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# Computational reinvestigation of the bithiophene torsion potential<sup>☆</sup>

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## Abstract

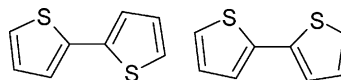
We present the results of *ab initio* calculations of the torsion potential of 2,2'-bithiophene, using the MP2, CCSD, CCSD(T) and B3LYP electron correlation methods. Special emphasis is given to the systematic investigation of basis set effects by the use of correlation-consistent bases. We find that the MP2 and coupled-cluster potential energy curves agree well with each other, for a given basis set. However, unlike B3LYP, they are rather sensitive to the quality of the basis. The previously observed disagreement between the B3LYP and MP2 methods, especially on the degree of ring coplanarity in the minimum-energy *cis* and *trans* conformations, is considerably reduced upon adoption of a large and flexible basis set for the latter.

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## 1. Introduction

Oligo- and polythiophenes are among the most promising and widely studied materials for organic electronic and optoelectronic applications [1–4]. Their aggregation and self-assembly properties are crucial for the charge mobility in organic thin film transistors or for the quantum yield of the luminescence in light-emitting diodes, to name two important examples [2,3]. As a first step in our effort to study many-chain interactions in oli-

gothiophenes by molecular dynamics simulations, we have re-examined the problem of the torsion potential in the dimer (2,2'-bithiophene or 2,2'-bithienyl), which is depicted below in its *trans*-planar (also known as anti-planar) and *cis*-planar (or syn-planar) conformations.



The main features of the torsion energy profile of bithiophene have been known for at least a decade [5–13]. The absolute minimum has a *trans*-distorted (TD, also known as anti-gauche) conformation, with an S–C–C–S torsion angle  $\phi \cong \pm 150^\circ$ . There is a second pair of minima

<sup>☆</sup> Dedicated to Prof. Giuseppe Allegra, on occasion of his 70th birthday.

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higher up in energy, at  $\phi \cong \pm 40^\circ$  (*cis*-distorted conformation, CD, also known as *syn-gauche*). The *trans*-planar (TP,  $\phi = 180^\circ$ ) and *cis*-planar (CP,  $\phi = 0^\circ$ ) conformations are actually transition states for the interconversion of two TD and two CD states, respectively. Finally, there are two more transition states (TS) at  $\phi \cong \pm 90^\circ$ , separating a CD from a TD minimum. The potential energy is of course an even function of the  $\phi$  angle.

A number of semiempirical and *ab initio* calculations of the torsion potential of bithiophene were carried out in the late 1980s and the first half of the 1990s. Orti et al. [5] have provided a useful summary of these early attempts, together with an extensive compilation and discussion of experimental studies (including gas-phase electron diffraction [9], high-resolution spectroscopy [10,11] or NMR in liquid crystalline solvents [12,13]). In their best calculation, these authors [5] obtained the torsion potential at the second-order Møller–Plesset (MP2) level using a 6-31G\* basis set. Agreement with the available gas-phase experiments [9,10] was not very satisfactory, but this could be partly attributed to the assumptions made in the interpretation of the raw data. Afterwards, Viruela et al. [6] recomputed the torsion potential using two hybrid density-functional methods (B3P86 and B3PW91) and a 6-31G\* basis set. These functionals gave virtually identical potential energy curves, and they roughly agreed with MP2 with respect to the CD–TD energy difference. On the other hand, these methods gave substantially different answers for other important features of the potential energy curves, such as the CP–CD and TP–TD energy differences and the height of the TS barrier (we shall have a chance to return to these in Section 3). In 1997, Karpfen et al. [7] attacked the same problem using MP2 and the B3LYP functional and a larger 6-311G\*\* basis, augmented with a further set of either diffuse or polarization functions. Again, the disagreement between the MP2 and density-functional methods could not be resolved in favour of either of them. These authors [7] also observed a strong dependence of the MP2 potential energy curve on the basis set, particularly upon inclusion of the diffuse functions. Eventually, they were unable to claim convergence of the MP2 potential with respect to

the basis set. Finally, Duarte et al. [8] studied the effects of several density functionals as well as CCSD (coupled-cluster with single and double excitations) and MP4(SDQ) (fourth-order Møller–Plesset, neglecting triple excitations). Interestingly, these authors observed a fair agreement between the MP4(SDQ)/cc-pVDZ and B3LYP/6-311G\*\* curves, thus reducing the ‘conflict’ between wavefunction-based and density-functional theories. However, their results are still inconclusive, mainly because of the lack of clear-cut convergence with respect to extension of the basis set.

The aim of the present Letter is to study the influence of the electron correlation method and of the quality of the basis set on the calculated torsion potential, and possibly come to a definite conclusion about its shape using state-of-the-art methods. A number of similar studies have been recently pursued on related systems, such as biphenyl [14,15] or bifuran and bipyrrrole [16]. The following section is devoted to the description of our computational methods. Note that some of our calculations with moderately sized basis sets reproduce previously published data [5–8] and are included mainly for the reader’s convenience, to facilitate comparison with the more accurate results. Afterwards, we shall illustrate our numerical results and discuss their dependence on the electron correlation method and on the quality of the basis set. Conclusions follow.

## 2. Calculations

We carried out a systematic investigation of the effect of the treatment of the electron correlation and of the basis set on the torsion potential of bithiophene. Thus, the correlation methods included MP2 [17,18], hybrid density functional (B3LYP) [19] and coupled-cluster theory [17,20], in the CCSD and CCSD(T) versions. Note that the overall accuracies (and computational cost) of the MP2 and B3LYP methods are generally considered to be comparable, mainly on the basis of their performance in the prediction of thermochemical quantities. On the other hand, there are rigorous theoretical arguments as well as much empirical evidence that the MP2, CCSD and CCSD(T)

methods form a well-defined hierarchy of increasingly accurate electron correlation models [21,22]. In particular, CCSD is considered to be roughly comparable in performance to MP4, while CCSD(T) often produces results of ‘full CI quality’ (of course, the coupled-cluster and perturbative methods can be expected to perform well only when the zero-order Hartree–Fock description is qualitatively correct).

The basis sets included the 6-31G\*\* basis from the Pople school [18] and Davidson’s contraction [23] of the correlation consistent [24,25] cc-pVDZ and cc-pVTZ bases. Further MP2 and B3LYP calculations were carried out with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, which include diffuse s and p functions on H, and diffuse s, p and d functions on C and S (diffuse d functions on H and diffuse f functions on the heavy elements were dropped from the standard aug-cc-pVTZ basis). In the B3LYP calculations, we employed atom-based spherical grids for the integration of the exchange-correlation functional, with  $96 \times 18 \times 36$  points distributed along the  $(R, \theta, \phi)$  polar coordinates (this is higher than the default program setting of  $96 \times 12 \times 24$  points, within the GAMESS-USA program [26]).

We used the full Cartesian basis set for most of the 6-31G\*\* calculations and spherical harmonic functions for all the calculations with the correlation consistent bases. We used a spherical harmonic basis also for the 6-31G\*\* coupled-cluster

calculations. Spherical harmonics are especially convenient for highly correlated methods, since the number of virtuals is sometimes greatly reduced by projecting out of the basis set some special combinations of Cartesian functions (such as  $x^2 + y^2 + z^2$ , for d-type orbitals). Thus, a Cartesian aug-cc-pVTZ basis for bithiophene contains 572 functions (529 virtuals), but the spherical harmonic basis contains ‘only’ 506 functions (463 virtuals). This truncation is more systematic and less prone to error than the ‘brute force’ one, whereby the 66 highest virtuals (as in the above example) are simply left out of the active space. One problem with the latter approach is that the nature and symmetry of these orbitals may change as a function of the torsion angle, leading to unphysical discontinuities in the potential energy curves. Finally, we point out that the calculations with the spherical harmonic cc-pVDZ basis (overall, 178 functions) always produced lower total energies than the analogous calculations with a Cartesian 6-31G\*\* basis (188 functions), thus demonstrating the superiority of the former over the latter (note however that the MP2 and coupled-cluster methods are not strictly variational).

Geometries were optimized at both MP2 and B3LYP levels, using both the 6-31G\*\* and the cc-pVDZ basis sets (overall, four series of calculations). Further optimizations were carried out at the MP2/aug-cc-pVDZ level. We performed full geometry optimizations of the TD and CD minima

Table 1

Summary of the computational methods and total energies (in a.u., 1 a.u. = 2625.4 kJ/mol) of the TP conformers ( $\phi = 180^\circ$ ,  $C_{2h}$  symmetry)

Energy evaluation method	Geometry optimization method	TP energy
MP2/6-31G** (cart.)	MP2/6-31G** (cart.)	–1102.751934
MP2/cc-pVDZ (s.h.)	MP2/cc-pVDZ (s.h.)	–1102.807086
MP2/aug-cc-pVDZ (s.h.)	MP2/aug-cc-pVDZ (s.h.)	–1102.879141
MP2/cc-pVTZ (s.h.)	MP2/6-31G** (cart.)	–1103.215357
MP2/aug-cc-pVTZ (s.h.)	MP2/6-31G** (cart.)	–1103.227119
CCSD/6-31G** (s.h.)	MP2/6-31G** (cart.)	–1102.786504
CCSD/cc-pVDZ (s.h.)	MP2/cc-pVDZ (s.h.)	–1102.854258
CCSD(T)/6-31G** (s.h.)	MP2/6-31G** (cart.)	–1102.851131
CCSD(T)/cc-pVDZ (s.h.)	MP2/cc-pVDZ (s.h.)	–1102.920113
B3LYP/6-31G** (cart.)	B3LYP/6-31G** (cart.)	–1104.504322
B3LYP/cc-pVDZ (s.h.)	B3LYP/cc-pVDZ (s.h.)	–1104.553641
B3LYP/cc-pVTZ (s.h.)	B3LYP/6-31G** (cart.)	–1104.676224
B3LYP/aug-cc-pVTZ (s.h.)	B3LYP/6-31G** (cart.)	–1104.678585

( $C_2$  symmetry group) and of the planar TP and CP states ( $C_{2h}$  and  $C_{2v}$  groups, respectively). We also carried out constrained optimizations with the S–C–C–S dihedral angle fixed at  $\phi = 30^\circ, 60^\circ, \dots, 150^\circ$  ( $C_2$  symmetry). Finally, we performed full transition state searches at  $\phi \cong 90^\circ$ . All the coupled-cluster as well as the MP2 energies with the larger basis sets were evaluated at the these MP2 geometries. Similarly, the B3LYP/cc-pVTZ and B3LYP/aug-cc-pVTZ energies were computed at the B3LYP/6-31G\*\* geometries. The validity of doing high-quality single point calculations at the geometries from a lower-level optimization – an assumption made in almost every quantum chemical study – was explicitly checked in [8] for bithiophene. Table 1 contains a summary of our calculations and provides the corresponding total energies of the TP states.

We used the GAMESS-USA suite of programs for all the calculations [26]. Its functionality has recently been extended by the inclusion of a coupled-cluster code [27].

### 3. Results and discussion

Figs. 1–3 display our results for the torsion potential of bithiophene, calculated at the B3LYP,

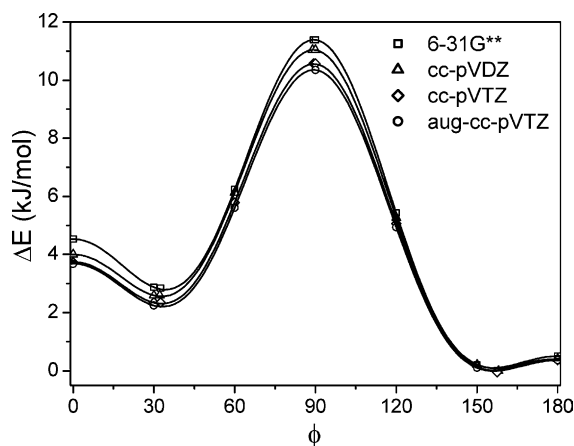


Fig. 1. Torsional potential of bithiophene, calculated by the B3LYP method with different basis sets. The points represent the relative energies calculated with respect to the TD conformation, and the continuous lines represent their interpolation by a Fourier expansion (see Table 2).

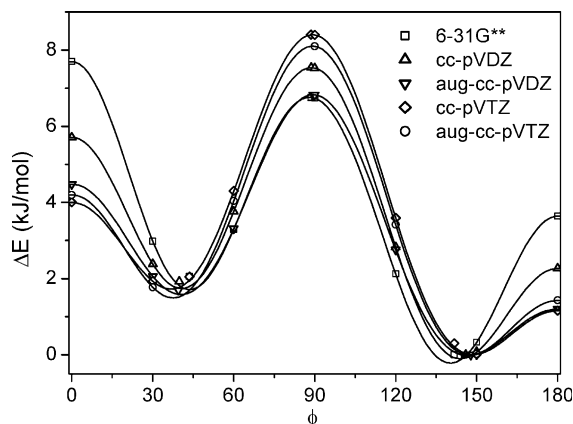


Fig. 2. Torsional potential of bithiophene, calculated by the MP2 method with different basis sets. See also the caption to Fig. 1.

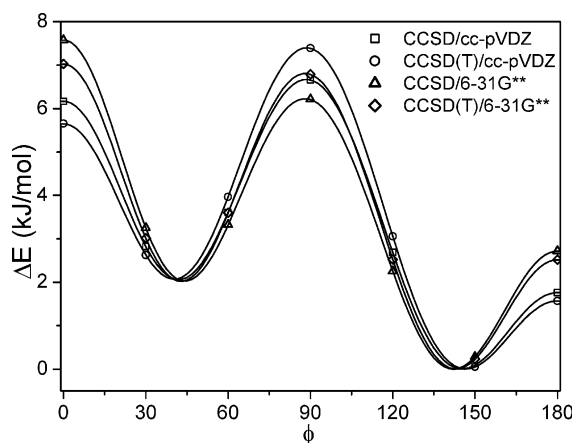


Fig. 3. Torsional potential of bithiophene, calculated by the CCSD and CCSD(T) methods with different basis sets. See also the caption to Fig. 1.

MP2 and coupled-cluster levels with the different basis sets. Relative energies were calculated with respect to the absolute TD minimum (or an interpolated value for it, see below). The plots contain both the calculated points (open symbols) and their interpolation by a truncated Fourier expansion (continuous curves):

$$V(\phi) = V_0 + \sum_{k=1}^6 V_k \cos\left(\frac{\pi k \phi}{180}\right). \quad (1)$$

The values of the coefficients are given in Table 2. The largest Fourier term often corresponds to the

Table 2

Coefficients (in kJ/mol) of the Fourier expansion of the torsion potentials [Eq. (1)]

Computational method	$V_1$	$V_2$	$V_3$	$V_4$	$V_5$	$V_6$
MP2/6-31G**	1.638	−0.708	0.283	2.682	0.108	0.173
MP2/cc-pVDZ	1.396	−1.870	0.263	2.333	0.061	0.100
MP2/aug-cc-pVDZ	1.232	−1.995	0.360	1.868	0.048	0.000
MP2/cc-pVTZ	1.146	−2.932	0.237	2.022	0.037	0.021
MP2/aug-cc-pVTZ	1.072	−2.705	0.252	2.098	0.061	0.062
CCSD/6-31G**	1.841	−0.693	0.457	2.267	0.132	0.163
CCSD/cc-pVDZ	1.676	−1.463	0.428	2.007	0.100	0.116
CCSD(T)/6-31G**	1.733	−1.152	0.393	2.294	0.128	0.145
CCSD(T)/cc-pVDZ	1.576	−1.985	0.377	2.048	0.087	0.095
B3LYP/6-31G**	1.580	−4.393	0.402	2.180	0.033	−0.044
B3LYP/cc-pVDZ	1.429	−4.378	0.312	2.048	0.055	−0.039
B3LYP/cc-pVTZ	1.318	−4.232	0.320	1.985	0.042	−0.014
B3LYP/aug-cc-pVTZ	1.283	−4.145	0.330	1.975	0.047	−0.020

fourth harmonic, while  $V_5$  and  $V_6$  are generally small. These two harmonics may be safely neglected in computationally intensive molecular dynamics simulations of oligothiophene assemblies (incidentally, we remind the reader that the potentials given in the figures and Table 2 should not be confused with the *intrinsic* torsion potentials of empirical force fields). The Fourier curves (containing seven adjustable parameters) agree exactly with energies at the seven evenly spaced points used to define them ( $\phi = 0^\circ, 30^\circ, 60^\circ, \dots, 180^\circ$ ), but they may deviate somewhat from those of the CD and TD states (where available). This problem occurs for example with the MP2/6-

31G\*\* curve in Fig. 2, which has a relatively sharp turn in the neighbourhood of these minima. Further information on the geometries and relative energies of the stationary points has been collected in Table 3.

The B3LYP method (Fig. 1) is much less sensitive than the MP2 and coupled-cluster ones to the choice of the basis set. As pointed out by other authors [6–8], this and similar density functionals predict two very shallow CD and TD minima lying very close to the planar states. The CD–TD energy difference is about 2.5 kJ/mol, in fair agreement with the MP2 and coupled-cluster calculations. On the other hand the TS barrier at  $90^\circ$  is relatively

Table 3

Stationary points on the torsional energy curves: the table provides the values of the  $\phi$  angle (in degrees) and the energies relative to global TD minimum (in kJ/mol)

Computational method	CP state	CD state	TS state	TD state	TP state
MP2/6-31G**	0.0; 7.70	43.6; 2.06	88.6; 6.86	141.7; 0.00	180.0; 3.64
MP2/cc-pVDZ	0.0; 5.71	39.8; 1.93	88.7; 7.54	145.9; 0.00	180.0; 2.27
MP2/aug-cc-pVDZ	0.0; 4.48	39.5; 1.70	89.5; 6.83	147.8; 0.00	180.0; 1.20
MP2/cc-pVTZ (&)	0.0; 4.00	36.8; 1.72	89.2; 8.40	148.7; 0.00	180.0; 1.16
MP2/aug-cc-pVTZ (&)	0.0; 4.20	37.5; 1.50	89.1; 8.11	147.5; 0.00	180.0; 1.43
CCSD/6-31G** (&)	0.0; 7.58	44.2; 2.03	88.0; 6.23	142.1; 0.00	180.0; 2.72
CCSD/cc-pVDZ (&)	0.0; 6.16	42.0; 2.06	88.5; 6.67	145.4; 0.00	180.0; 1.76
CCSD(T)/6-31G** (&)	0.0; 7.03	42.8; 2.02	88.1; 6.81	143.0; 0.00	180.0; 2.52
CCSD(T)/cc-pVDZ (&)	0.0; 5.65	40.4; 2.07	88.6; 7.39	146.6; 0.00	180.0; 1.57
B3LYP/6-31G**	0.0; 4.53	32.5; 2.84	89.3; 11.49	157.5; 0.00	180.0; 0.50
B3LYP/cc-pVDZ	0.0; 4.00	32.2; 2.59	88.9; 11.04	158.0; 0.00	180.0; 0.41
B3LYP/cc-pVTZ (&)	0.0; 3.73	32.8; 2.29	89.3; 10.54	156.3; 0.00	180.0; 0.37
B3LYP/aug-cc-pVTZ (&)	0.0; 3.68	33.1; 2.20	89.4; 10.36	156.2; 0.00	180.0; 0.36

The lines marked by the (&) symbol have been obtained from the Fourier expansion of the potential [see Eq. (1) and Table 2].

high, about 10–11 kJ/mol above the minimum-energy TD state, to be compared with 7–8 kJ/mol for MP2 and coupled-cluster (see also below, however). Adding diffuse functions to the cc-pVTZ basis set makes very little difference for B3LYP.

The MP2 (Fig. 2) and the coupled-cluster (Fig. 3) curves show comparably strong dependencies on the basis set. The variations mostly concern the CP–CD and the TP–TD energy differences. Remarkably, they are quite systematic. They are largest (3–6 kJ/mol) with the lower-quality 6-31G\*\* basis and smallest (1–2 kJ/mol) with the higher-quality cc-pVTZ, with cc-pVDZ falling in between. Thus, using a high-quality basis set reduces the disagreement with B3LYP with respect to the degree of coplanarity in the *cis* and *trans* states. The CD–TD energy difference is consistently predicted to be about 2 kJ/mol, and the TS barrier is found 7–8 kJ/mol above the global TD minimum. In relative terms, its variation is much smaller than the one concerning the planar geometries. However, it is interesting that also the MP2 and B3LYP barrier heights seem to come closer together, as the size of the basis grows from 6-31G\*\* to cc-pVTZ. Thus, the energy of the TS state *increases* from 6.9 to 8.4 kJ/mol at the MP2 level, and *decreases* from 11.5 to 10.5 kJ/mol at the B3LYP one.

Adding diffuse functions to the cc-pVDZ basis set (aug-cc-pVDZ) changes somewhat the MP2 potential energy curve, which becomes rather similar to cc-pVTZ. Only the TS barrier height seems to be underestimated. This may be due to a deficiency in the basis set, but possibly also to the fact the geometries of the MP2/aug-cc-pVDZ points were fully optimized at the same level of theory (the MP2/6-31G\*\* geometries were used for the MP2/cc-pVTZ curve, instead). On the other hand, adding diffuse functions to the cc-pVTZ basis (aug-cc-pVTZ) changes the MP2 curve by less than 0.5 kJ/mol over the whole  $\phi$  range. This contrasts with a previous study by Karpfen et al. [7], who observed a strong variation in the MP2 curves upon going from 6-311G\*\* to 6-311++G\*\*. We are probably close to a converged MP2 torsion potential. However a definite and clear-cut demonstration of this may only come from further calculations with an even larger basis set.

We also see in Fig. 3 that the coupled-cluster curves roughly fall in two groups, with the basis set (6-31G\*\* or cc-pVDZ) being a more important factor than the level of electron correlation treatment (CCSD or CCSD(T)). The predominant role of the basis set over the electron correlation level is confirmed by Fig. 4, where the MP2 and coupled-cluster curves with the same cc-pVDZ basis set have been collected in order to facilitate the comparison. These appear to be rather close over the whole  $\phi$  range, suggesting that a CCSD(T) calculation with the larger basis sets would behave very similarly to MP2 or CCSD.

In Fig. 5, we compare the MP2 and restricted Hartree–Fock (RHF) curves, calculated using the 6-31G\*\* and cc-pVTZ basis sets (the RHF curves did not involve separate geometry optimizations, but they were simply obtained as a byproduct of the MP2 calculations). We see that the RHF/6-31G\*\* curve is very similar to the RHF/cc-pVTZ one. We may readily conclude that the strong basis set dependence of the MP2 curves comes from the correlated part of the calculations. Since distortion from coplanarity has much to do with *intramolecular* non-bonded interactions between the rings, it is tempting to draw a parallel with a well-known problem in the *ab initio* calculation of *intermolecular* forces [28]. On the one hand, the MP2 and coupled-cluster methods are superior to RHF

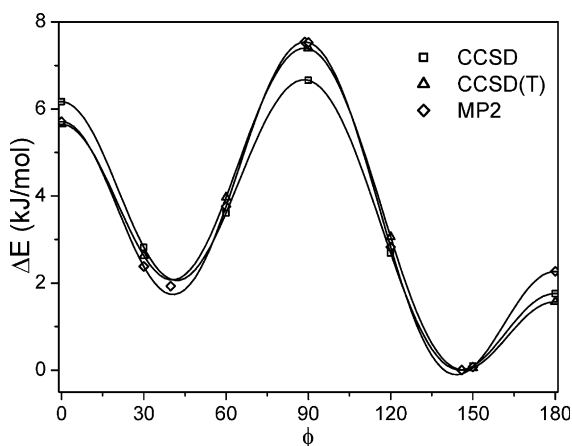


Fig. 4. Comparison of the MP2 and coupled-cluster potential energy curves, calculated using the cc-pVDZ basis set. See also the caption to Fig. 1.

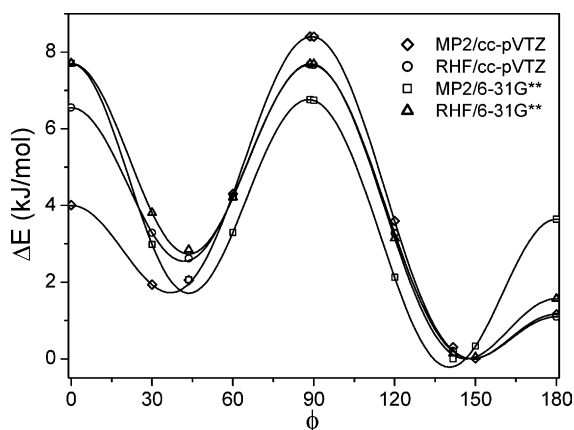


Fig. 5. Comparison of the MP2 and RHF potential energy curves, calculated using the 6-31G\*\* and the cc-pVTZ basis sets. See also the caption to Fig. 1.

(and, indeed, also density-functional theory) because of the inclusion of dispersion interactions. On the other hand, application of these correlated methods can be problematic because of their greater sensitivity to the ‘basis set superposition error’ [29–33]. It seems that, in the present and similar cases, the best solution is simply to adopt a sufficiently large and flexible basis set. When the system size prevents this (as for example in higher oligothiophenes), the ‘second best’ solution is probably to stick to the B3LYP or even the RHF method, where the basis set is not so critical. Indeed, we see in Fig. 5 that the RHF curves agree rather well with the MP2/cc-pVTZ one. The only point where they depart significantly from it is at  $\phi \cong 0^\circ$ , where they overestimate the energy of the CP state by about 2.5 kJ/mol.

Finally, we compare our results with the available gas-phase experiments. We limit the discussion to the largest basis set, for each electron-correlation method (MP2/aug-cc-pVTZ, B3LYP/aug-cc-pVTZ, CCSD/cc-pVDZ and CCSD(T)/cc-pVDZ). Samdal et al. [9] interpreted their electron-diffraction data on the basis of coexisting CD and TD states at  $\phi \cong 36^\circ$  and  $\phi \cong 148^\circ$  with relative populations of 44% and 56%, at a temperature of 98 °C. Our results for the *average* torsion angles and populations of these conformations are collected in Table 4. These were obtained by integrating the classical Boltzmann probabilities in the

Table 4

Comparison of the calculated torsion potentials with the (interpretation of the) electron diffraction data of [9]

Method	CD state	TD state
MP2/aug-cc-pVTZ	37°; 37%	147°; 63%
CCSD/cc-pVDZ	43°; 33%	145°; 67%
CCSD(T)/cc-pVDZ	41°; 33%	146°; 67%
B3LYP/aug-cc-pVTZ	33°; 33%	152°; 67%
Experiment	36 ± 5°; 44 ± 4%	148 ± 3°; 56 ± 4%

For each table entry, the first figure is an average torsion angle, the second figure is a relative population.

[0°, 90°] and [90°, 180°] ranges (the evaluation of quantum states and populations is unnecessary for our present purposes, considering the high temperature in the electron-diffraction experiments and the relatively crude information obtained from their interpretation). The MP2/aug-cc-pVTZ curve seems to give the best overall agreement with experiment. The MP2 torsion angles fall almost exactly in the middle of the experimental uncertainty range. The populations are not altogether satisfactory, but they are clearly better than those from the other methods, or from MP2 with a smaller basis (33% and 67%, for 6-31G\*). Note that the average torsion angles are less than 1° away from the minimum-energy states (see Table 3), with one interesting exception. At the B3LYP level, the average TD angle is 4° smaller (i.e., further away from coplanarity, and closer to the experimental value) than predicted by simple energy minimization. This effect is due to the flatness and asymmetry of the B3LYP potential energy curve in the neighbourhood of the TD states.

The work of Takayanagi et al. [11] represents another important source of experimental information, which has been mostly overlooked by the other theoretical studies [5–8]. These authors criticized an earlier interpretation of the fluorescence excitation and fluorescence spectra of bithiophene, which had led to an estimate of the TD–CD energy difference of 4.9 kJ/mol [10]. Indeed, this value appears to be far too high, on the basis of both the theoretical calculations and the populations from the electron diffraction experiments [9]. Instead, their interpretation of similar experimental data [11] led to a detailed description of the potential



energy curve about the TD minima ( $\phi \cong 120^\circ$  to  $180^\circ$ ). In particular, according to these authors the TP state should be only  $25 \text{ cm}^{-1} = 0.30 \text{ kJ/mol}$  higher than the TD ones, which are located at  $\phi = 159^\circ$ . These data are in excellent agreement with the B3LYP result (see again Table 3), while the MP2 and coupled-cluster ones are less satisfactory.

#### 4. Conclusions

We have carried out an investigation of the torsion potential of 2,2'-bithiophene, using different electron correlation methods and basis sets. We have used highly correlated CCSD and CCSD(T) calculations with moderately sized bases in order to judge the relative merits of the computationally cheaper MP2 and B3LYP methods. These have then been carried forward by calculations with larger basis sets, up to aug-cc-pVTZ. Compared to previous computational studies [5–8], special emphasis has been placed on the achievement of properly converged results by the systematic use of correlation consistent bases. The size of the system, and the constraints imposed by our present computational resources, have prevented us from carrying out this program to the level which was seen, for example, in calculations of hydrogen bonding interactions between smaller molecules (MP2 and CCSD(T) with aug-cc-pV5Z bases [33]). Still, we believe that reasonably converged potential energy curves (i.e., relative energies, not total energies) have been obtained at the B3LYP and probably also the MP2 level.

The MP2 and coupled-cluster curves are much more sensitive than B3LYP and RHF to the choice of the basis set. Thus, even though our CCSD(T) results are in computational terms the 'heaviest' attempt so far at the bithiophene torsion potential, we do not wish to overemphasize their significance. Calculations with more extensive basis sets can be expected to produce significant changes to our coupled-cluster curves. As mentioned above, these are useful mainly as a way to assess the strengths and weaknesses the other methods. In any case, the quality of the basis appears to be a more im-

portant factor than the level of electron correlation, since the MP2, CCSD and CCSD(T) calculations with a cc-pVDZ basis produce rather similar potentials.

Surprisingly, the MP2/aug-cc-pVTZ potential is in many ways closer to the B3LYP/6-31G\*\* one than to the MP2/6-31G\*\* one. Thus, the previously discussed disagreement [6–8] between the MP2 and B3LYP results is greatly reduced by the adoption of a high-quality basis set. According to one particular set of experimental data [11], giving a very detailed picture of the torsion potential in the neighbourhood of the global TD minimum, B3LYP even appears to be superior to MP2. However, considering also other features such as the relative energies of the TD and CD states, the height of the TS barrier at  $90^\circ$  and the good agreement with the coupled-cluster results, we trust the MP2/aug-cc-pVTZ curve to provide the best overall description of the torsion potential.

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