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The torsional potential in 2,2'-bipyrrole revisited: High-level ab initio and DFT results

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Abstract

A systematic study of torsional potentials for inter-ring rotation in 2,2'-bipyrrole is accomplished. Highly accurate calculations were performed at the second-order Møller–Plesset theory (MP2) and at the very demanding coupled-cluster with single, double, and perturbatively estimated triple excitations CCSD(T) level, together with the hierarchy of (aug)-cc-pVnZ basis sets. These large-scale state-of-the-art calculations ensure virtual convergence in both N- and one-particle space. The reliability of density-functional theory (DFT) is thoroughly assessed along the whole rotational profile by root-mean-squared energy differences with respect to benchmark values. The best agreement is obtained for large fractions of Hartree–Fock (HF) exchange introduced into the functionals.

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1. Introduction

Polypyrrole is currently included among the most studied π -conjugated polymers; a broad set of applications for the emerging but rapidly growing fields of nanoelectronics and information technology is thus envisioned [1–4]. The thorough understanding of the chemistry of π -conjugation, at both molecular and supra-molecular orders, is readily placed at the origin of this promising field. Since many chemical phenomena involved in the operation mechanism of optoelectronic devices may be usually rationalised from the theoretical study of finite-size π -conjugated systems [5], when experimental information is scarce and difficult to obtain, pyrrole oligomers are a very attractive source of information [6,7] while computational modelling becomes a very valuable tool. Therefore, an accurate

knowledge of the evolution of the electronic properties of these oligomers as a function of torsional angle between adjacent rings is still a topic of ongoing research. For instance, torsions on going from planar to perpendicular conformations drive their possible thermochromic and/or solvatochromic behaviours. Fluorescence quantum yields, the occurrence of inter-system crossing processes, or variations of electrophilicity may be also affected by deviations from planarity. Additionally, torsions between monomer units is expected to largely influence the vibronic progressions in the absorption and emission spectra recorded for 2,2'-bipyrrole [8]. The inter-ring torsion plays also a key role in the conductance mechanism of a molecular wire created by contacting a 2,2'-bipyrrole molecule to bulk electrodes [9]. A reliable description of torsional energy profiles is thus required to rationalise many properties of pyrrole-based materials. These features have motivated the investigation performed here. Although several preliminary studies are found in the literature [10–14] the question still remains open since torsional properties are largely

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dependent on the theoretical method chosen. This elusive character clearly deserves systematic application of *ab initio* methods in order to firmly establish a set of benchmark results to be further exploited; cost-effective and widely used density-functional methods are then carefully applied in a second step. Since some weaknesses of this theory have been recently detected for closely related systems [15,16], the present study will also analyse the way these functionals describe, not only the torsional barrier heights, but also the entire torsional curve of 2,2'-bipyrrrole.

2. Computational methodology

All calculations have been performed with the GAUSSIAN 03 suite of programs [17] in the gas-phase. Full optimisation of the geometric structure of all conformers was done at MP2 and DFT levels for each fixed value of the torsional angle ϕ . A regular grid of 10° was imposed for ϕ in the region from 0° to 180° . CCSD(T) single-point corrections were subsequently performed at the respective MP2 optimised geometries. The correlation consistent (aug)-cc-pVnZ basis sets [18] were applied due to its large coverage of the one-particle space while keeping a good asymptotic behaviour. The best-estimated benchmark value was thus obtained by adding the correction [19,20]

$$\begin{aligned} \Delta\text{CCSD(T)} \\ = \text{CCSD(T)}/\text{aug-cc-pVDZ} // \text{MP2}/\text{aug-cc-pVDZ} \\ - \text{MP2}/\text{aug-cc-pVDZ} \end{aligned} \quad (1)$$

to the MP2/cc-pVQZ//MP2/cc-pVTZ calculated energy. The parallel convergence found at higher levels of perturbation theory, $\Delta\text{MP4(SDQ)}/\text{cc-pVTZ}$ was extremely close to $\Delta\text{MP4(SDQ)}/\text{aug-cc-pVDZ}$, justifies the use of this correction; thus, the possible impact of further basis sets extension is not expected to significantly influence the conclusions.

The expression we adopt to define the exchange-correlation functional in a general fashion is

$$E_{xc}[\rho] = a_x E_x^{\text{HF}} + (1 - a_x) E_x[\rho] + E_c[\rho], \quad (2)$$

where E_x^{HF} is the exact HF energy and $E_i[\rho]$ is one of the most employed exchange ($i = x$) or correlation ($i = c$) functionals. The coefficient a_x has been introduced to probe in a systematic way the influence of the exact exchange; the main interest in this term arises by the fact that this contribution primarily governs the torsional energy profiles of π -conjugated systems. We have selected, as exchange functional, the well-known B [21], PBE [22], or OPTX [23] expressions; note that the latter is a recently developed functional which is claimed to be close to the accuracy limit that can be achieved by a gradient-corrected functional. On the other hand, these

functionals are coupled respectively to the LYP [24], PBE [22], or B95 [25] correlation counter-parts. The hybrid versions resulting from Eq. (2) are named in our notation B1LYP, PBE0, or O1B95 ($a_x = 0.25$) [26,27] and BHHLYP, PBEHH, or OHB95 ($a_x = 0.5$) [28] by analogy with standard procedures. PW91- [29] or B3LYP-based [30] results are also included since these functionals are often used as reference. Sufficiently converged DFT results were obtained at the cc-pVTZ level in close agreement with many previous studies.

Multicoefficient (MC) protocols constitute, on the other hand, a new suite of computational tools; more specifically, DFT schemes have been recently combined with HF and MP2 methods in a three-parameter (MC3) version [31]

$$\begin{aligned} E_{\text{MC3F}} = c_2 [E_{\text{HF/DIDZ}} + c_1 (E_{\text{MP2/DIDZ}} - E_{\text{HF/DIDZ}})] \\ + (1 - c_2) E_{\text{F}[\rho]/\text{MG3S}}, \end{aligned} \quad (3)$$

where $F[\rho]$ is a modified version of either the BB1k [32] (MC3BBX) or the MPW1k [33] (MC3MPWX) exchange-correlation functional. We note that the portion of HF exchange in the formulation of the BBX (39%) or MPWX (38%) functionals is slightly lower than for the BB1k (42%) or MPW1k (42.8%) case. The set of parameters entering into Eq. (3) are easily extracted from the original reference. The DIDZ and MG3S 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 Database¹. These methods have recently provided remarkable accuracy when dealing with torsional energy profiles of other π -conjugated molecules [34]; thus, the inclusion here can be considered as an attempt to further confirm their reliability as a general-purpose method.

3. Results and discussion

3.1. Benchmark *ab initio* calculations

One open question in view of the scarcity of the existing data is to determine if large-scale *ab initio* calculations may substantially change the barrier heights with respect to previously published results [10–14]. We have thus collected in Table 1 the MP2 barriers calculated

¹ Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the US Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information.

Table 1

Energetics (kcal/mol) of stationary points in 2,2'-bipyrrole relative to the *anti*-planar conformation, as calculated at the MP2 level with different basis sets

Method	<i>anti</i> -gauche	TS- <i>syn</i> - <i>anti</i>	<i>syn</i> -gauche	<i>syn</i>
MP2/cc-pVDZ	−1.00 (142.4°)	0.78 (75.2°)	0.63 (50.5°)	3.15 (0°)
MP2/aug-cc-pVDZ	−0.76 (143.2°)	0.85 (78.7°)	0.72 (44.4°)	2.91 (0°)
MP2/cc-pVTZ	−0.72 (146.8°)	1.35 (79.2°)	0.95 (44.8°)	3.02 (0°)
MP2/aug-cc-pVTZ ^a	−0.53 (147.8°)	1.53 (80.1°)	1.14 (46.0°)	2.92 (0°)
MP2/cc-pVQZ ^a	−0.62 (147.8°)	1.48 (80.1°)	1.06 (45.5°)	2.94 (0°)
MP2/cc-pVQZ ^a + ΔCCSD(T)	−0.43 (153.9°)	1.70 (82.1°)	1.07 (41.5°)	2.86 (0°)

The corresponding angle (in degrees) is reported between parentheses.

^a At the corresponding MP2/cc-pVTZ optimised geometry.

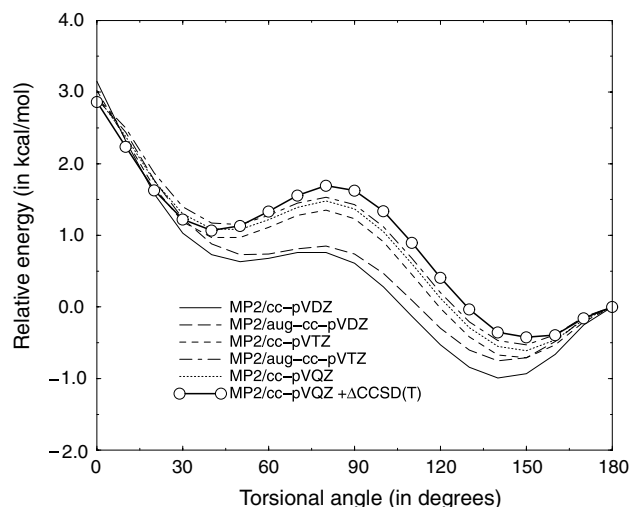


Fig. 1. Torsional potential of 2,2'-bipyrrole, as calculated at the MP2 level with different basis sets.

with the set of (aug)-cc-pVnZ basis functions; the corresponding torsional curves being shown in Fig. 1. As it is easily seen, we have exploited the systematic convergence of these basis sets to show how the results are highly influenced by their size. The MP2 results can be considered as converged at the stage of the cc-pVQZ level; however, treatments of the electron correlation beyond MP2 also deserve to be further explored. To do so, approximate CCSD(T) results were constructed by adding the energy difference between CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ and MP2/aug-cc-pVDZ to the MP2 energies obtained with the largest basis. The impact on the torsional curves, see Fig. 1, clearly indicates that augmenting the basis sets up to the large cc-pVQZ was in fact crucial to obtain the highest accurate results presented here; which could not be afforded by previous computational studies. While the energy difference between the *syn* or *syn*-gauche conformers with respect to the global minimum was changed by less than 0.1 kcal/mol, the curves deviate the most around the 90° region; which, however, can be considered as a marginal deviation compared with the energy differences between the MP2/(aug)-cc-pVDZ curves and those

calculated with larger basis sets. Since experimental information is not available, our best results, named MP2/cc-pVQZ+ΔCCSD(T), will be used next as a solid and trustworthy reference for systematic assessment of DFT theory.

3.2. Density-functional theory accuracy

We focus in the following section on the performance of DFT methods for the prediction of relative energies; the corresponding results being thus compiled in Table 2. The respective torsional potentials are displayed in Fig. 2 for the largest DFT-used basis sets, all of them having very similar shapes. Independently of the basis sets employed, analysis of the results allows us to deduce that: (i) all the DFT methods are able to provide rather accurate results for the *antisyn* energy separation; (ii) the curves progressively deteriorate in the 30°–150° region which translates into a larger overestimation of barrier heights between the *syn*- or *anti*-gauche conformers and the global minimum; (iii) the largest overestimation is, however, found for the energy barrier needed to reach the highly twisted TS-*syn*-*anti* form; and (iv) it appears that DFT results are more sensitive to the introduction or a larger portion of HF exchange than to the basis used, which is in agreement with previous studies [11,15,16].

In spite of the above-summarised general trends, it is not so straightforward to judge if one of the studied DFT methods behaves more accurately than the others; thus, a more detailed analysis of the local behaviour along the whole torsional profile has been also performed. We define in a statistical manner the so-called 'discrepancy function' (DF) according to the expression

$$DF = \sqrt{\int_0^{180^\circ} \varepsilon^2(\phi) d\phi}, \quad (4)$$

$\varepsilon(\phi)$ being the difference between the relative energy of the assessed method and the reference value taken from the previous section, as a function of the torsional angle ϕ . This function is further normalised by the number of scanned torsional angles. The results are presented in Fig. 3; which clearly quantify the results found upon inspection of Table 2. Of particular interest is the

Table 2

Energetics (kcal/mol) of stationary points in 2,2'-bipyrrole relative to the *anti*-planar conformation, as calculated with different DFT approaches

Basis set	Method	<i>anti</i> -gauche	TS- <i>syn</i> - <i>anti</i>	<i>syn</i> -gauche	<i>syn</i>
cc-pVDZ	BLYP	−0.33 (154.4°)	2.77 (83.3°)	1.50 (35.0°)	2.78 (0°)
	B1LYP	−0.39 (152.8°)	2.52 (83.2°)	1.44 (37.5°)	2.91 (0°)
	BHHLYP	−0.43 (151.9°)	2.37 (83.3°)	1.38 (39.2°)	3.02 (0°)
	PBE	−0.30 (155.0°)	2.92 (82.7°)	1.68 (35.4°)	2.95 (0°)
	PBE0	−0.38 (152.8°)	2.57 (82.4°)	1.58 (38.2°)	3.06 (0°)
	PBEHH	−0.44 (151.5°)	2.32 (82.5°)	1.48 (40.5°)	3.16 (0°)
	OB95	−0.29 (155.8°)	2.56 (81.8°)	1.65 (38.5°)	2.94 (0°)
	O1B95	−0.34 (153.9°)	2.38 (81.8°)	1.60 (40.4°)	3.06 (0°)
	OHBB95	−0.37 (152.6°)	2.28 (82.1°)	1.54 (41.6°)	3.15 (0°)
	PW91PW91	−0.28 (156.4°)	2.97 (82.7°)	1.68 (34.7°)	2.94 (0°)
aug-cc-pVDZ	B3LYP	−0.38 (156.3°)	2.60 (82.7°)	1.49 (36.9°)	2.92 (0°)
	BLYP	−0.03 (162.2°)	2.74 (83.4°)	1.72 (36.4°)	2.52 (0°)
	B1LYP	−0.10 (156.0°)	2.55 (83.4°)	1.65 (38.8°)	2.68 (0°)
	BHHLYP	−0.16 (154.4°)	2.42 (83.5°)	1.59 (40.4°)	2.83 (0°)
	PBE	−0.06 (160.0°)	2.94 (82.8°)	1.86 (36.0°)	2.71 (0°)
	PBE0	−0.15 (155.5°)	2.64 (82.8°)	1.75 (38.8°)	2.85 (0°)
	PBEHH	−0.23 (153.4°)	2.42 (82.8°)	1.63 (41.0°)	3.00 (0°)
	OB95	−0.14 (158.7°)	2.57 (81.9°)	1.79 (39.1°)	2.79 (0°)
	O1B95	−0.18 (156.3°)	2.42 (82.0°)	1.72 (41.0°)	2.91 (0°)
	OHBB95	−0.22 (154.6°)	2.35 (82.3°)	1.66 (42.1°)	3.03 (0°)
cc-pVTZ	PW91PW91	−0.03 (156.4°)	2.97 (82.8°)	1.88 (35.8°)	2.72 (0°)
	B3LYP	−0.08 (158.7°)	2.61 (83.2°)	1.68 (38.3°)	2.67 (0°)
	BLYP	−0.29 (155.0°)	2.76 (83.9°)	1.40 (34.4°)	2.65 (0°)
	B1LYP	−0.32 (154.1°)	2.60 (83.8°)	1.42 (36.6°)	2.81 (0°)
	BHHLYP	−0.34 (153.6°)	2.52 (84.0°)	1.44 (38.2°)	2.95 (0°)
	PBE	−0.26 (156.1°)	3.00 (83.5°)	1.62 (34.3°)	2.83 (0°)
	PBE0	−0.30 (154.8°)	2.76 (83.4°)	1.62 (36.8°)	2.98 (0°)
	PBEHH	−0.32 (153.9°)	2.61 (83.4°)	1.60 (38.7°)	3.10 (0°)
	OB95	−0.29 (155.8°)	2.61 (82.8°)	1.60 (37.2°)	2.86 (0°)
	O1B95	−0.30 (154.9°)	2.53 (82.8°)	1.61 (38.9°)	2.99 (0°)
	OHBB95	−0.29 (154.4°)	2.53 (83.2°)	1.63 (39.8°)	3.10 (0°)
	PW91PW91	−0.23 (158.0°)	3.05 (83.1°)	1.64 (34.0°)	2.86 (0°)
	B3LYP	−0.29 (156.1°)	2.68 (83.2°)	1.48 (36.2°)	2.82 (0°)

The corresponding angle (in degrees) is reported between parentheses.

performance of the newly developed OB95-based schemes. The nonhybrid OB95 functional performs at least as accurate as the well-known B3LYP model; larger

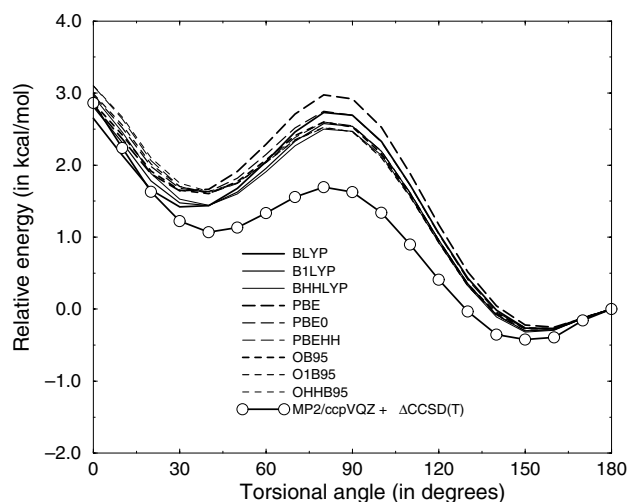


Fig. 2. Torsional potential of 2,2'-bipyrrole, as calculated at various DFT levels with the cc-pVTZ basis.

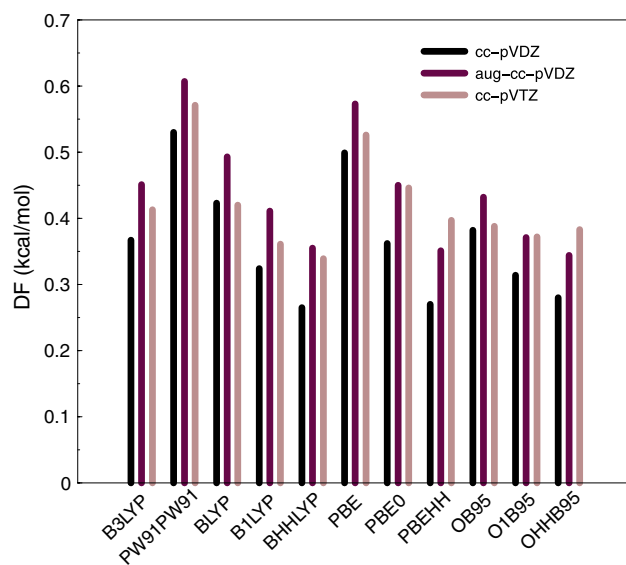


Fig. 3. Values of the discrepancy function for the torsional potential of 2,2'-bipyrrole, as calculated by different DFT-based approaches.

Table 3

MC3-calculated energetics (kcal/mol) of stationary points in 2,2'-bipyrrole relative to the *anti*-planar conformation; results from its individual components are also listed as well as the 'discrepancy function' (kcal/mol, see text for details)

Method	<i>anti</i> -gauche	TS- <i>syn</i> - <i>anti</i>	<i>syn</i> -gauche	<i>syn</i>	DF
HF/DIDZ	−0.66 (146.6°)	1.20 (84.7°)	0.69 (47.3°)	3.01 (0°)	0.239
MP2/DIDZ	−1.94 (134.1°)	−0.84 (76.5°)	−0.85 (66.3°)	2.76 (0°)	1.268
MPWX/MG3S	−0.24 (155.0°)	2.63 (83.2°)	1.64 (38.5°)	2.89 (0°)	0.414
MC3MPWX	−0.69 (148.5°)	1.51 (82.2°)	0.95 (44.1°)	2.84 (0°)	0.146
BBX/MG3S	−0.16 (157.8°)	2.76 (83.4°)	1.74 (38.1°)	2.87 (0°)	0.490
MC3BBX	−0.50 (151.1°)	1.88 (82.6°)	1.20 (42.1°)	2.83 (0°)	0.081

The corresponding angle (in degrees) is reported between parentheses.

portions of HF exchange, in contrast to the BLYP- or PBE-based schemes, do not largely modify the results. Its use can therefore be envisioned in applications where low cost is of primary importance as for instance, in the study of conformational changes in longer pyrrole oligomers [7] or closely related systems. Although the preference for the *anti*-gauche conformation is predicted by all the DFT methods, and this feature will also survive for longer chains, the relative stability of all possible conformations might be altered depending of the functional used.

3.3. Multicoefficient strategies

The application of composite MC3 computational strategies has been finally explored. A summary of the results is provided in Table 3, where the relative energies

and the corresponding DF are listed, and in Fig. 4, where the respective torsional curves are shown. Note that the main problem associated with all DFT functionals, the overestimation of relative energies in the 30°–150° region, still persists for the MPWX and BBX functionals. The large portion of HF exchange in the formulation of the MPWX (38%) and BBX (39%) models may serve, however, as a good starting point for further customised methods. In fact, inspection of the results show how the MC3-based methods are much more accurate than the former DFT ones. The optimised mixing of wave function (HF, MP2) and DFT terms (MPWX or BBX) given by Eq. (3) performs surprisingly well in view of the poor performance found for the MP2 method alone; which is traced back to the inadequately small DIDZ basis. This situation is reminiscent of the case of butadiene [19], where converged MP2 and CCSD(T) calculated potential curves display also significant lower torsional barriers than the best DFT results. These protocols behave thus very accurately when faced to other approaches having comparable computational cost. However, as a note of caution, we warn about the lack of implemented analytical gradients; which might limit somehow the range of applicability of these methods yet.

3.4. Analytical Fourier fits

The point-wise calculated energies were subjected to simple Fourier fits of the form

$$V(\phi) = \sum_{n=1}^m V_n [1 - \cos n(180 - \phi)], \quad (5)$$

where V_n are the coefficients to be determined and ϕ is the torsional angle around the inter-ring bond. Such a potential energy function is virtually included in all

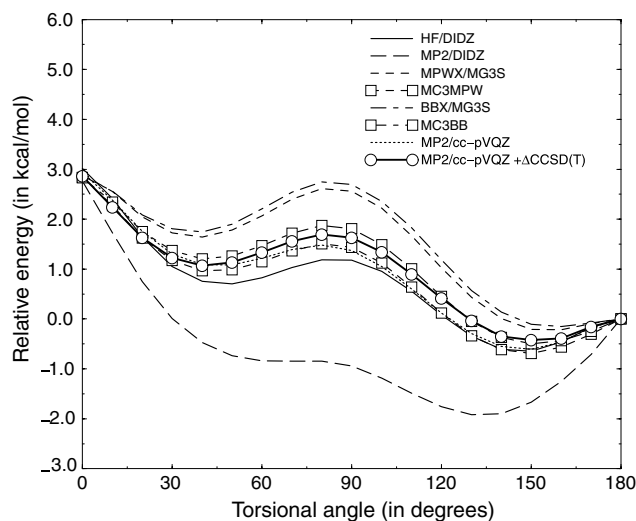


Fig. 4. Torsional potential of 2,2'-bipyrrole, as calculated by MC3-based approaches.

Table 4

Fitted expansion coefficients (kcal/mol) for the analytical torsional potential of 2,2'-bipyrrole

Method	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8
MP2/cc-pVQZ+ΔCCSD(T)	2.163	0.558	0.258	−1.043	0.197	−0.251	0.092	−0.144
MC3MPWX	2.332	0.384	0.208	−1.151	0.143	−0.252	0.055	−0.168
MC3BBX	2.328	0.706	0.218	−1.078	0.143	−0.221	0.054	−0.136

current force fields and, consequently, it is of much interest to accurately determine these expansion coefficients. Fits extended up to the eight order to have a sufficiently negligible difference between calculated and fitted values. The corresponding results are gathered in Table 4.

4. Concluding remarks

We have presented a large set of correlated ab initio and DFT calculations on the torsional potential curves for 2,2'-bipyrrole. Increasing time and effort is being lately devoted to the accurate calculation of these torsional profiles since they are essential models for the evaluation of any suitable method for π -conjugated molecules. Sufficiently converged MP2 results were obtained at the cc-pVQZ level; the CCSD(T) correction was still added to ensure that convergence has also been virtually achieved with respect to correlation effects. Thus, very accurate Fourier series representation of the torsional curve was reported for the first time. Former discrepancies between ab initio and DFT calculations are still found at these higher correlated levels. This previously found contradiction, given the strong dependence of the MP2 method, was indeed not due to the result of using relatively small basis sets. The use of MC3-based composite methods substantially remedied the divergence of both theories. These methods might soon become an appealing tool for electronic structure calculations as far as they start to be promisingly applied out of the training set. We expect the detailed calculations performed in this Letter will help experimentalists when deducing conformational information from measurements. We also tried to provide for theoreticians a systematic assessment of newly developed methods within present day computational capabilities.

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