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Assessment of Recently Developed Multicoefficient Strategies for the Treatment of π-Conjugated Molecules

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Newly developed hybrid functionals (MPW1k and BB1k) have been systematically applied for the description of conjugation effects in organic molecules. These functionals are also used as part of the recently developed general-purpose multicoefficient methods MC3MPW and MC3BB. The performance of the various approaches is compared not only for relative energies but also through the calculation of torsion energy profiles for critical comparison with available reference data; thus, a numerical criterion depending on local behavior could be correspondingly defined. The results show that MC3-based methods are very accurate when faced to other approaches having comparable computational cost; thus, paving the way toward new applications and achievements in the field of conjugated materials.

1. Introduction

The search for improved approximations to make density functional theory (DFT)[1−4] an even more accurate and generally applicable computational tool is still a topic of ongoing research. Most exchange-correlation functionals currently in use are known to exhibit a number of limitations for chemically important systems. Thus, the development and systematic assessment of new functionals, or computational strategies based on them, still deserves considerable efforts. Among the previously detected weaknesses, the treatment of conjugation effects in organic molecules[5−7] is well-documented. The thorough understanding of the chemistry of π-conjugation has become a fundamental step toward the rationalization of more applied phenomena. For instance, the field of organic electronics would definitively benefit from new cost-effective but accurate computational protocols.

The first-generation of generalized gradient approximation (GGA) functionals has shown to behave erratically when dealing with torsion energy profiles in π-conjugated systems;[8,9] this also includes the widely applied Becke[10] Lee−Yang−Parr[11] functional either in its pure form (BLYP) or in its hybrid three-parameter B3LYP[12] version. A second-generation of functionals was subsequently developed, with the aim of covering a larger number of properties. These were elaborated within one of the several theoretical frameworks now firmly established for improving such expressions: (i) intense (re)parametrization of GGA functionals on the basis of a relatively large number of reference data [HCTH (Hamprecht-Cohen-Tozer-Handy[13−15]), or those derived from Becke's B97 functional form[16−18]]; (ii) refinement of the GGA expression by careful reformulation of the model [PBE (Perdew-Burke-Ernzerhof[19]), or OPTX/OPTC (OPTimized eXchange/Correlation[20−22])]; and (iii) inclusion of new variables, explicitly dependent on Kohn−Sham orbitals, that go beyond the density $\rho(\mathbf{r})$ and its gradient $\nabla\rho(\mathbf{r})$, in the mathematical form of the so-called meta-GGA functionals [B95 (Becke[23]), PKZB (Perdew-Kurth-Zupan-Blaha[24]), VSXC (Van Voorhis-Scuseria[25]), or TPSS (Tao-Perdew-Staroverov-Scuseria[26])]. Furthermore, since a larger weight was previously put on thermochemistry, the development of exchange-correlation functionals for thermochemical kinetics constitutes another avenue currently being pursued.[27−29] The first successful attempt (MPW1k[27]) has been enhanced recently by the development of the BB1k[28] and the BMK[29] models.

Although the application of most of these GGA and meta-GGA functionals to the torsion energy profiles of π-conjugated systems has been recently accomplished,[30−32] the results are not completely free of ambiguity. Even the most modern exchange density functionals over-stabilize the strength of π-conjugation; thus, aromatic structures are systematically more favored, which translates into an overestimation of the torsional barriers between the planar and highly twisted forms. Consequently, hybrid versions that include a portion of Hartree−Fock (HF) exchange are still needed to reduce the over-stabilitazation but at the price of being less cost-effective than the nonhybrid variants. The combination of the OPTX exchange with the B95 correlation functional currently seems to be one of the most accurate models for predictive applications to π-conjugated molecules.[32] This brings us to the subject of this work; that is, to evaluate if even more accurate results can be achieved by recently developed multicoefficient methods. This issue has been addressed through a critical comparison of torsion energy profiles in model π-conjugated systems (1,3-butadiene, styrene, biphenyl, bithiophene) and a computational study of the energy barriers between three stable [10]annulene conformations. In all cases, benchmark coupled-cluster (CC) results will be used as reference. These multicoefficient methods, which include the MPW1k and the BB1k functionals in their formulation, are briefly presented next.

2. Computational Details

The multicoefficient three-parameter MC3BB and MC3MPW methods were recently derived by Truhlar et al.[33] by allowing a customized mixing of wave function based methods with hybrid density functionals. The MC3BB method was defined as

$$E_{\mathrm{MC3BB}} = c_2[E_{\mathrm{HF/DIDZ}} + c_1(E_{\mathrm{MP2/DIDZ}} - E_{\mathrm{HF/DIDZ}})] + (1 - c_2)E_{\mathrm{BBX/MG3S}} \quad (1)$$

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TABLE 1: Relative Energies (in kcal/mol) of Various Conformations of 1,3-Butadiene with Respect to the Global *s*-trans Minimum

method	s-cis	gauche[a]	TS[a]	SE[b]
HF/DIDZ	3.96	3.09 (39.7°)	5.94 (101.7°)	0.15
MP2/DIDZ	3.72	2.51 (40.1°)	5.56 (100.8°)	0.31
MPW1k/MG3	4.06	3.38 (36.1°)	6.81 (101.5°)	0.34
BB1k/MG3	3.92	3.27 (35.0°)	6.82 (101.4°)	0.32
MC3MPW	3.94	3.12 (37.2°)	6.48 (101.1°)	0.18
MC3BB	3.86	3.10 (36.1°)	6.56 (101.1°)	0.19
CC reference[c]	3.46	2.88 (35.0°)	6.09 (101.0°)	
exp.[d]	4.0	2.9 (43.2°)	6.0 (102.8°)	

[a] The corresponding angle (in degrees) is reported between parentheses. [b] Surface error, see text for details. [c] Taken from ref 40. [d] Taken from ref 42.

where MP2 is the Möller−Plesset perturbed energy at second order and BBX is the same as the BB1k functional but with a newly determined method-dependent percentage of HF exchange. An equivalent definition exists for the MC3MPW scheme. The DIDZ and MG3 basis sets[34,35] are used for the ab initio (HF, MP2) and DFT terms, respectively. These basis sets correspond, in standard notation, to the 6-31+G(d,p) and 6-311++G(2df,2p) and were obtained from the Extensible Computational Chemistry Environment Basis Set Database.[36] Note that it has been preferred to use here the complete MG3 basis set instead of the originally proposed MG3S; this is not, however, expected to significantly influence the conclusions. The parameters were determined by optimizing the set of values (c_1, c_2, and percentage of HF exchange in the BBX term) against thermochemistry (atomization energies) and thermochemical kinetic (reaction barrier heights) data; thus, application of the methods outside of the training set is highly recommended to assess their performance as reliable general-purpose methods.

For the calculation of torsion potentials, the geometric structure of each conformer was fully optimized for each fixed value of the dihedral angle; thus, dealing with $3N - 7$ degrees of freedom. The torsion angle ϕ between the two moieties being rotated (i.e., the double bonds in butadiene, the double bond and the phenyl ring in styrene, and the phenyl or thiophene rings in biphenyl or bithiophene, respectively) was varied in a stepwise fashion between 0° and 180° in steps of 10°. Solid-state packing effects and zero-point energy corrections associated with the vibrations are neglected; the latter typically modify the torsional barriers by up to 1 kJ/mol in conjugated systems.[9,37] The different conformations of [10]annulene were fully optimized, and their relative energies were estimated. All calculations have been performed with the Gaussian98[38] and Gaussian 03[39] packages in the gas phase.

3. Results and Discussion

3.1. 1,3-Butadiene. Table 1 summarizes the relative energies, with respect to the global *s*-trans minimum, of the *s*-cis conformation, the gauche local minimum, and the transition state (TS). Analysis of the values allows us to deduce the following: (i) all of the methods, in agreement with previous studies,[8,40,41] provided reasonably accurate results for the energy barriers between the *s*-cis and *s*-trans conformers; (ii) the DFT methods MPW1k and BB1k, however, produced the largest overestimation of barrier height between the gauche and the global minimum by about 0.4−0.5 kcal/mol compared to experimental values; (iii) the DFT methods also provided much less accurate values for the energy barriers needed to reach the highly twisted TS; (iv) although exchange and correlation effects are required to qualitatively describe partial π-bond breaking, it appears that the results are quite independent of the exchange-correlation functional used; and (v) the ab initio results under-estimate the experimental barrier heights. All of these factors suggest multicoefficient procedures as a possible source of improvement; the combination of ab initio correlated methods with reoptimized exchange density functionals might thus lead to better results. This view is supported by the values reported in Table 1. It is clear that use of the MC3MPW and MC3BB methods largely decrease the errors with respect to the corresponding MPW1k and BB1k functionals. The corresponding torsional potentials are displayed in Figure 1 all of them having very similar shapes. The DFT-based results have the largest deviation from the CC reference or the experimental curve[42] in the region where the π-conjugation is severely reduced.

In view of the promising results obtained above by using the multicoefficient methods, a more detailed analysis of the local behavior along the whole rotational profile it has been performed. This required a so-called "surface error" (SE) to be defined in a statistical manner by the following expression:

$$\sqrt{\int_{0°}^{180°} \epsilon^2(\phi)\, \mathrm{d}\phi} \tag{2}$$

where $\epsilon(\phi)$ is the difference between the relative energy of the assessed method and the reference value, as a function of the torsion angle ϕ. The SE is further normalized by the number of scanned torsion angles; thus, the resulting quantity can be viewed as an average of the root-mean-squared error over the entire torsion potential curve. The results are graphically presented in Figure 2; which fully correspond to the trends found upon inspection of Table 1. The MC3MPW and MC3BB methods roughly halves the errors in the 30°−150° region by partly compensating for the well-known overestimation of the π-conjugation caused by the density functionals.

3.2. Styrene. In the following section, we focus on the performance of the methods for the prediction of relative energies of styrene conformers, with the corresponding results being collected in Table 2. The DFT methods MPW1k and BB1k wrongly predict a planar conformation as the global minimum, with the energy barrier (ΔE) between the transition state of styrene (located at 90°) being overestimated by around 0.8−1.0 kcal/mol. The introduction of multicoefficient schemes yields a greatly improved estimation of the barrier height. Moreover, this includes the prediction of a nonplanar global minimum; thus, the correct curvature of the torsional potential is fully recovered. The rotational curves are also included in Figure 1, whereas the above-defined error measurement is presented in Figure 2. By comparing the results obtained at the MPW1k (BB1k) and MC3MPW (MC3BB) levels for the barrier heights and for the surface error, we are led to the conclusion that an improved performance for the DFT methods when dealing with π-conjugated systems is being achieved.

3.3. Biphenyl. Biphenyl constitutes another well-known prototype of conjugated systems. A number of recent DFT studies[43−45] provided better agreement with experimental results than the much more costly ab initio methods.[46−48] It is now well established that the barriers separating the global minimum from the planar ($\phi = 0°$) and perpendicular ($\phi = 90°$) conformations are almost similar. This is also observed from the results of our calculations based on the MPW1k and BB1k functionals, which are summarized in Table 3. We would like also to stress that the overall shape of the curve obtained with DFT methods, see Figure 1, is quite similar to that derived from CC theory.[49] These abilities are also shared by the multicoefficient methods, and consequently, their errors presented in

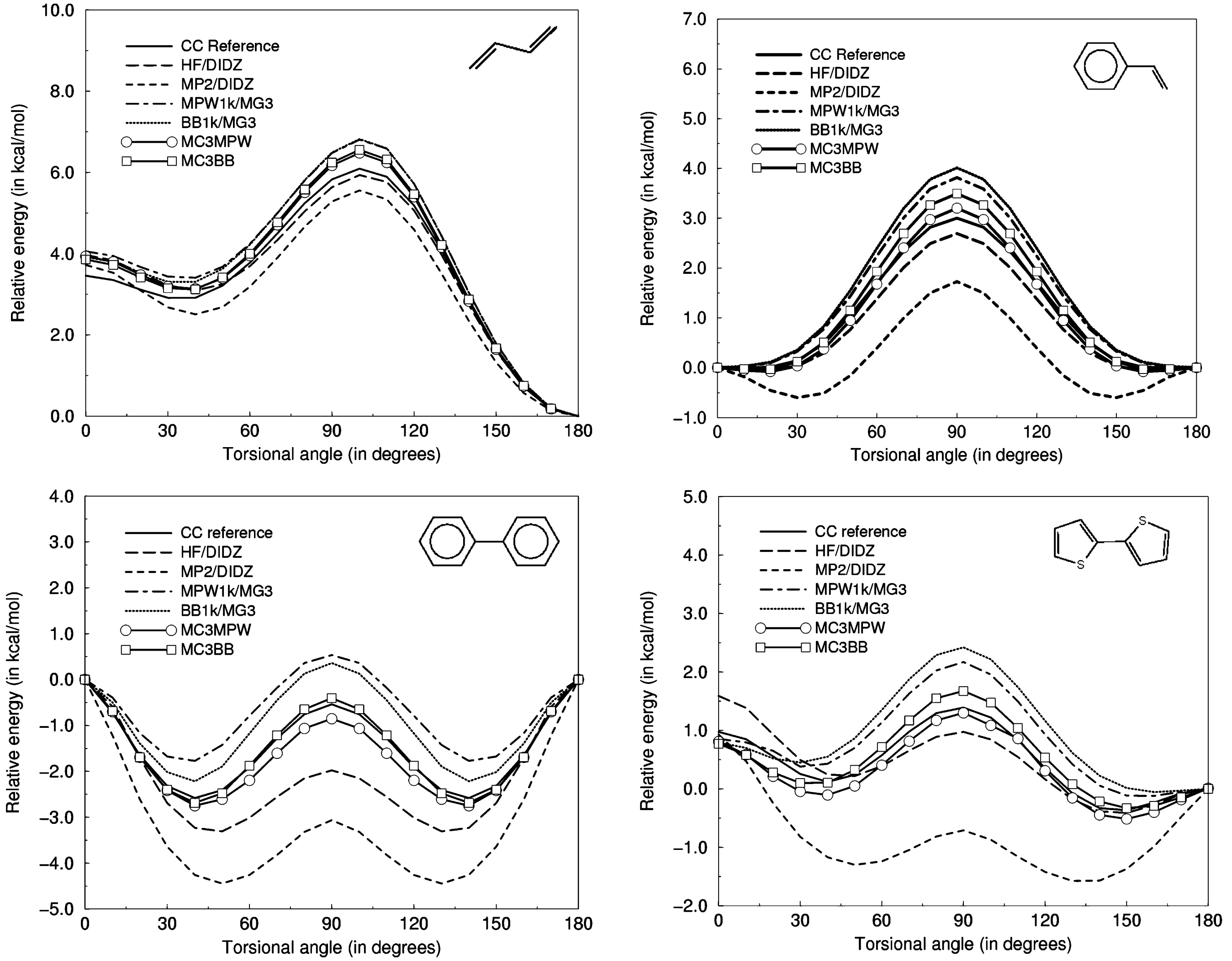

Figure 1. Torsion potential of conjugated systems, as calculated by different approaches.

Figure 2 are almost negligible, especially compared to previously reported results. The dihedral angles are also in excellent agreement with the reference value.

3.4. Bithiophene. The torsion potential of bithiophene has been the object of numerous DFT studies,[50−53] partly due to the lack of satisfactory agreement between ab initio and DFT results as well as the strong basis set dependence of the ab initio results. The performance of the multicoefficient methods can again be judged from the results of Table 4, where the relative energies of various conformers are listed, and from the curves depicted in Figure 1. The main problem associated with the hybrid MPW1k and BB1k functionals, the overestimation of the TS-syn-anti barrier height, is largely reduced by the MC3-based methods. Inspection of the locally calculated errors from the correponding curves shown in Figure 2 reinforces once more the whole analysis. At the current stage, it was concluded that the MC3-based methods are among the most accurate computational tools in describing the physics of π-conjugation, as already deduced from the previous sections.

3.5. [10]Annulene. In this final section, the conformational surface of [10]annulene has been explored. This constitutes today one of the most intriguing tests for a quantum-chemical method;[54] thus, the inclusion here should be considered as an attempt to discuss potentially difficult cases. The structures for the "twist", "naphthalene-like", and "heart" conformations are illustrated in Figure 3. Most of the previous attempts (including semiempirical, HF, MP2, and B3LYP-based DFT methods) have been reviewed in ref 55. In general, all of the approximations were deemed to be clearly inadequate for the [10]annulene problem with erratic behavior found; only the CCSD(T) method was able to provide accurate structures and relative energies.

The portion of HF exchange in the formulation of the MPW1k (43%) and BB1k (42%) functionals is larger than in other previously used DFT hybrid methods; this, may thus lead to greater success since the understabilization of the "twist" form is expected to be reduced. A summary of the results is provided in Table 5. The lowest-energy conformer is predicted to be the twist form only by the HF method, whereas the MP2, DFT, and MC3-based methods predict the heart conformation to be energetically favorable. Note that, even when this severe divergence is considered, the BB1k results are much more realistic than the former B3LYP values.[55] Unfortunately, the MC3-based results still differ from the reference values. Possible solutions to this apparent questionable behavior are (i) as DFT rapidly saturates with basis set,[56−60] one possible enhancement to obtain more reliable energies might be the use of larger basis functions for the MP2 component of the multicoefficient methods; and (ii) as the energetics of these conformers can be finely tuned[54] using exact exchange as an adjustable parameter, reliable results are only expected with larger percentages of HF exchange. Thus, this system may be considered as a delicate test case.

MC3-based methods are expected to perform definitively better than hybrid DFT (B3LYP is often used as reference)

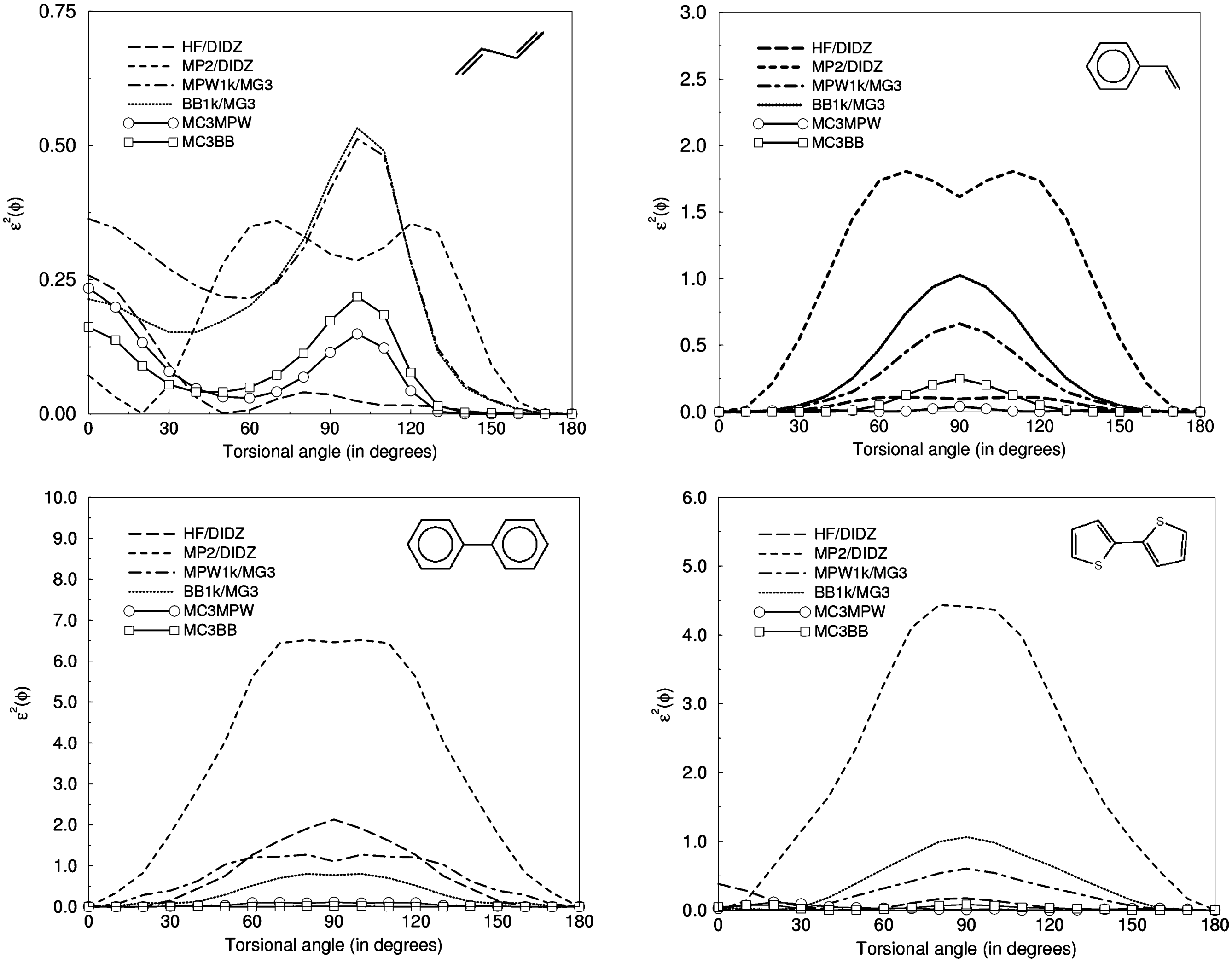

Figure 2. Local calculated errors for the torsion potential of conjugated systems.

TABLE 2: Relative Energies (in kcal/mol) of the Planar (ΔE^0) and Perpendicular (ΔE^{90}) Conformations of Styrene, as Compared to the Global Twisted Minimum, Whose Corresponding Angle (in degrees) Is Also Reported

method	ΔE^0	ΔE^{90}	$\phi_{\min}$	SE [a]
HF/DIDZ	−0.05	2.69	19.0°	0.17
MP2/DIDZ	−0.60	1.73	31.6°	0.72
MPW1k/MG3		3.82		0.33
BB1k/MG3		4.01		0.41
MC3MPW	−0.08	3.20	16.2°	0.07
MC3BB	−0.04	3.50	15.8°	0.17
CC reference [b]	−0.01	3.01	13.0°	

[a] Surface error, see text for details. [b] Taken from ref 9.

TABLE 3: Relative Energies (in kcal/mol) of the Planar (ΔE^0) and Perpendicular (ΔE^{90}) Conformations of Biphenyl, as Compared to the Global Twisted Minimum, Whose Corresponding Angle (in degrees) Is Also Reported

method	ΔE^0	ΔE^{90}	$\phi_{\min}$	SE [a]
HF/DIDZ	3.33	1.35	46.6°	0.63
MP2/DIDZ	4.45	1.39	49.5°	1.32
MPW1k/MG3	1.79	2.32	37.2°	0.61
BB1k/MG3	2.21	2.58	39.0°	0.41
MC3MPW	2.76	1.90	41.6°	0.15
MC3BB	2.69	2.29	40.9°	0.06
CC reference [b]	2.58	2.04	40.9°	

[a] Surface error, see text for details. [b] Taken from ref 49.

mostly in those cases where too little percentage of exact exchange is provided by the most common hybrid exchange functionals (typically around 20−25%). This feature is certainly true when dealing with torsion potentials of conjugated molecules. However, the accurate energetics of the conformers of [10]annulene is an example where fair agreement with CCSD(T) results would need at least 50% of exact HF exchange; which can be viewed as a pathological case since other properties as molecular geometries then progressively deteriorate.[54,61]

Following on from our analysis in previous sections, we briefly suggest an additional set of systems that might enlarge the calibration/benchmark database for these and others multicoefficient methods; their inclusion in the training set is expected to improve the performance for π-conjugated systems: (i) scan of the torsion energy profiles of heterobutadienes,[36,62] and other conjugated backbones with heteroatoms;[31] (ii) calculation of the relative energies of C_3H and C_3H_2 isomers;[63,64] (iii) reproduction of the reorganization energies in oligoacenes[65,66] and related systems;[67] and (iv) estimation of the energy differences between cumulenes and poly-ynes.[68] The existence in all cases of highly accurate results would allow critical comparison to be performed.

4. Concluding Remarks

With the increased computational resources of the last several years, DFT has emerged as one of the most used computational

TABLE 4: Relative Energies (in kcal/mol) of Various Conformatios of Bithiophene with Respect to the Antiplanar Conformation

method	TS-syn-planar[a]	syn-gauche[a]	TS-syn-anti[a]	anti-gauche[a]	SE[b]
HF/DIDZ	1.59 (0°)	0.20 (45.9°)	0.98 (89.1°)	−0.42 (146.4°)	0.20
MP2/DIDZ	0.93 (0°)	−1.30 (51.6°)	−0.71 (89.1°)	−1.59 (134.9°)	1.04
MPW1k/MG3	0.85 (0°)	0.36 (33.2°)	2.17 (89.1°)	−0.13 (155.2°)	0.33
BB1k/MG3	0.80 (0°)	0.45 (29.6°)	2.42 (88.8°)	−0.05 (161.0°)	0.46
MC3MPW	0.81 (0°)	−0.11 (37.8°)	1.31 (88.4°)	−0.52 (148.2°)	0.12
MC3BB	0.77 (0°)	0.08 (34.8°)	1.68 (88.9°)	−0.33 (152.0°)	0.13
CC reference[c]	0.98 (0°)	0.12 (40.4°)	1.39 (88.7°)	−0.37 (146.6°)	

[a] The corresponding angle (in degrees) is reported between parentheses. [b] Surface error, see text for details. [c] Taken from ref 52.

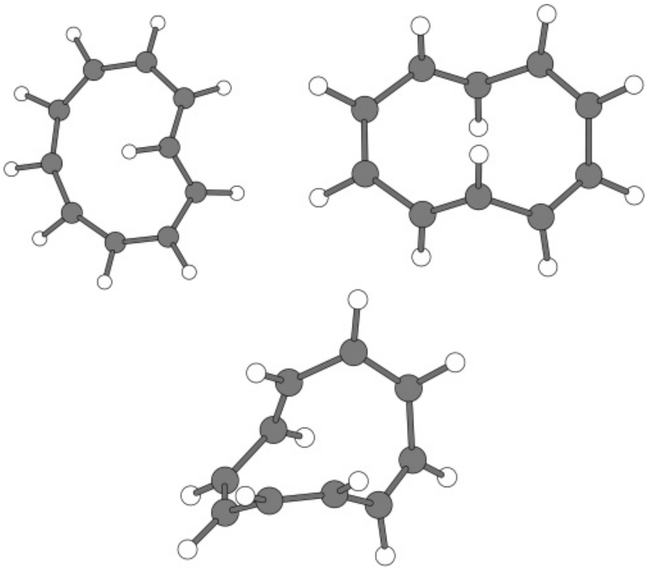

Figure 3. Optimized structures of "heart" (top, left), "naphthalene-like" (top, right), and "twist" (bottom) conformations of [10]annulene.

TABLE 5: Relative Energies (in kcal/mol) of Various Conformations of [10]Annulene

method	C_s heart	C_2 naphthalene	C_2 twist
HF/DIDZ	12.37	3.24	0.0
MP2/DIDZ	−2.66	1.02	0.0
BB1K/MG3	−2.04	0.21	0.0
MPW1K/MG3	−9.86	−5.16	0.0
MC3BB	−1.57	2.13	0.0
MC3MPW	−9.31	−3.72	0.0
CC reference[a]	4.24	1.40	0.0

[a] Taken from ref 55.

procedures for the fields of Chemistry and Materials Science. We believe that the field of organic electronics, where cost-effective methods need to be accurately applied to π-conjugated materials[69] in order to design new materials with optimized properties, is expected to be one suitable candidate for further applications. As a result, increasing time and effort is being devoted to the accurate calculation of torsion energy profiles; which are essential models for the evaluation of any method able to describe the physics of π-conjugation. The extension to prototypical π-conjugated materials of recently developed doubly hybrid density functionals has demonstrated that these methods might soon become an appealing tool for electronic structure calculations. The extent to which these new methods will impact the community depends on their applications outside of the training set; thus, the systematic assessment of the multicoefficient methods motivated the present paper.

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under contract DE-AC06−76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

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