intramolecular BSSE caused by interaction between the benzene ring and the –SCH<sub>3</sub> group. However, there is no connecting group between these two fragments, and the same CP procedure as used for Tyr-Gly is therefore not feasible here. In the current work, we simply break the C(sp<sup>2</sup>)–S

bond, creating two open-shell radical molecules to be used as the monomers in the CP procedure. This procedure is similar to the intramolecular counterpoise correction employed previously for the N<sub>2</sub><sup>87</sup> and HCl<sup>88</sup> molecules.

Other schemes to correct intramolecular BSSE have been proposed. Palermo et al. published the so-called rotation method.<sup>89</sup> According to this method, for a molecule with two interacting groups that may be affected by intramolecular BSSE, one of the interacting groups is rotated to a position where no interaction is observed, and ghost orbitals are placed corresponding to the rotated group in its original position. In addition, a geometry is created by fixing the interacting group in its original, optimal position and placing ghost orbitals corresponding to the group in its rotated position. The interaction energy is then obtained by taking the difference in energy of these two geometries. It was however shown that this method underestimates the magnitude of the intramolecular BSSE.<sup>90</sup> In addition, this method cannot be easily used to compute BSSE-free rotational energy profiles. Other proposed schemes to correct intramolecular BSSE are all variants of the CP procedure. Jensen<sup>91</sup> investigated intramolecular BSSE in different conformations of H<sub>2</sub>O, NH<sub>3</sub>, and ethane by taking the union of the basis sets of the two different conformations. However, this scheme cannot be used when the atoms in the two conformations are in similar positions, as the ghost orbitals would be very close to atomic basis functions, leading to numerical problems. More recently, the same author devised an atomic counterpoise scheme where the BSSE is estimated as a sum of atomic contributions, calculated as differences in energies computed in a regular basis set and in a subset of basis functions on atoms separated by a minimum number of bonds.<sup>92</sup> This method does not require the somewhat ambiguous definition of the molecular fragments as in the CP approach used for thioanisole in the current paper. However, the atomic counterpoise method does require the definition of the atomic reference states and the subset of basis functions to be included in the CP calculations and is therefore also not explicitly defined. Baladin<sup>93</sup> used the close relationship between intramolecular BSSE and basis set incompleteness to derive a power-law linking basis set incompleteness and intramolecular BSSE. This could in principle be used to obtain MP2/CBS values using only one energy value and the intramolecular BSSE (or, alternatively, compute the intramolecular BSSE if the CBS limit is known). However, the law has a large uncertainty (25%) and has so far only been tested on a number of small molecules (ranging from N<sub>2</sub> to C<sub>2</sub>H<sub>4</sub>) using nondiffuse basis sets. Salvador et al.<sup>94,95</sup> showed that intramolecular BSSE is responsible for the surprising result that *ab initio* calculations on aromatic systems such as benzene and the nucleic acid bases yield nonplanar structures. They corrected the intramolecular BSSE in these molecules using small moieties (the C–H, C=O, N–H, and CCH<sub>3</sub> groups) as the counterpoise fragments (while noting that the unambiguous, but expensive, way to do the counterpoise calculations would be to take atomic fragments). A similar method, employing CH<sub>2</sub> and CH<sub>3</sub> fragments, was used to estimate the intramolecular BSSE in different conformations of *n*-butane and *n*-hexane.<sup>96</sup> This

approach is basically identical to the one adopted in the current paper to compute the intramolecular BSSE in thioanisole.

In the current paper, we show that the discrepancies between the B3LYP and MP2 results for the ethyne methyl isocyanide complex are due primarily to missing dispersion in the B3LYP calculations and, to a smaller extent, overestimation of the interaction by the MP2 method. This molecule shows the typical characteristics of a dispersion-bound system: the binding energy is underestimated by B3LYP and slightly overestimated by MP2, and good performance is achieved with the M05-2X, DFT-D, and mPW2-PLYP-D methods. The situation is very different for thioanisole. We find that the shape of the potential energy curve for rotation around the thioanisole C(sp<sup>2</sup>)-S bond is very method- and basis-set-dependent. The CCSD(T) reference profile shows the global minimum at the planar conformation and a plateau region at the perpendicular conformation. This can be reasonably reproduced by MP2 calculations with basis sets of at least triple- $\zeta$  quality and B3LYP calculations with basis sets of double- $\zeta$  quality. The electronic structure methods assessed show a very mixed performance: B3LYP-D and M06-L considerably overestimate the relative stability of the planar conformer, whereas the M05-2X and mPW2-PLYP(-D) results are in closer agreement with the CCSD(T) reference values. This shows that DFT methods designed to give good results for weak interactions, like DFT-D and the M0x ( $x = 5, 6$ ) functionals, do not always give good results, and more studies assessing the performance of these methods are required, particularly for challenging molecular systems like thioanisole.

## 2. Methodology

**2.1. The Ethyne Methyl Isocyanide Complex.** The ethyne methyl isocyanide complex was optimized using B3LYP, MP2, and M05-2X, all employing the aug-cc-pVTZ basis set. The geometry optimizations were done both with and without counterpoise (CP) corrections, and the interaction energy was computed according to the CP procedure.<sup>84</sup> The CP-corrected interaction energy follows from:

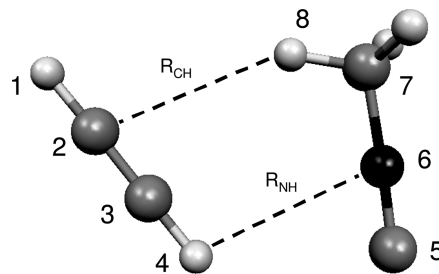
$$\Delta E^{\text{CP}} = E_{\text{EM}}^{\{\text{EM}\}} - E_{\text{E}}^{\{\text{EM}\}} - E_{\text{M}}^{\{\text{EM}\}} + E_{\text{E}}^{\text{def}} + E_{\text{M}}^{\text{def}} \quad (1)$$

Here, the monomer deformation energy  $E_X^{\text{def}}$  ( $X = \text{E}$  or  $\text{M}$ ;  $\text{E} = \text{ethyne}$ ;  $\text{M} = \text{methyl isocyanide}$ ) is defined as

$$E_X^{\text{def}} = E_X^{\{\text{X}\}}(\text{EM}) - E_X^{\{\text{X}\}}(\text{X}) \quad (2)$$

In eqs 1 and 2, the subscripts denote the molecular system. The superscripts denote the basis set used for the calculation (the monomer basis set  $\{\text{E}\}$  or  $\{\text{M}\}$  or the dimer basis set  $\{\text{EM}\}$ ), whereas the terms in parentheses indicate the geometry used in the calculation (the geometry of the dimer (EM) or the optimized monomer geometry (E) or (M)).

Interaction energy profiles were computed by optimizing the structures at fixed C<sub>3</sub>-N<sub>6</sub> distances in the range 2.0–4.5 Å, using B3LYP/aug-cc-pVTZ, MP2/6-31+G(d), and MP2/aug-cc-pVTZ (see Figure 1 for the atom labeling). The



**Figure 1.** Atom labeling in the ethyne methyl isocyanide complex.

geometry optimizations were performed on the uncorrected potential energy surfaces. Uncorrected and CP-corrected interaction energies were computed at the same levels of theory as used to obtain the optimized structures.

The uncorrected B3LYP/aug-cc-pVTZ-optimized geometry was used to compare the performance of a range of electronic structure methods for evaluating the ethyne methyl isocyanide interaction energy. Uncorrected as well as CP-corrected interaction energies were computed. To avoid artificially large monomer deformation energies, the calculation of the monomer energies  $E_{\text{E}}^{\{\text{E}\}}(\text{E})$  and  $E_{\text{M}}^{\{\text{M}\}}(\text{M})$  used the B3LYP/aug-cc-pVTZ-optimized geometries. The levels of theory considered include HF, B3LYP, MP2, M05-2X, M06-L, B3LYP-D, and mPW2-PLYP-D, all employing the aug-cc-pVTZ basis set. The MP2 calculations were also done with the aug-cc-pVDZ and aug-cc-pVQZ basis sets. From the mPW2-PLYP-D calculations, the mPW-LYP and mPW2-PLYP interaction energies can be extracted as well. mPW-LYP is a nonhybrid functional.

The results were compared with the estimated CCSD(T)/CBS interaction energy, which was obtained by subtracting the CCSD(T)/CBS monomer energies from the CCSD(T)/CBS dimer energy. As above, the dimer and monomer structures were optimized with B3LYP/aug-cc-pVTZ. The interaction energy obtained like this is free of BSSE, as the BSSE vanishes at the CBS limit. The CCSD(T)/CBS energies were obtained by the method introduced by Klopper and Lüthi<sup>97</sup> and used by Hobza and co-workers,<sup>98</sup> which involves the addition of a higher-order correlation correction term to the MP2/CBS energies, obtained by extrapolation. The CCSD(T)/CBS dimer and monomer energies then follow from

$$E(\text{CCSD(T)/CBS}) = E(\text{HF/av5z}) + E(\text{MP2corr/CBS(avtz/avqz)}) + E(\text{CCSD(T)corr/avtz}) \quad (3)$$

In eq 3, the aug-cc-pV $x$ Z basis sets are abbreviated as av $x$ z ( $x = \text{t}, \text{q}, 5$ ). The MP2 correlation energy term,  $\Delta E(\text{MP2corr/CBS})$ , was obtained by extrapolating the aug-cc-pVTZ and aug-cc-pVQZ MP2 correlation energies to the CBS limit using the extrapolation formula of Halkier et al.:<sup>99</sup>

$$E(\text{MP2corr/CBS}) = \frac{x^3}{x^3 - (x-1)^3} \times E_{\text{MP2corr},x} - \frac{(x-1)^3}{x^3 - (x-1)^3} E_{\text{MP2corr},x-1} \quad (4)$$



**Table 1.** Interaction Energies  $\Delta E$  (in kJ/mol) and Key Structural Features (Distances in Å, Angles in Degrees) of the Ethyne Methyl Isocyanide Complex<sup>a</sup>

	geometry <sup>b</sup>	$\Delta E^{\text{noCP}}$	$\Delta E^{\text{CP}}$	$R(\text{H}_4\text{C}_5)$	$\angle(\text{H}_4\text{C}_5\text{N}_6)$	$R(\text{H}_8\text{C}_2)$	$\angle(\text{C}_7\text{H}_8\text{C}_2)$	$R(\text{C}_3\text{N}_6)$
B3LYP	no CP	−5.25	−5.07	2.941	84.2	3.407	147.0	3.602
	CP	−5.24	−5.07	2.959	84.2	3.400	147.3	3.611
MP2	no CP	−14.32	−12.62	2.759	83.8	2.916	150.2	3.305
	CP	−14.26	−12.68	2.790	84.9	2.972	149.1	3.341
M05-2X	no CP	−11.12	−10.80	2.836	83.3	3.057	149.8	3.402
	CP	−11.12	−10.80	2.838	83.3	3.066	149.6	3.407

<sup>a</sup> All calculations employed the aug-cc-pVTZ basis set. <sup>b</sup> No CP/CP: geometries optimized on the uncorrected/CP-corrected potential energy surface.

Here,  $x$  is the cardinal number of the largest basis set used in the extrapolation (in this case, 4 for aug-cc-pVQZ).

The CCSD(T) correction term for higher-order correlation energy,  $E(\text{CCSD(T)corr})$ , was obtained by taking the difference in the MP2 and CCSD(T) correlation energies, computed with the aug-cc-pVTZ basis set. As the basis set dependence of the CCSD(T) correction term is small,<sup>100–102</sup> the aug-cc-pVTZ basis set should be sufficiently large to give an accurate estimate of the higher-order correlation energy.

The B3LYP, MP2, and M05-2X calculations were done with Gaussian,<sup>103</sup> the mPW2-PLYP-D and B3LYP-D calculations were done with Orca,<sup>104</sup> and the Molpro program package<sup>105</sup> was used for the CCSD(T) calculations. For consistency with the Gaussian results, the B3LYP-D calculations with Orca employed the VWN1<sup>106</sup> correlation functional (Gaussian's definition of the B3LYP functional).

**2.2. Thioanisole.** Potential energy curves for rotation around the  $\text{C}(\text{sp}^2)\text{--S}$  bond were computed by optimizing the thioanisole structure at fixed  $\tau(\text{CCSC})$  torsion angles ranging from 0 (planar) to 90° (perpendicular) using M05-2X/6-31+G(d). Single-point calculations employing the M05-2X-optimized geometries were performed at different levels of theory, including MP2 and B3LYP employing the 6-311G(d,p) and (aug)-cc-pV $x$ Z ( $x = \text{D, T, Q}$ ) basis sets; HF/cc-pV $x$ Z ( $x = \text{D, T, Q, 5}$ ); CCSD(T)/aug-cc-pVDZ; B3LYP-D/aug-cc-pVDZ; and the M05-2X, M06-L, and mPW2-PLYP(-D) methods combined with the (aug)-cc-pV $x$ Z ( $x = \text{D, T}$ ) basis sets. M05-2X and M06-L calculations were also done with the aug-cc-pV( $n+\text{d}$ )Z ( $n = \text{D, T}$ )<sup>107</sup> basis sets, obtained from the EMSL Basis Set Exchange Web site.<sup>108,109</sup> An estimated CCSD(T)/CBS potential energy curve was constructed by estimating the CCSD(T)/CBS thioanisole energy at each  $\tau(\text{CCSC})$  value similar to eq 3, but at slightly lower basis set levels:

$$E(\text{CCSD(T)/CBS}) = E(\text{HF/v5z}) + E(\text{MP2corr/CBS}(\text{avtz/avqz})) + E(\text{CCSD(T)corr/avdz}) \quad (5)$$

Selected single-point energies were CP-corrected by considering as the monomers the two radical fragments obtained by breaking the  $\text{C}(\text{sp}^2)\text{--S}$  bond, i.e., the benzene ring and the  $\text{--SCH}_3$  group.

### 3. Results

**3.1. The Ethyne Methyl Isocyanide Complex.** **3.1.1. Geometry Optimization.** Table 1 shows the interaction energies and key structural features of the ethyne methyl isocyanide

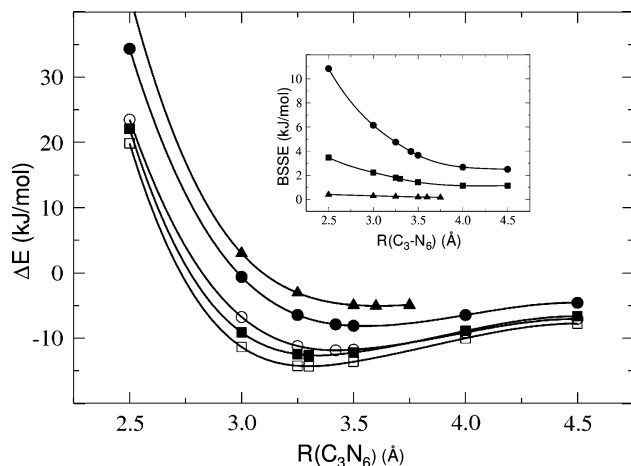
complex optimized at different levels of theory. In agreement with the results of Cao et al.,<sup>26</sup> MP2 predicts shorter intermolecular distances than B3LYP. The small differences in the results obtained in ref 26 and by us may be due to different convergence criteria (we used Gaussian's "tight" convergence threshold) or different integration grid sizes in the DFT calculations (we used Gaussian's default integration grid). In line with the larger intermolecular distances, B3LYP predicts much less intermolecular stabilization than MP2. The M05-2X results are between the B3LYP and MP2 results but closer to the MP2 results.

The effect of CP correction on the geometries is very small. Even the MP2 geometries are only negligibly affected by BSSE: CP correction increases the intermolecular distances by less than 0.1 Å. As expected, the effects are even smaller for the DFT calculations. The interaction energies, on the other hand, are more noticeably affected by BSSE: CP correction decreases the MP2 interaction energy by about 10%. We conclude that CP-corrected geometry optimization is, in this case, not required, but the ethyne methyl isocyanide interaction energies should be corrected for BSSE.

These results suggest that the differences in the geometries optimized by B3LYP and MP2 are not due to large BSSE effects in the MP2 calculations. It is therefore likely that missing dispersion interactions in the B3LYP calculations are the cause of the discrepancies between the MP2 and B3LYP results. We explore this further in the next section.

**3.1.2. Interaction Energy Profiles.** To investigate further the effect of the method and BSSE on the intermolecular separation, we performed geometry optimizations at fixed  $\text{C}_3\text{--N}_6$  distances, in the range 2.5–4.5 Å. At distances outside this range, the geometry did not resemble the minimum-energy structure displayed in Figure 1. Figure 2 shows the uncorrected and CP-corrected interaction energy profiles. The B3LYP/aug-cc-pVTZ profile is shown only up to 3.75 Å, as the ethyne methyl isocyanide structure changes significantly beyond this distance, yielding a structure slightly more stable than the minimum at 3.60 Å. Full optimization of this structure generated a linear complex, which was found to be more stable than the  $\pi$ -bonded structure investigated in this work. This conforms to the water–acetonitrile system, for which the linear H-bonded isomer was also found to be more stable than the  $\pi$ -bonded isomer.<sup>51</sup>

The inset of Figure 2 shows the variation of the BSSE with  $\text{C}_3\text{--N}_6$  distance. The B3LYP/aug-cc-pVTZ BSSE is small for all  $\text{C}_3\text{--N}_6$  distances considered, with the result that the uncorrected and CP-corrected B3LYP/aug-cc-pVTZ curves are nearly identical, and therefore, only the CP-

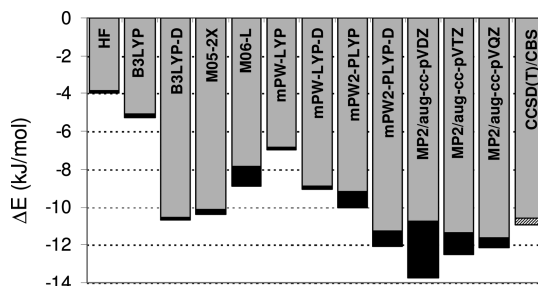


**Figure 2.** Interaction energy profiles obtained by optimizing the ethyne methyl isocyanide structure at fixed  $C_3-N_6$  distances. Circles: MP2/6-31+G(d) profiles. Squares: MP2/aug-cc-pVTZ profiles. Triangles: B3LYP/aug-cc-pVTZ profile. Open symbols: uncorrected results. Closed symbols: CP-corrected results. The inset shows the variation of the BSSE as a function of the  $C_3-N_6$  distance.

corrected profile is shown in Figure 2. The BSSE is somewhat larger in the MP2/aug-cc-pVTZ calculations and increases with decreasing separation between the two fragments. This is expected, as the basis-set stealing process, which underlies the cause of BSSE, becomes more difficult the further apart the fragments are. The MP2/aug-cc-pVTZ BSSE is however still sufficiently small not to affect significantly the interaction energy profiles; the CP-corrected MP2/aug-cc-pVTZ curve is just slightly shifted upward as compared to the uncorrected profile. These results are in agreement with the results in Table 1, which show a negligible effect of BSSE on the ethyne methyl isocyanide geometries obtained with DFT and MP2 employing the aug-cc-pVTZ basis set. However, the MP2/6-31+G(d) results in Figure 2 show much larger BSSE effects. The magnitude of the BSSE changes significantly over the  $C_3-N_6$  distance range considered, and the application of the CP procedure shifts the minimum to a longer interfragment distance (uncorrected:  $R(C_3N_6) = 3.423$  Å; CP-corrected:  $R(C_3N_6) = 3.554$  Å). Thus, the effect of BSSE on the ethyne methyl isocyanide structure is only negligible if a sufficiently large basis set is employed in the MP2 calculations. In the current case, the aug-cc-pVTZ basis set fulfills this requirement.

**3.1.3. Comparison of Different Electronic Structure Methods.** Figure 3 shows a comparison of the ethyne methyl isocyanide interaction energy computed with different methods, using the uncorrected B3LYP/aug-cc-pVTZ optimized geometry. The estimated CCSD(T)/CBS interaction energy ( $-10.68$  kJ/mol), obtained using eq 3, was used to assess the performance of the various methods.

As we used the estimated CCSD(T)/CBS interaction energy to assess other electronic structure methods, a knowledge of its accuracy is of considerable importance. The CCSD(T)/CBS interaction energy has three main sources of uncertainty: (i) the degree of basis-set convergence of the HF/aug-cc-pV5Z interaction energy, (ii) the accuracy of the aug-cc-pVTZ/aug-cc-pVQZ extrapolation of the MP2 cor-



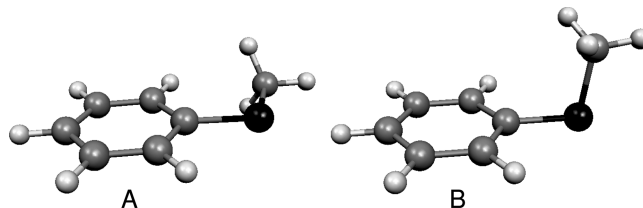
**Figure 3.** Ethyne methyl isocyanide interaction energies computed with different methods. Light gray: CP-corrected interaction energies. Black: BSSE. The sum of the black and gray fields equals the uncorrected interaction energy. The diagonally striped area shows the estimated uncertainty in the CCSD(T) interaction energy. All calculations were done using the uncorrected B3LYP/aug-cc-pVTZ optimized geometry. The aug-cc-pVTZ basis set was employed, unless stated otherwise.

relation energies, and (iii) the accuracy of the CCSD(T) correction term. Let us consider these three issues separately: (i) The HF interaction energies decrease by 0.73, 0.14, and 0.04 kJ/mol, from aug-cc-pVDZ to aug-cc-pVTZ, aug-cc-pVTZ to aug-cc-pVQZ, and aug-cc-pVQZ to aug-cc-pV5Z, respectively. Thus, the differences decrease by a factor of 5.6 and 3.0, respectively. Assuming this trend continues (i.e., the factor with which the differences decrease continues to halve), we expect the decrease from aug-cc-pV5Z to aug-cc-pV6Z to be  $0.04/1.5 = 0.03$  kJ/mol. We therefore estimate the HF/aug-cc-pV5Z interaction energy to be too large (i.e., too negative) by 0.03–0.05 kJ/mol. (ii) The accuracy of the MP2 extrapolation procedure can be deduced from the convergence of the MP2 correlation interaction energies. The correlation interaction energies decrease by 0.49 and 0.28 kJ/mol, from aug-cc-pVDZ to aug-cc-pVTZ and from aug-cc-pVTZ to aug-cc-pVQZ, respectively. Extrapolation to the CBS limit, using the aug-cc-pVTZ and aug-cc-pVQZ results, leads to a further decrease of 0.20 kJ/mol. The aug-cc-pVxZ ( $x = D, T, Q$ ) MP2 interaction energies appear to converge smoothly toward the estimated CBS interaction energy, which therefore seems a realistic estimate of the true CBS limit. It seems reasonable to estimate the MP2/CBS limit to be accurate to  $\sim 0.1$  kJ/mol. It may appear unusual that the correlation interaction decreases when the basis set is enlarged. The reason for this is the use of uncorrected energies for the extrapolation, and the decrease in interaction reflects a reduced BSSE when more complete basis sets are employed. (iii) The CCSD(T) correction term differs by 0.15 kJ/mol for the aug-cc-pVDZ and aug-cc-pVTZ basis sets. This is in excellent agreement with Sinnokrot and Sherrill's results for different benzene dimer configurations, for which the CCSD(T) correction term also differed by less than 0.2 kJ/mol when evaluated with aug-cc-pVDZ or aug-cc-pVTZ.<sup>100</sup> As the aug-cc-pVTZ correction term should be more accurate than the aug-cc-pVDZ value, we estimate the aug-cc-pVTZ correction term to be accurate to  $\sim 0.1$  kJ/mol. In principle, we can avoid the correction term by using directly extrapolated CCSD(T) energies. Thus, we computed a second estimate of the CCSD(T)/CBS interaction energy, by extrapolation of the aug-cc-pVDZ and aug-cc-pVTZ

CCSD(T) correlation energies of the complex and the two fragments, using Halkier et al.'s extrapolation method<sup>99</sup> given in eq 4, and adding these to the HF/aug-cc-pV5Z total energies. The CCSD(T)/CBS interaction energy was then obtained by subtracting the thus obtained CCSD(T)/CBS monomer energies from the CCSD(T)/CBS dimer energy. This procedure yields a CCSD(T)/CBS value of  $-10.89$  kJ/mol. Inspection of the aug-cc-pVDZ/aug-cc-pVTZ and aug-cc-pVTZ/aug-cc-pVQZ extrapolations of the MP2 results shows that the former yields an MP2/CBS interaction energy that is  $0.28$  kJ/mol larger than that obtained from the (more accurate) aug-cc-pVTZ/aug-cc-pVQZ extrapolation. Subtracting this extrapolation correction from the directly extrapolated CCSD(T)/CBS interaction energy yields a value of  $-10.62$  kJ/mol, in excellent agreement with the CBS value obtained according to eq 3. Note that the CBS value obtained using directly extrapolated CCSD(T) energies differs from that obtained according to eq 3 only by the CCSD(T) correction term, taking the difference in the MP2 and CCSD(T) correlation energies extrapolated using the aug-cc-pVDZ and aug-cc-pVTZ basis sets instead of those computed with the aug-cc-pVTZ basis set. The good agreement between the two CBS values therefore confirms the small basis set dependence of the CCSD(T) correction term. Overall, we estimate the error in the estimated CCSD(T)/CBS interaction energy to be  $+0.25/-0.15$  kJ/mol.

Figure 3 clearly demonstrates that the HF method and the B3LYP and mPW-LYP functionals severely underestimate the ethyne methyl isocyanide interaction energy. Also, the double hybrid mPW2-PLYP predicts too little stabilization. This is in agreement with previous work, where the mPW2-PLYP method was shown to underestimate the intramolecular dispersion in two conformers of the Tyr-Gly dipeptide.<sup>64,74</sup> In addition, Benighaus et al. found that double hybrid functionals capture only about 50% of the interaction energy of dispersion-dominated complexes.<sup>82</sup> The addition of an empirical dispersion term to the B3LYP, mPW-LYP, and mPW2-PLYP functionals brings the results in closer agreement with the CCSD(T) reference value, although mPW-LYP-D still underestimates, whereas mPW2-PLYP-D slightly overestimates the interaction energy. Note the significantly larger BSSE for the double hybrid functionals as compared to the standard DFT methods, which is caused by the added MP2 correlation term. The M05-2X functional gives a very good result, only slightly underestimating the CCSD(T) interaction energy. The CP-corrected MP2/aug-cc-pVDZ result is also very close to the CCSD(T) interaction energy. However, this is due to a cancellation of errors: basis set incompleteness vs MP2's tendency to overestimate dispersion interactions.<sup>100,101,110-112</sup> When larger basis sets are used, the MP2 method overestimates the interaction energy, and the CCSD(T) correction term in eq 3 is therefore positive. Note also here the sizable BSSE, particularly when using the aug-cc-pVDZ basis set.

The CCSD(T)/CBS reference interaction energy was computed at the B3LYP/aug-cc-pVTZ optimized geometry and is therefore likely too small, as geometry relaxation at the CCSD(T) level is expected to increase the stability of the ethyne methyl isocyanide complex. Let us therefore return



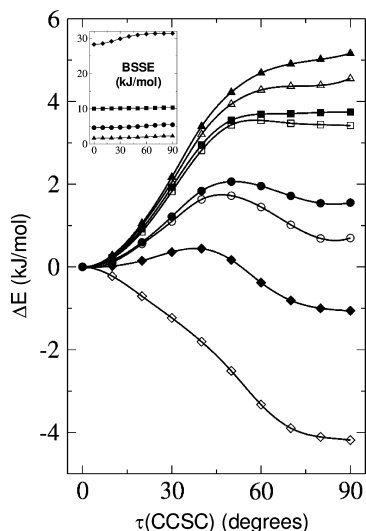
**Figure 4.** The planar (A) and perpendicular (B) conformations of thioanisole.

to the results displayed in Table 1, which were obtained using geometries optimized at the same level of theory as used for the energy calculation. The analysis above shows that MP2/aug-cc-pVTZ slightly overestimates, whereas M05-2X/aug-cc-pVTZ slightly underestimates. We therefore estimate the ethyne methyl isocyanide interaction energy to be  $12 \pm 1$  kJ/mol.

**3.2. Thioanisole.** *3.2.1. B3LYP and MP2 Potential Energy Curves.* Previous computational and experimental work indicates that there are two possible configurations for the thioanisole molecule, with the thiomethyl group either planar or perpendicular with respect to the benzene ring (see Figure 4). The calculations done by Suzuki et al. showed that the global minimum geometry is drastically dependent on the level of theory used:<sup>27</sup> whereas B3LYP/cc-pVTZ yields a planar structure, MP2/6-311G(d,p) calculations result in the perpendicular conformer. MP2/cc-pVTZ finds both structures, with the planar one the most stable of these. The large basis set dependence of the MP2 results suggests that BSSE effects may be significant. We have therefore computed B3LYP and MP2 potential energy curves for rotation around the C(sp<sup>2</sup>)-S bond with and without CP corrections (Figure 5).

In agreement with Suzuki et al.,<sup>27</sup> the uncorrected MP2/6-311G(d,p) curve shows the perpendicular conformer at  $90^\circ$  as the only minimum. CP correction reveals a second, shallow minimum at  $0^\circ$ , though the perpendicular conformer remains the more stable one. All other curves show the planar conformer as the global minimum. The uncorrected MP2/cc-pVTZ curve shows a second, very shallow minimum at  $90^\circ$  (barely visible in Figure 5), which disappears after CP correction. The uncorrected and CP-corrected MP2/cc-pVTZ curves are very close to each other, even though the BSSE is fairly large in the MP2/cc-pVTZ calculations ( $\sim 10$  kJ/mol, see inset). However, the MP2/cc-pVTZ BSSE appears to be rather insensitive to the orientation of the thiomethyl group and therefore hardly affects the shape of the potential energy curve. The two B3LYP/6-311G(d,p) curves show a very shallow minimum around  $80^\circ$ . Such a secondary minimum was also found with some functionals in the study by Bossa et al.<sup>34</sup> With both basis sets, B3LYP predicts the relative stability of the perpendicular conformer to be larger as compared to MP2. As the potential energy curves appear to be rather sensitive to the basis set employed, we have investigated the basis set dependence in greater detail. To provide a reference to assess the convergence of the results obtained with different basis sets, we have constructed an estimated MP2/CBS and CCSD(T)/CBS profile. The CCSD(T)/CBS energies were obtained according to eq 5, whereas





**Figure 5.** Potential energy curves for rotation around the  $C(sp^2)$ –S bond computed with B3LYP/6-311G(d,p) (circles), B3LYP/cc-pVTZ (triangles), MP2/6-311G(d,p) (diamonds), and MP2/cc-pVTZ (squares). Open symbols denote uncorrected results; closed symbols denote CP-corrected results. The structures were optimized at fixed  $\tau(\text{CCSC})$  torsion angles with M05-2X/6-31+G(d). The planar conformer ( $\tau(\text{CCSC}) = 0^\circ$ ) was taken as the reference point for the relative energies. The inset shows the variation of the BSSE as a function of the  $\tau(\text{CCSC})$  torsion angle.

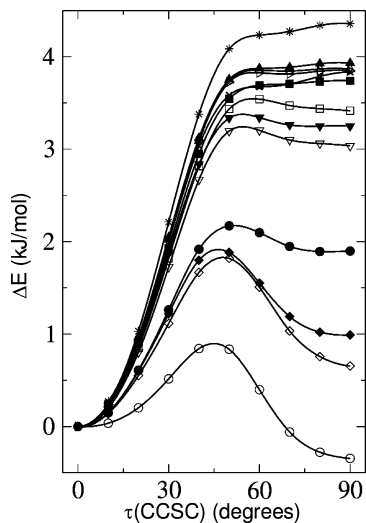
the MP2/CBS energies were obtained in the same way, but without the CCSD(T) correction term.

Let us first discuss the accuracy of the CBS profiles. Here, we focus on the stability gap between the planar and perpendicular conformer (which for some, but not all, levels of theory corresponds to the rotational barrier). The stability gap is estimated to be 4.4 kJ/mol for MP2/CBS and 3.8 kJ/mol for CCSD(T)/CBS. As above, there are three main sources of uncertainty in this property: (i) the degree of basis-set convergence of the HF/cc-pV5Z energies, (ii) the accuracy of the aug-cc-pVTZ/aug-cc-pVQZ extrapolation of the MP2 correlation energies, and, for the CCSD(T)/CBS profile, (iii) the accuracy of the CCSD(T) correction term. (i) At the HF level, the stability gap decreases from 4.78 to 2.18, 1.71, and 1.53 kJ/mol for cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z, and from 3.89 to 1.85 for aug-cc-pVDZ to aug-cc-pVTZ, respectively. On the basis of the convergence of these numbers, we estimate that the HF/cc-pV5Z stability gap would decrease by less than 0.2 kJ/mol upon a further increase of the basis set. (ii) The extrapolations of the MP2 correlation energy were performed both using the uncorrected and CP-corrected correlation energies. This should in principle lead to the same limits, as the BSSE vanishes at the CBS limit. Differences in the standard and CP-corrected CBS limits will therefore provide information on the accuracy of the extrapolation procedure. We focus again on the stability gap between the planar and perpendicular conformer. Using cc-pVTZ/cc-pVQZ extrapolation, this gap is 5.55 and 5.56 kJ/mol, for the standard and CP-corrected extrapolation, respectively, evidencing that CP correction does not have a noticeable effect on the cc-pVTZ/cc-pVQZ extrapolation. The uncorrected and CP-corrected

cc-pVTZ/cc-pVQZ extrapolated energies are almost identical over the whole  $\tau(\text{CCSC})$  torsion angle range (Figure S1, Supporting Information). Using the less accurate cc-pVDZ/cc-pVTZ and aug-cc-pVDZ/aug-cc-pVTZ extrapolation, the differences between the standard and CP-corrected extrapolation are somewhat larger. Thus, CP-correction appears necessary when extrapolating using basis sets of DZ and TZ quality, and for such extrapolations we will only discuss the CBS limits obtained using the CP-corrected energies. The stability gap changes little from cc-pVTZ to cc-pVQZ (from 5.60 to 5.57 and from 5.48 to 5.53 kJ/mol, for the uncorrected and CP-corrected correlation energies), and the cc-pVTZ/cc-pVQZ-extrapolated CBS limit of 5.55/5.56 kJ/mol therefore seems entirely reasonable. The cc-pVDZ/cc-pVTZ CP-corrected extrapolated CBS limit is also in close agreement with the cc-pVTZ/cc-pVQZ-extrapolated limits. Aug-cc-pVDZ/aug-cc-pVTZ extrapolation using the CP-corrected correlation energies gives a somewhat lower CBS limit (5.25 kJ/mol) as compared to extrapolation using nonaugmented basis sets. However, the stability gap increases significantly (by 0.6 kJ/mol) from aug-cc-pVTZ to aug-cc-pVQZ, and the aug-cc-pVTZ/aug-cc-pVQZ extrapolation yields a CBS value of 5.9 kJ/mol, 0.3 kJ/mol larger than the CBS limits obtained using the unaugmented basis sets. There therefore is some uncertainty in the extrapolation of the MP2 correlation energies. The most accurate CBS limit is probably the one obtained with the largest basis sets employed (aug-cc-pVTZ/aug-cc-pVQZ), but the above analysis suggests that this CBS limit is more likely too large than too low. We therefore estimate the aug-cc-pVTZ/aug-cc-pVQZ extrapolation to be accurate to within  $+0.2/-0.5$  kJ/mol. (iii) The last source of uncertainty in the CCSD(T)/CBS profile is related to the CCSD(T)/aug-cc-pVDZ correction term. On the basis of our analysis for the ethyne methyl isocyanide molecule above (section 3.1.3) and Sinnokrot and Sherrill's results for different benzene dimer configurations, we estimate that the CCSD(T)/aug-cc-pVDZ correction term is accurate to within 0.3 kJ/mol. Thus, the uncertainty in the MP2/CBS and CCSD(T)/CBS profiles is estimated to be  $-0.7/+0.2$  kJ/mol and  $-1.0/+0.5$  kJ/mol, respectively.

Let us now investigate the basis set dependence of the potential energy profiles. Figure 6 shows MP2 potential energy curves for rotation around the  $C(sp^2)$ –S bond computed with different correlation consistent basis sets. The uncorrected cc-pVDZ results predict the perpendicular conformer to be more stable than the planar conformer. Counterpoise correction reverses this preference. All other basis sets predict the planar conformation as the global minimum. The results obtained with basis sets of triple- or quadruple- $\zeta$  quality, as well as the CCSD(T) reference profile, do not show a clear minimum or maximum at  $90^\circ$ ; instead the profile displays a plateau-like region around this torsion angle. Both CP correction and increasing the basis set size decreases the relative stability of the perpendicular conformer. Upon increasing the basis set quality, the uncorrected and CP-corrected curves converge toward each other. The CP-corrected cc-pVTZ and cc-pVQZ profiles and the uncorrected cc-pVQZ and aug-cc-pVQZ profiles are very close to each other. The aug-cc-pVTZ profiles, however,



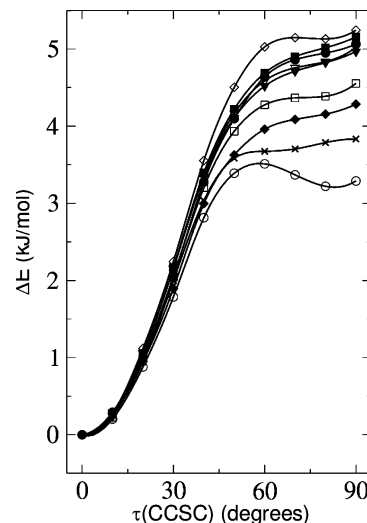


**Figure 6.** Potential energy curves for rotation around the C(sp<sup>2</sup>)–S bond computed with MP2 and various basis sets. Circles: cc-pVDZ. Squares: cc-pVTZ. Up triangles: cc-pVQZ. Diamonds: aug-cc-pVDZ. Down triangles: aug-cc-pVTZ. Right triangles: aug-cc-pVQZ. Open symbols denote uncorrected results; closed symbols denote CP-corrected results. The structures were optimized at fixed  $\tau(\text{CCSC})$  torsion angles with M05-2X/6-31+G(d). The planar conformer ( $\tau(\text{CCSC}) = 0^\circ$ ) was taken as the reference point for the relative energies. The estimated MP2/CBS potential energy curve is denoted by stars, whereas the estimated CCSD(T)/CBS potential energy curve is denoted by crosses.

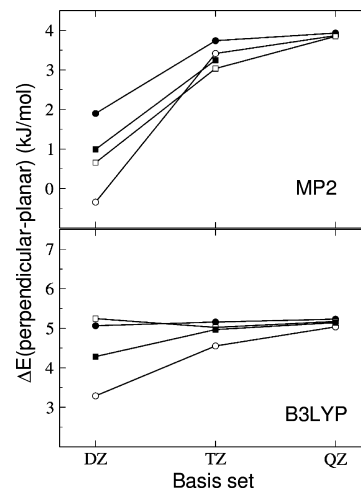
show a smaller stability gap between the two thioanisole isomers. The estimated MP2/CBS profile, which is about 0.5 kJ/mol above the quadruple- $\zeta$  profiles at  $90^\circ$ , suggests that the calculations are not yet converged with respect to basis set quality, and basis sets beyond quadruple- $\zeta$  quality may be required to obtain converged results. Comparison with the CCSD(T)/CBS results suggests that, at the CBS limit, MP2 overestimates the relative stability of the planar conformer. However, the large uncertainty in the CBS profiles prevents solid conclusions on this.

Figure 7 shows the potential energy curves computed with B3LYP and the (aug)-cc-pVxZ basis sets of DZ and TZ quality. For the sake of clarity, the (aug)-cc-pVQZ results, which are close to the corresponding (aug)-cc-pVTZ values, are not shown. The QZ-quality results are included in the discussion on the convergence of the energy difference between the planar and perpendicular conformers (see section 3.2.2 below). All basis sets predict the planar conformer as the global minimum, whereas the perpendicular structure is not a minimum with any of the basis sets employed. The uncorrected B3LYP/cc-pVDZ shows a shallow minimum at  $80^\circ$ , which disappears after CP correction. All B3LYP curves (except the uncorrected cc-pVDZ curve) predict a larger stability gap between the planar and perpendicular configurations (barrier height 4–5 kJ/mol) as compared to CCSD(T)/CBS.

In summary, the thioanisole potential energy curves appear to be very basis set dependent, which also causes relatively large uncertainties in the estimated CBS profiles. When the MP2 method is used with small basis sets and no CP corrections, the perpendicular conformer is predicted to be



**Figure 7.** Potential energy curves for rotation around the C(sp<sup>2</sup>)–S bond computed with B3LYP and various basis sets. Circles: cc-pVDZ. Squares: cc-pVTZ. Diamonds: aug-cc-pVDZ. Down triangles: aug-cc-pVTZ. Open symbols denote uncorrected results; closed symbols denote CP-corrected results. The structures were optimized at fixed  $\tau(\text{CCSC})$  torsion angles with M05-2X/6-31+G(d). The planar conformer ( $\tau(\text{CCSC}) = 0^\circ$ ) was taken as the reference point for the relative energies. The estimated CCSD(T)/CBS potential energy curve is denoted by crosses.



**Figure 8.** The energy gap between the planar and perpendicular conformers as a function of basis set size calculated with MP2 (upper plot) and B3LYP (lower plot). Circles: cc-pVxZ. Squares: aug-cc-pVxZ. Open symbols denote uncorrected results; closed symbols denote CP-corrected results.

the global minimum. Larger basis sets, however, show the planar conformer as the global minimum. MP2 appears to overestimate the energy gap between the planar and perpendicular configurations. B3LYP predicts the global minimum to be planar, irrespective of the basis set employed. However, like MP2, B3LYP overestimates the relative stability of this conformer.

**3.2.2. Convergence of the Energy Difference between the Planar and Perpendicular Configurations.** Figure 8 shows the B3LYP and MP2 energy gap between the planar and perpendicular conformers as a function of basis set

quality. Both uncorrected as well as CP-corrected results are shown. All MP2 curves and all B3LYP curves clearly converge toward a limiting value. The limiting value is 4.4 kJ/mol for MP2 (see above) and is estimated from Figure 8 to be about 5.2 kJ/mol for B3LYP. Both limits are higher than the CCSD(T) estimate of 3.8 kJ/mol.

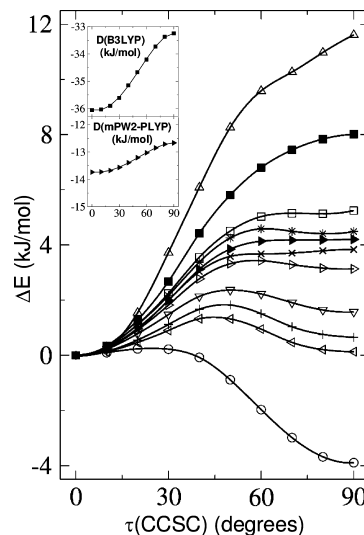
The B3LYP curves vary less with basis set improvement than the MP2 curves (note that the energy range on the y axis is identical for the two plots). This is consistent with the smaller basis set dependence of DFT as compared to MP2. CP correction brings the results closer to the limiting value, except for the B3LYP/aug-cc-pVDZ calculation. However, CP correction does restore the regular convergence of the B3LYP/aug-cc-pVxZ curve. This is consistent with earlier work that showed that, in many cases, the convergence behavior of molecular properties calculated with the correlation consistent basis sets is significantly improved if BSSE is taken into account.<sup>113</sup> This agreement indicates that the simple CP scheme to correct for the intramolecular BSSE used in the current study works well.

Even though the BSSE is significantly smaller in the B3LYP calculations (ranging from 6.8–8.6 kJ/mol for B3LYP/cc-pVDZ compared to 22.4–24.6 kJ/mol for MP2/cc-pVDZ), the effect on the B3LYP/cc-pVDZ and MP2/cc-pVDZ results is similar (B3LYP, 1.8 kJ/mol; MP2, 2.2 kJ/mol). CP correction of the B3LYP/cc-pVDZ calculation brings the energy gap in close proximity to the limiting value.

The corresponding uncorrected and CP-corrected curves using the aug-cc-pVxZ basis sets are closer to each other than those computed with the unaugmented basis sets. This is particularly evident for the MP2 method. This does not mean that the BSSE is smaller for the augmented basis sets. In fact, the BSSE has a similar magnitude for the corresponding standard and augmented basis sets. The close agreement between the uncorrected and CP-corrected aug-cc-pVxZ curves results from the fact that the magnitude of the BSSE is very similar for the planar and perpendicular conformers in the aug-cc-pVxZ calculations.

**3.2.3. Comparison of Different Electronic Structure Methods.** Figure 9 shows the potential energy curves for rotation around the C(sp<sup>2</sup>)–S bond computed with different electronic structure methods, the aug-cc-pVDZ basis set, and no CP corrections.

The HF curve shows the perpendicular structure as the global minimum, in agreement with previous studies,<sup>28–30</sup> with only a very shallow minimum at 0°. The curve is similar to the uncorrected MP2/6-31G(d,p) profile (Figure 5). However, unlike for MP2, increasing the basis set does not result in the planar structure becoming the global minimum, even though the energy gap between the two conformations reduces somewhat (Figure S2, Supporting Information). CCSD(T)/aug-cc-pVDZ predicts only a very small stability difference (0.13 kJ/mol) between the planar and perpendicular conformer. At the CBS limit, however, the planar conformer is 3.83 kJ/mol more stable than the perpendicular structure. The MP2/aug-cc-pVDZ stability difference between the two conformers is also small (0.65 kJ/mol), but we have seen above that, at the CBS limit, MP2 overestimates the stability gap. As we have seen above, B3LYP



**Figure 9.** Potential energy curves for rotation around the C(sp<sup>2</sup>)–S bond computed at different levels of theory. All profiles (except the CCSD(T)/CBS reference curve) were computed with the aug-cc-pVDZ basis set. Open circles: HF. Left triangles: CCSD(T). Pluses: MP2. Down triangles: mPW-LYP. Open right triangles: mPW2-PLYP. Closed right triangles: mPW2-PLYP-D. Open squares: B3LYP. Closed squares: B3LYP-D. Up triangles: M06-L. Stars: M05-2X. The inset shows the van der Waals/dispersion corrections (D) computed by the B3LYP-D and mPW2-PLYP-D methods. The structures were optimized at fixed  $\tau(\text{CCSC})$  torsion angles with M05-2X/6-31+G(d). The planar conformer ( $\tau(\text{CCSC}) = 0^\circ$ ) was taken as the reference point for the relative energies. The estimated CCSD(T)/CBS potential energy curve is denoted by crosses.

predicts a too large stability gap between the two conformers. The addition of a dispersion term exacerbates this (B3LYP-D profile). The inset clearly shows the dispersion contribution's preference for the planar conformation. Because the dispersion term, as calculated in the Orca program, is by default independent of the basis set employed, B3LYP-D exhibits the same basis set dependence as B3LYP. It can thus be inferred from Figure 7 that the use of larger basis sets in the B3LYP-D calculations (or CP-correction) would only slightly decrease the discrepancy with the CCSD(T) curve, but the B3LYP-D stability gap would remain significantly too large. Interestingly, other systems for which DFT-D was found to give results in disagreement with CCSD(T) also include an anisole unit: anisole–water and anisole–ammonium.<sup>79</sup> For these systems, the overestimated interaction energies obtained by DFT-D were attributed to an overestimated dispersion correction or to double counting of electron correlation effects by the DFT and van der Waals parts of the method. The mPW2-PLYP/aug-cc-pVDZ and mPW2-PLYP-D/aug-cc-pVDZ profiles are very close to the reference CCSD(T)/CBS curve and also show the plateau region around 90°. Increasing the basis set quality in the mPW2-PLYP-D calculations deteriorates the results somewhat (Figure S3, Supporting Information). Note that the dispersion contribution is smaller for mPW2-PLYP than for B3LYP (inset), as the nonlocal perturbation term in the double hybrid functional already accounts for part of the dispersion energy. The M05-2X/aug-cc-pVDZ profile is also close to the reference profile.

Like the mPW2-PLYP results, the M05-2X profile is very basis set dependent (Figure S4, Supporting Information), and basis sets of at least aug-cc-pVDZ or cc-pVTZ quality are required to obtain good agreement with the CCSD(T)/CBS curve. Here, we also investigated the performance of the aug-cc-pV( $n+d$ )/Z basis sets,<sup>107</sup> which contain additional tight d functions for second-row elements. Figure S4 shows that these basis sets give only slightly revised profiles compared to those obtained with basis sets without the tight d-functions. M06-L significantly overestimates the stability gap between the planar and perpendicular conformation. Improving the basis set and correcting for BSSE does not change the M06-L profile significantly (Figure S5, Supporting Information).

#### 4. Summary and Conclusions

We have investigated two molecular systems, the ethyne methyl isocyanide complex and thioanisole; for both molecules, previous studies had shown significant discrepancies between the results obtained with the MP2 and B3LYP methods. The ethyne methyl isocyanide complex exhibits two  $\pi$  bonds. Earlier work by Cao et al.<sup>26</sup> showed that B3LYP/cc-pVTZ predicts significantly longer H-bond distances than MP2/cc-pVTZ. In the current work, we show that this is likely due to missing dispersion in the B3LYP calculations. Comparison with estimated CCSD(T)/CBS results shows that B3LYP significantly underestimates the stability of the complex, whereas MP2 slightly overestimates (when basis sets larger than aug-cc-pVDZ are employed). Other methods that give results in close proximity to the CCSD(T)/CBS reference value include M05-2X, B3LYP-D, and (CP-corrected) mPW2-PLYP-D.

The thioanisole molecule can adopt two different structures, with the thiomethyl group planar or perpendicular with respect to the benzene ring. An earlier study by Suzuki et al.<sup>27</sup> showed that B3LYP/cc-pVTZ geometry optimizations yield the planar conformer, whereas MP2/6-311G(d,p) geometry optimizations lead to the perpendicular conformer. MP2/cc-pVTZ shows both structures as a minimum, with the planar conformer as the global minimum. By comparison with estimated CCSD(T)/CBS results, we show in this work that the preferred thioanisole structure is planar. The energy landscape is very shallow around the perpendicular configuration, and the CCSD(T)/CBS energy profile for rotation around the C(sp<sup>2</sup>)-S bond shows a plateau region, rather than a true minimum or maximum, near the perpendicular configuration. The energy barrier for rotation around the C(sp<sup>2</sup>)-S bond is estimated to be 3.8  $\pm$  1.0/0.5 kJ/mol. This small energy barrier indicates nearly free rotation around this bond, which may explain the varied conformations found experimentally for thioanisole. The stability gap between the planar and perpendicular conformations is found to be very method and basis set dependent. Thus, the 6-311G(d,p) basis set is too small to give the correct conformer in MP2 calculations. Both B3LYP (with basis sets of at least triple- $\zeta$  quality) and MP2 (at the CBS limit) appear to slightly overestimate the stability gap between the two thioanisole conformations. B3LYP predicts a maximum instead of a plateau region at the perpendicular structure. This is presumably not due to missing dispersion in the B3LYP calculations,

as the addition of an empirical dispersion term further disfavors the perpendicular conformer. Other density functionals, like M06-L and M05-2X, also show a maximum in the profile at the perpendicular conformer. Note that the uncertainty in the estimated CCSD(T)/CBS limit is relatively large, due to the large basis set dependence of the results. Results that are within the estimated error bars of the CCSD(T)/CBS reference value of the stability gap between the planar and perpendicular conformer include MP2 with basis sets of at least triple- $\zeta$  quality, B3LYP with cc-pVDZ or CP-corrected aug-cc-pVDZ, M05-2X/cc-pVTZ, mPW2-PLYP/aug-cc-pVDZ, and mPW2-PLYP-D/(aug-cc-pVDZ). B3LYP calculations with basis sets larger than aug-cc-pVDZ and mPW2-PLYP-D calculations with basis sets of at least triple- $\zeta$  quality yield overestimated values of the stability gap. M05-2X calculations with basis sets smaller than cc-pVTZ underestimate, whereas larger basis sets overestimate the stability gap.

The ethyne methyl isocyanide complex shows the typical characteristics of a dispersion-dominated system: B3LYP underestimates the interaction; MP2 slightly overestimates; and methods like M05-2X, B3LYP-D, and mPW2-PLYP-D give good results. The situation is different however for the thioanisole molecule. The energy profile for rotation around the C(sp<sup>2</sup>)-S bond is very method and basis set dependent, and methods that could be expected to yield good results, like B3LYP-D, do not agree with the reference profile. Surprising is also the vastly different results obtained with M05-2X and M06-L, two basis sets taken from the related M05 and M06 density functional families of the Minnesota group. One possible explanation for the difficulty in describing this system may be the presence of the sulfur atom. Indeed, previous studies indicate that the rotational profile is less method-dependent for anisole as compared to thioanisole.<sup>30,34</sup> We have not systematically explored the addition of tight d functions, which were found to improve the convergence of the results for molecules with second-row atoms.<sup>107</sup> However, exploratory M05-2X and M06-L calculations using the (aug-cc-pV( $n+d$ ))/Z ( $n = 2, 3$ ) basis sets indicate that the tight d functions only have a moderate influence upon the results.

For both systems, the effects of BSSE were investigated. The standard CP method was used to correct the *intermolecular* BSSE in the ethyne methyl isocyanide complex as well as the *intramolecular* BSSE in thioanisole. For ethyne methyl isocyanide, it is found that CP-corrected geometry optimization is not required when basis sets of at least triple- $\zeta$  quality are used. However, as BSSE increases the MP2/aug-cc-pVTZ interaction energy by 10%, for accurate results the interaction energies should be corrected for BSSE. The intramolecular BSSE in thioanisole affects the relative stability of the planar and perpendicular conformers at both the MP2 and B3LYP levels of theory, particularly when basis sets of less than triple- $\zeta$  quality are employed. In general, CP correction brings the result closer to the limiting value for the method employed. Though this is not the case for the B3LYP/aug-cc-pVDZ calculation, CP correction does improve the convergence behavior of the energy gap computed with B3LYP/aug-cc-pV<sub>x</sub>Z. Thus, the simple CP



scheme used here to correct the intramolecular BSSE in thioanisole appears to work well.

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**Supporting Information Available:** Plots containing potential energy curves for rotation around the C(sp<sup>2</sup>)–S bond computed with various methods and basis sets. Cartesian coordinates of the ethyne methyl isocyanide complex and the ethyne and methyl isocyanide monomers optimized at different levels of theory. Cartesian coordinates of thioanisole optimized with M05-2X/6-31+G(d) at fixed  $\tau$ (CCSC) torsion angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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