J. Phys. Chem. A 2008, 112, 12469–12474 12469

On the Importance of Electron Correlation Effects for the Intramolecular Stacking Geometry of a Bis-Thiophene Derivative

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Received: June 12, 2008; Revised Manuscript Received: October 7, 2008

The structure of dithienobicyclo[4.4.1]undeca-3,8-diene-11-one ethylene glycol ketal (database code RESVAN) was determined using the wave function theory (WFT) as well as density functional theory (DFT) methods combined with various Gaussian AO basis sets. The apparently most accurate procedure, employing the CCSD(T)/complete basis set (CBS), provides an S−S distance and an angle between the two thiophene rings which differ considerably from experimental values. The best agreement with the experimental data among all WFT methods was surprisingly obtained at the MP3/aug-cc-pVDZ and MP3/CBS(B) levels (the correction term to CBS was obtained by the aug-cc-pVDZ basis set). The very good results obtained by the CCSD(T)/6-31G* method are clearly a consequence of fortunate error compensation. MP2 calculations, even with a small basis set, overestimate the attraction between the thiophene rings, and the worst agreement with experimental data was found in full MP2/QZVP method optimizations (i.e., a strong distortion of the thiophene rings was observed). The SCS(MI)-MP2 and SCS-MP2 methods exhibit improvement over the MP2 procedure. All standard DFT approaches fail to predict reasonable S−S distances. The lack of intramolecular London dispersion energy results in too great distance between the thiophene rings. Much better agreement with experiment was obtained if advanced DFT methods, covering dispersion effects, were used. The best results were obtained at the TPSS–D/TZVP, M06-L/TZVP and B2PLYP-D/def2-TZVP levels. When a larger basis (LP in the case of TPSS functional) or more advanced versions of the new Truhlar functionals (M06-2X) was used, the agreement with experiment deteriorated. The accurate description of this molecule is highly functional/basis dependent and this dependence is hardly predictable. To estimate effects of neighboring molecules in the experimental crystal structure, an optimization in the electric field of the 26 closest RESVAN molecules was performed, which, however, leads to only moderate (<0.05 Å) changes of the S−S distance.

Introduction

Noncovalent interactions (NI) determine the energetics and structure of both molecular clusters and nonrigid floppy molecules.[1] The theoretical treatment of NI is difficult and still represents one of the most challenging tasks in today's computational chemistry. It was originally believed that the determination of interaction (stabilization) or relative energies is more complicated, because typically the energy is more sensitive to the theoretical level than molecular structures are. Recent studies from our laboratory as well as others have shown, however, that the determination of structures involving NI is difficult and reliable data can only be obtained when high-level quantum mechanical procedures are implemented. Reliable stabilization and relative energies of DNA base pairs,[2,3] amino acid pairs,[4] and oligopeptides[5,6] were obtained at the CCSD(T)/complete basis set (CBS) level. The CCSD(T)/CBS level was constructed[7] as a sum of the MP2/CBS stabilization (relative) energies and the CCSD(T) correction term (the difference of the CCSD(T) and MP2 interaction energies) determined by means of a small basis set (e.g., 6-31G**). The accuracy of this procedure has recently been verified in the case of the smallest DNA base pair, the uracil dimer.[8] It was shown that the stabilization energies of H-bonded and stacked structures determined at the CCSD(T)/CBS levels (with the values having been obtained by the direct extrapolation of the CCSD(T) energies calculated using the aug-cc-pVDZ and aug-cc-pVTZ basis sets) are within 0.5 kcal/mol of the original values obtained as mentioned above. A similar accuracy is expected also for relative energies of oligopeptides.

A frequently asked question concerns the determination of the structure of extended molecular clusters and oligopeptides. The task is certainly more complex, as gradient techniques need to be used when determining structure, and the use of the above-mentioned procedure is evidently impractical. In the case of molecular clusters, we recommended[9] the use of a counterpoise-corrected gradient optimization performed at the MP2/cc-pVTZ level. Using augmented basis sets yields less accurate geometries, which is mainly attributable to the MP2 interaction energy being overestimated. It is evident that the good performance of the described procedure is a consequence of some error compensation. The determination of the structures of such floppy systems as peptides is further complicated by the fact that in these cases it is not easy to eliminate the role of the intramolecular basis set superposition error.[10,11] The only straightforward

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10.1021/jp8051664 CCC: $40.75

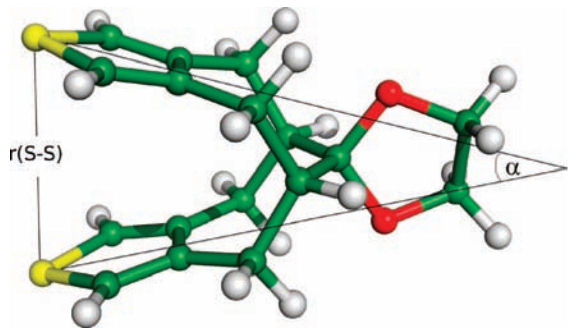

Figure 1. The structure of RESVAN optimized at the TPSS-D/TZVP level of theory (sulfurs, yellow; oxygens, red). Distance between the sulfurs *r*(S−S) is equal to 4.25 Å and angle α is equal to 27°.

TABLE 1: Sulfur−Sulfur Distances and Angles α Formed by the Two Thiophene Rings[a]

method/basis set	*r*(S−S) [Å]	α [°]
X-ray	4.29	28
B3LYP/TZVP	4.65	34
B2PLYP/def2-TZVP	4.37	29
B2PLYP-D/def2-TZVP	4.16	25
TPSS/LP	4.53	31
TPSS-D/LP	4.11	24
TPSS-D/TZVP	4.25	27
M06-2X/MIDI	3.78	19
M06-2X/TZVP	4.00	22
M06-L/TZVP	4.20	26
BH&H/TZVP	4.15	25
MP2/cc-pVDZ	3.91	21
MP2/cc-pVTZ	3.80	19
MP2/QZVP	3.87	20
SCS-MP2/def2-TZVP	4.12	24

[a] The values have been obtained by standard gradient optimization using various methods and basis sets.

way to do so is to use the theory at the CBS level, which has been confirmed by our recent studies on peptides.[12] However, a direct comparison of geometrical characteristics for these systems is lacking, because the experimental evidence is limited to IR frequencies and the structures (obtained via rotational constants) are generally not available.

In the study being presented, we have investigated the structure of a rather complicated system containing heteroatoms from the second period, namely dithienobicyclo[4.4.1]undeca-3,8-diene-11-one ethylene glycol ketal (RESVAN code, cf. Figure 1) using a wide range of wave function theory (WFT) and density functional theory (DFT) methods, which have recently been shown to be applicable for the evaluation of the accurate stabilization energies of molecular clusters. The reasons for selecting this example were several, namely that the X-ray structure of this extended system has been determined and the S−S distance and angle α have been obtained (cf. Table 1); another reason is the presence of a stacking motif of the two thiophene rings (see Figure 1). The presence of two rather polarizable sulfur atoms makes the role of dispersion energy, which strongly influences the stacking,[13] even more important.

We should mention here that the stacking motifs in peptides and other complex molecular systems make it difficult to determine the structure on the level of theory, as obtaining the correct dispersion energy (which covers the stacking) is complicated. First, the standard DFT techniques are impractical, because they do not take into account the London dispersion energy. Second, the MP2 method in conjunction with extended basis sets overestimates the dispersion energy, and reliable energies are thus obtained only when a medium basis set is used. This is, however, due to error compensation, and the method is in general impossible to rely on. There are two possible ways to reduce this overestimation: either by a more sophisticated treatment of the electron correlation problem or by using some empirical treatments within the MP2 method. The first option is represented by the use of MP3 or, preferably, the CCSD(T) method, whereas the second is based on a spin component scaled (SCS) modification of the MP2 method (termed SCS-MP2), originally introduced by one of the authors.[14] The use of the MP3 method is attractive as it is computationally considerably easier than the CCSD(T) method. As shown recently, MP3 overcomes the most serious drawback of the MP2: the overestimation of the dispersion energy. The question remaining to be answered is whether MP3 can yield results as accurate as CCSD(T) does. In our recent paper on peptides[15] we have shown that the results obtained at the MP3/CBS level are satisfactory but very CPU demanding. Both the MP3 and CCSD(T) methods should be performed with extended basis sets or, better yet, at the CBS level. The MP3 method was recently applied also to H-bonded and stacked structures of uracil dimer.[8] The error at the MP3/CBS level (i.e., the difference between CCSD(T) and MP3 interaction energies) was negligible for the H-bonded structure. In the case of the stacked structure MP3 underestimates the stabilization energy and this underestimation is of similar magnitude than the overestimation by the MP2 method. An important advantage of MP3 (and contrary to SCS-MP2) is that no empirical parameters are used. The SCS-MP2 method effectively reduces the overestimation of the MP2 for stacking, but for H-bonded complexes it yields binding energies that are too small.[14] On the other hand, the SCS(MI)-MP2 procedure by Head-Gordon et al.[16] provides stabilization and relative energies which compare well with the CCSD(T)/CBS values. The procedure parametrized the scaling factors for the parallel and antiparallel spin contributions on the basis of accurate CCSD(T) data (the S22 set).[9]

Theoretical Methods

Structures. The structure of RESVAN was determined by gradient optimization using both DFT as well as MP2 methods with different basis sets. The following DFT calculations were performed: B3LYP/TZVP,[17,18] B2PLYP/def2-TZVP,[19] B2PLYP-D/def2-TZVP,[19,20] TPSS/LP,[21,22] TPSS-D/LP,[23] TPSS-D/TZVP, BH&H/TZVP,[24] M06-2X/MIDI!,[25,26] M06-2X/TZVP, and M06-L/TZVP.[27] The extension -D stands for added London dispersion energy.[23,28] The MP2 calculations were done using the cc-pVDZ and cc-pVTZ[29,30] as well as QZVP[31] basis sets. For the SCS-MP2 geometry optimization we have used the cc-pVTZ basis set. We have used the RI approximation[32] where possible. The abbreviation LP stands for Pople's basis set 6-311++G(3df,3pd).[22]

The gradient optimization was performed only for the DFT, MP2, and SCS-MP2 methods. In cases where no analytical gradient is available (CCSD(T), MP3, and SCS(MI)-MP2), we performed a one-dimensional potential energy surface scan the S−S distance being the "reaction coordinate" while reoptimizing the rest of the molecule by the PBE1PBE functional and the 6-31G** basis set. We have generated 9 geometries with the S−S distance ranging from 3.9 to 4.7 Å with a 0.1 Å step (with the experimental value of the S−S distance being 4.29 Å).[33] See Figure 2.

The quantum mechanical optimizations provide the structure of an isolated system which strictly correspond to the gas-phase state. The experimental structure of RESVAN was determined

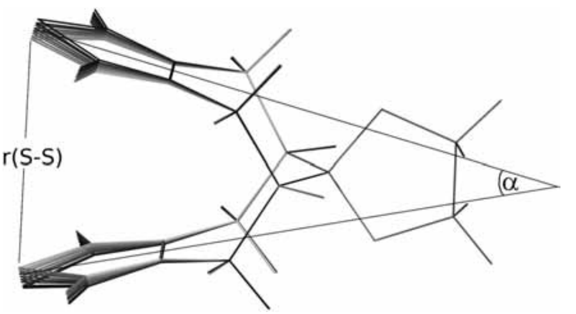

Figure 2. Structures of RESVAN differing in the S−S distance (3.9−4.7 Å with a 0.1 Å step).

in the crystal. The closest intermolecular distances were found to be 2.45 Å (H−H distance) and this might affect the internal structure of one molecule. To estimate part of crystal packing effects we performed geometry optimizations in the electric field of point charges. For the construction of the field, we used an experimental crystal structure of 27 RESVAN molecules. The central molecule was optimized in this field by keeping the position of the charges placed on the Cartesian coordinates of the rest of the molecules constant. The charges in the individual molecules were obtained using a restrained electrostatic potential (RESP) procedure,[34] employing the B3LYP functional and utilizing the cc-pVTZ basis set.

Energies. ***WFT Relative Energies.*** Here we have used the procedure originally developed for the CCSD(T)/CBS interaction energy. Instead of the interaction energy, the relative energy defined as the energy difference between the global minimum and the structure being studied was utilized.

The CCSD(T)/CBS energy is approximated as

$$E^{\mathrm{CCSD(T)}}_{\mathrm{CBS}} = E^{\mathrm{MP2}}_{\mathrm{CBS}} + (E^{\mathrm{CCSD(T)}} - E^{\mathrm{MP2}})\Big|_{\text{medium basis set}} \qquad (1)$$

where the first and second terms represent the CBS limit of the MP2 energy and the CCSD(T) correction term (the difference of the CCSD(T) and MP2 relative energies) calculated in the smaller basis set. This means the MP2 energies required for MP2/CBS extrapolation (aug-cc-pVDZ to aug-cc-pVTZ) as well as CCSD(T) and MP2 energies calculated in small basis (6-31G*) are determined for all structures on the energy scan.

The MP2 relative energy is extrapolated to the CBS limit using the two-point scheme of Helgaker et al.[35,36] Because of the different convergences of the Hartree−Fock (HF) and MP2 energies, both energies were extrapolated to their CBS limits separately on the basis of the aug-cc-pVDZ and aug-cc-pVTZ energies.[37]

The CCSD(T) correction term is determined with the small basis set (6-31G*), which can be implemented, because the [CCSD(T)-MP2] interaction energy difference of the molecular complexes is known to be less basis-set dependent than the MP2 and CCSD(T) interaction energies themselves.[38] Further details on the construction of CCSD(T)/CBS interaction energies can be found in our previous work.[39]

The MP3 calculations were done using a modified CCSD(T) code,[40] based on the Cholesky-decomposed two electron AO integrals, as implemented in the MOLCAS 7 program package.[41] Integrals decomposition threshold was set to 10^{-6}, which leads to an accuracy of better than 0.01 kcal/mol for the relative energy. The MP3/CBS relative energies were obtained in the same way as the CCSD(T) values, i.e.,

$$E^{\mathrm{MP3}}_{\mathrm{CBS}} = E^{\mathrm{MP2}}_{\mathrm{CBS}} + (E^{\mathrm{MP3}} - E^{\mathrm{MP2}})\Big|_{\text{medium basis set}} \qquad (2)$$

As a basis set for the MP3 extrapolation in eq 2, we have used beside the 6-31G* basis set the aug-cc-pVDZ one. The corresponding MP3/CBS energies are named MP3/CBS(A) in the former case and MP3/CBS(B) in the later case.

Besides the MP2 and MP3 methods, we used the original spin-component scaled second-order Møller−Plesset (SCS-MP2) method[14] with a scaling factor of 6/5 for antiparallel and 1/3 for parallel spin electron pairs. Another SCS(MI)-MP2[16] variant with reverse scaling factors, namely 6/5 for parallel and 1/3 for antiparallel spins, was also utilized. Both the SCS-MP2 calculations were accelerated with density-fitting (DF) approximation as implemented in the Molpro quantum chemistry package.

Density Functionals. The B3LYP[17] functional is a hybrid functional including a mixture of the Hartree−Fock exchange with a DFT exchange-correlation.

The B2PLYP[19] functional belongs to a new class of double-hybrid density functionals (DHDF) that add nonlocal electron correlation effects to a standard hybrid functional by second-order perturbation theory. The B2PLYP functional is based on a mixing of standard generalized gradient approximations (GGAs) for exchange by Becke (B) and for Lee, Yang, and Parr (LYP) with Hartree−Fock (HF) exchange and a perturbative second-order correlation part (PT2) that is obtained from the Kohn−Sham (GGA) orbitals and eigenvalues. This virtual orbital-dependent functional contains only two global parameters that describe the mixture of HF an GGA exchange and of the PT2 and GGA correlation, respectively.

The TPSS[21] functional is a nonempirical meta-generalized gradient approximation functional. TPSS as well as B3LYP despite being among the most popular functionals, fail to describe major parts of the London dispersion energy, which prevents them from being used in biological systems where dispersion energy plays an important role. This failure[42,43] (which is characteristic of many commonly used functionals) has recently been resolved simply by adding a classical, atom-pairwise expression for the dispersion energy (indicated by added "-D").[23,44,45] In addition to the standard functionals, we have in this study used TPSS-D and B2PLYP-D, which have recently been proven to perform reasonably well when studying noncovalent complexes[23,46] and isolated systems.[15,20,46]

The BH&H[24] functional is a hybrid functional constructed as a sum of the Lee, Yang, and Parr correlation functional and 50% of both a local density approximation and exact Hartree−Fock exchange. It has recently been shown that this potential covers some portion of the dispersion energy and thus provides rather reliable results for molecular stacking, but it has also been demonstrated to be less efficient for clusters with H-bonds.[47]

The M06-2X[26] functional from the Truhlar laboratory is one of a new generation of hybrid meta-generalized-gradient-approximation exchange-correlation functionals that were parametrized to include medium- and long-range correlation energy. Since the parametrization was done including typical van der Waals complexes, the M06-2X functional seems to provide satisfactory results also for systems where noncovalent interactions play a significant role. This has been shown by testing the performance against the S22 benchmark set.[48]

The M06-L[27] functional is a semilocal (nonhybrid) meta GGA functional from the same laboratory.

The B3LYP, TPSS, B2PLYP and SCS-MP2 calculations were carried out with the Turbomole code[49] while the M06-2X and M06-L calculations with the NWChem code[50] and the BH&H calculations with the Gaussian code/program package.[51] The CCSD(T) and part of the SCS-MP2 calculations were performed with the Molpro code[52] and the MP3 calculations with a modified CCSD(T) code, employing Cholesky-decomposed two-electron integrals,[40] in the MOLCAS 7 program package.[41]

Results and Discussion

Table 1 shows the two most important geometrical parameters obtained from the gradient optimizations namely the sulfur−sulfur distance in the two thiophene rings and the angle α between them. By comparing our results with the experimental data[33] shown in the first line of Table 1, we can estimate the performance of the individual methods. To begin with, all the standard density functionals, which are known not to cover the London dispersion energy, overestimate the S−S distance and the angle α. The worst results were obtained using the most widely used B3LYP functional, with the performance of the TPSS functional being only slightly better. The large S−S distance and angle α evidently arise from the missing dispersion energy between the two thiophene rings. When functionals covering dispersion effects are utilized, the trend is opposite. The shortest S−S distance was obtained with the M06-2X functional combined with the recommended MIDI! basis set, clearly suggesting that the dispersion effects are now overestimated mainly by intramolecular basis set superposition errors. On the other hand, the M06-L functional with the TZVP basis set performs surprisingly well (with deviations of 0.09 Å and 2°). Also the results obtained with the BH&H functional were relatively satisfactory, and those using the TPSS or B2PLYP functional augmented with the London dispersion energy were even better. The B2PLYP-D structure deviated from the X-ray structure only by 0.13 Å and 3°, respectively. Note, that due to the inclusion of some dispersion effects by perturbation theory, the results of the uncorrected B2PLYP method (4.37 Å and 29°) are already relatively close to the experimental value. To our surprise, in the case of TPSS better results were obtained with a smaller basis set (TZVP), when the closest agreement with the experimental results was found (deviations of only 0.04 Å and 1°). Using a larger basis set (LP), which in the case of molecular clusters yields close agreement with the CCSD(T)/CBS data, brought slightly worse results.

In line with expectations, MP2 overestimated the interaction between the thiophene units. Even in conjunction with a small cc-pVDZ basis set, where the effects of the dispersion energy overestimation and the small basis set were expected to compensate, rather poor results were obtained (difference of 0.38 Å and 7° from the X-ray structure). When a larger cc-pVTZ basis set was applied, the difference from X-ray data became even larger and these values were among the worst in Table 1. With larger basis sets only minor changes are observed and a value of about 3.8−3.85 Å for r(S−S) can be estimated at the CBS level from our calculations using the very large QZVP basis. However the structure of RESVAN began to change due to a repulsion of the two thiophene rings that are forced to be too close by the QZVP basis set. In Figure 3 the thiophene rings' distortion of 7° is shown. The S−S distance is in this case slightly longer 3.86 Å than we would probably expect but this is caused by the distortion. In fact the distance between the thiophene rings is shorter than this. The SCS-MP2 method gave better results (deviations of 0.17 Å and 4°) compared to MP2 but in global they are still not satisfactory.

The results obtained from the potential energy curves with the S−S distance as variable, which was implemented where the analytical gradients were either not available or their calculations would be (at present) impractical, are accumulated in Table 2. By comparing the TPSS-D/TZVP results in Tables 1 and 2 we conclude that the difference resulting from the one-dimensional scan in comparison to full gradient optimization is negligible. The MP2/CBS results are one of the worst of the techniques investigated here. This is, however, fully in accord with our expectations (cf. Introduction) and should serve as a warning to refrain from using this method. As already mentioned, the overestimation of the dispersion energy (upon increasing the basis set while using the MP2 method) is reduced by a more sophisticated treatment of correlation effects, i.e., by passing to the MP3 and CCSD(T) levels. Both MP3/CBS results are considerably improved over the MP2/CBS ones but the MP3/CBS(A) results are still far from the X-ray data. On the other hand, the MP3/CBS(B) results are in very good agreement with experiment (with deviations of 0.07 Å and 2°). The difference between the relative energy MP3 correction terms determined with small (6-31G*) and medium (aug-cc-pVDZ) basis set amount to a maximum of 0.5 kcal/mol. Since energy curves are very flat (see Figure 4) even this small difference yields rather large geometry change (S−S distance changes by 0.14 Å). It must be mentioned that the energy difference mentioned above is comparable to the corresponding CCSD(T) correction term determined previously for the uracil dimer[8] using small (6-31G*), medium (aug-cc-pVDZ) and large (aug-cc-pVTZ) basis sets. This indicates that large basis sets have to be used for the determination of the MP3 correction term to obtain reasonable structures. Contrary to our expectations, passing from the MP3/CBS to the CCSD(T)/CBS level does not improve the situation. Quite the opposite, the CCSD(T)/CBS S−S distance and angle α differed from experiment by more than 0.29 Å and 6°. At present we have no explanation for this unexpected finding. The best agreement with the X-ray data was obtained when the CCSD(T)/6-31G* level was used. It must be, however, emphasized that the excellent performance on the CCSD(T)/6-31G* level is a result of error compensation. Tentatively we

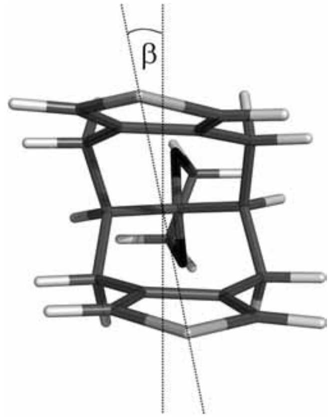

Figure 3. Front view of RESVAN molecule optimized by MP2/QZVP level of theory. The distortion angle β (equal to 7.4°) of the two sulfurs clearly depicts the strength of their repulsion at shorter distance.

TABLE 2: Sulfur−Sulfur Distances and Angles α Formed by the Two Thiophene Rings[a]

method/basis set[b]	r(S−S) [Å]	α [°]
TPSS-D/TZVP	4.27	27
MP2/CBS	3.91	21
SCS-MP2/cc-pVTZ	4.13	25
SCS(MI)-MP2/cc-pVTZ	4.06	23
MP3/aug-cc-pVDZ	4.25	27
MP3/CBS(B)	4.22	26
MP3/CBS(A)	4.08	24
CCSD(T)/ 6-31G*	4.26	27
CCSD(T)/CBS	4.00	22

[a] Both values have been calculated from the energy dependence on the S−S distance after smoothing the parabola. (See second paragraph in section named "Structures" in part "Theoretical Methods".) [b] The abbreviation CBS stands for a complete basis set.

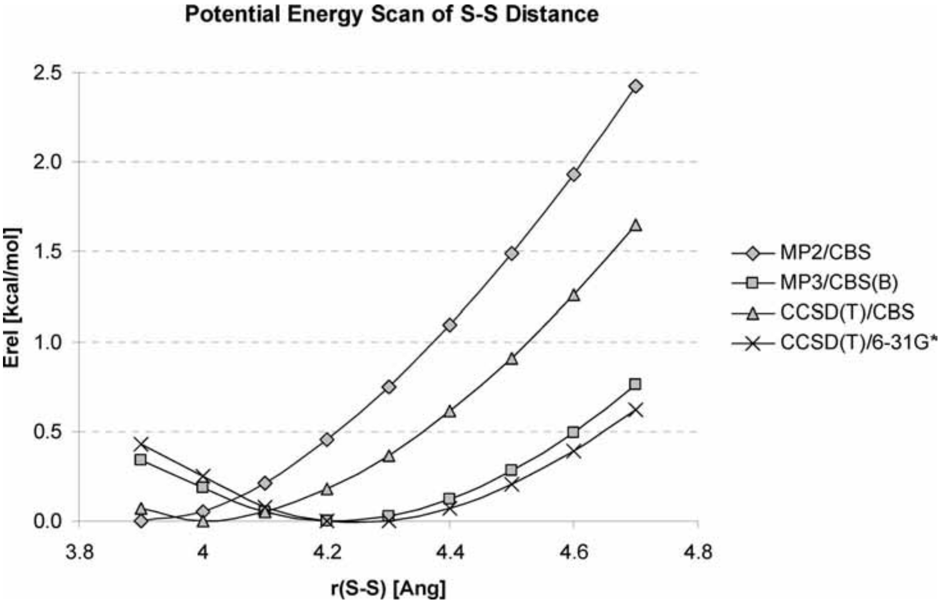

Figure 4. Graph of potential energy scans for chosen methods.

assign the problem to a insufficient basis for the determination of the ΔCCSD(T) term in a similar way as shown for the ΔMP3 term. Evidently, further studies in this direction are required.

The other possibility to reduce the overbinding effects at the MP2 level is to use the SCS-MP2 technique. This method is, unlike the MP3 and CCSD(T) methods, based on empirical parameters, which scale both the parallel and antiparallel spin contributions. In this study, we used the original SCS-MP2[14] as well as Head-Gordon et al.'s modified SCS(MI)-MP2[16] procedures. Table 2 shows that the SCS(MI)-MP2/cc-pVTZ calculations provided good estimations of the r(S−S) and α values and were rather close to the more expensive MP3/CBS(A) values. Here we should mention that in the case of molecular clusters, the SCS(MI)-MP2 procedure yielded stabilization energies which are very close to CCSD(T)/CBS values. The original SCS-MP2 procedure is known to yield reliable stabilization energies for stacked complexes whereas the values for H-bonded complexes are typically underestimated. Table 2 presents the SCS-MP2/cc-pVTZ values along with the respective values generated by the MP2 and SCS(MI)-MP2 methods (using the same basis set). Evidently, the original SCS values are better than those obtained by means of the MP2 method and also better than the SCS(MI)-MP2 values, which is slightly surprising but supports SCS-MP2 as a robust quantum chemical method for general use. When S−S distances obtained by one-dimensional scan and full gradient optimization are compared we can see just a negligible difference. This clearly shows that mainly the position of the thiophene rings is affected along the reaction coordinate and thus, RESVAN can be considered as a good intramolecular model for a thiophene dimer.[53,54]

The effect of the neighboring molecules on the structure of RESVAN was studied at the MP2/cc-pVDZ and M06-L/TZVP levels. Table 3 clearly shows that the electric field created by atoms of 26 neighboring molecules has only a small influence on the S−S distance and angle α. The distance between the two thiophene rings changes only slightly (0.05 Å) toward a larger value. Applying such a correction would bring the results of all methods that slightly underestimate the S−S distance (e.g., B2PLYP-D, TPSS-D, and SCS-MP2) in closer agreement with the experimental value. However, intermolecular dispersion effects in the crystal may also have an impact on the results (possibly in the other direction) which seems to be an interesting topic for future studies on this system.

TABLE 3: Sulfur−Sulfur Distances and Angles α Formed by the Two Thiophene Rings Obtained in Vacuo and in a Field of Point Charges by Full Gradient Optimization, Providing Information on the Effect of Neighboring Molecules in the Crystal

	vacuum		field of point charges[a]	
method/basis set	r(S−S) [Å]	α [°]	r(S−S) [Å]	α [°]
MP2/cc-pVDZ	3.91	21	3.96	22
M06-L/TZVP	4.20	26	4.25	27

[a] The field of charges was constructed from a crystal structure of 26 RESVAN molecules. A crystal cell contains 4 molecules.

Conclusions

The determination of the structure of the system investigated (RESVAN) is difficult. The best agreement with the experimental data among all WFT methods was surprisingly obtained at the MP3/aug-cc-pVDZ and MP3/CBS(B) levels. This good performance is clearly due to the use of large basis set as well as an accurate and balanced covering of electron correlation effects. The very good results obtained by CCSD(T)/6-31G* method are clearly a consequence of fortunate error compensation. The method theoretically considered to be most accurate (CCSD(T)/CBS) provides an S−S distance and an angle α which differ considerably from the experimental values. This may be explained by the fact that the CCSD(T) correction term determined with a small basis set (6-31G*) is not accurate enough. A larger basis set should thus be used similarly as we did in the MP3/CBS(B) calculation. However, such calculations are extremely CPU time demanding and are impractical at present.

MP2 calculations even with a small basis set overestimate the attraction between thiophene rings, and one amongs the worst agreement with the experimental data was found for the MP2/CBS method. When MP2 method was combined with QZVP basis set the structure of RESVAN molecule changed substantialy (the thiophenes distorted from the plane of molecule due to nuclear repulsion of sulfur atoms). The SCS(MI)-MP2 and SCS-MP2 methods exhibit improvement over the MP2 procedure.

All the standard density functionals fail to predict reasonable S−S distances. The lack of London dispersion energy results in a much too large distance between the thiophene rings. Much better agreement with experiment was achieved if advanced DFT methods that include dispersion effects were used. The best results were obtained with the TPSS-D/TZVP, M06-L/TZVP, and B2PLYP-D/def2-TZVP methods. When a larger basis (LP in the case of TPSS functional) or more advanced versions of a functional (e.g., M06-2X) was used, the agreement with experiment deteriorated, which evidently arises from the fact that the correct description of this molecule is rather sensitive to details of the theoretical treatment.

With the aim of comparing the calculated (isolated) and crystal structures, an optimization in the field of the 26 neighboring RESVAN molecules was performed. It was shown that the field exhibited only minor change in its relevant structural parameters.

Acknowledgment. This work is part of the research project No. Z4 055 0 506. It was supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant No. LC 512 and MSM 6198958216) and the Grant Agency of the Academy of Science of the Czech Republic (Grant No. A 400 550 510). P.H. acknowledges the support from Praemium Academiae of the Academy of Sciences of the Czech Republic, awarded to him in 2007.

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JP8051664