Single-Bond Torsional Potentials in Conjugated Systems: A Comparison of *ab Initio* and Density Functional Results

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The fully relaxed single-bond torsional potentials in typical conjugated systems were evaluated with the aid of ab initio self-consistent-field and Møller−Plesset second-order calculations and, additionally, with several recently developed variants of the density functional theory. For this systematic investigation, 1,3-butadiene, styrene, biphenyl, 2,2′-bithiophene, 2,2′-bipyrrole and 2,2′-bifuran have been selected as model molecules. As representative examples for nonconjugated systems, the molecules *n*-butane and 1-butene have been treated at the very same calculational levels. For all conjugated molecules, the electron correlation corrections to the self-consistent-field torsional potentials, as obtained with the density functional methods, are dramatically different from those resulting from the more conventional Møller−Plesset second-order approximation. For those cases where experimental data for torsional barriers are available, the self-consistent-field and the Møller−Plesset second-order results agree reasonably, whereas the density functional results consistently predict too large barriers. This behavior is most probably caused by an overestimation of the stability of the planar π-systems by the density functional theory variants in question.

Introduction

Recent applications of density functional theory (DFT) in many areas of chemistry have proven its promising performance in obtaining accurate molecular properties. Its explicit treatment of electron correlation effects opens a new way of understanding chemical properties where traditional noncorrelated methods may not be applicable. In combination with the recent developments of linear scaling Coulomb interaction methods,[1] DFT could be even applicable to large molecules such as proteins soon. However, its model exchange-correlation functional dependencies make it difficult to generalize its performance to any molecular property.

In this paper, extensive tests of the applicability of current exchange-correlation functionals to the rotational potential surfaces shall be discussed.

The detailed shape of single-bond torsional potentials in organic molecules is critical for understanding the structure and relative energetics of the lowest-lying rotational isomers. Accurate torsional potentials as obtained from high-level quantum mechanical calculations often form the basis for simple analytical potentials to be used either in the subsequent solution of the nuclear Schrödinger equation for that soft degree of freedom or for the use in empirical force field methods, molecular dynamics simulations, and Monte Carlo studies.[2−4]

The quantitative evaluation of torsional potentials in conjugated systems poses particularly difficult problems from the experimental as well as from the theoretical side. Even for the smallest conceivable conjugated hydrocarbon, 1,3-butadiene, the relative stabilities of anti and gauche isomers, the barrier height between these two minima, and the small barrier to the syn saddle point were intensely under debate a few years ago.[5−26] For a most recent discussion see ref 27.

To explore the predictive potential of the currently very popular density functional methods, several recent investigations were devoted to the computation of torsional potentials in small organic molecules.[28−30] While in the case of nonconjugated systems mostly acceptable agreement between the predictions of gradient-corrected density functional methods and the more expensive Møller−Plesset second-order (MP2) results could be achieved, significant discrepancies were found in the case of 1,3-butadiene.[29,30] The calculated energy difference between anti and gauche structures, and the barrier height between these two minima were too high by about 1 kcal mol^{-1} within the framework of the density functional methods. Full torsional potentials were not reported in those investigations, except in ref 31.

It has been known that the partial bond breaking of conjugated single-bonds by internal rotations is accompanied by large changes in electron correlation contributions, and post-Hartree−Fock methods are necessary to describe it correctly.[26]

In this work, the performance of DFT for the description of torsional potential surfaces has been systematically studied and compared with those of self-consistent-field (SCF) and MP2 methods. The set of molecules includes pure hydrocarbons such as 1,3-butadiene, styrene, and biphenyl and the dimeric heterocycles 2,2′-bithiophene, 2,2′-bipyrrole, and 2,2′-bifuran (see Figure 1). The nonconjugated systems *n*-butane and 1-butene are included for reference purposes. For most of the conjugated molecules listed above, either experimental or theoretical (ab initio SCF or MP2) investigations of the torsional potentials are already available in the literature (styrene,[26,32−43] biphenyl,[26,41,42,44−55] 2,2′-bithiophene,[56−73] 2,2′-bipyrrole,[74−76] 2,2′-bifuran[77]). With the exception of the 1,3-butadiene[29−31] and 2,2′-bithiophene[73] cases, we are, however, not aware of any previously published density functional calculations on these systems. The torsional potentials of *n*-butane[27−30,78−85] and 1-butene[20,27,30,86] can be considered as well understood.

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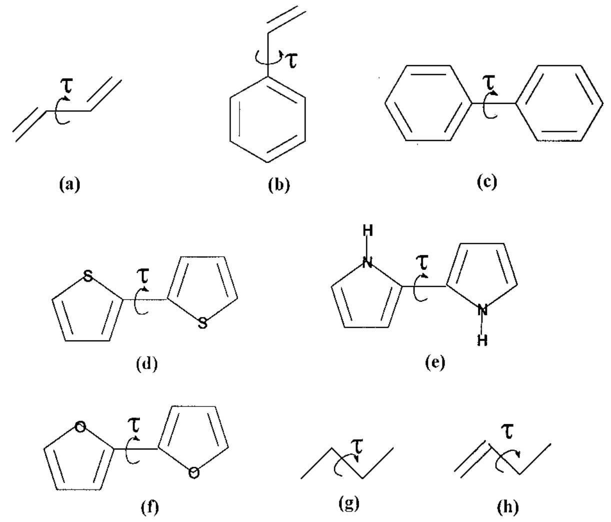

Figure 1. Molecules discussed in this work; (a) 1,3-butadiene, (b) styrene, (c) biphenyl, (d) 2,2′-bithiophene, (e) 2,2′-bipyrrole, (f) 2,2′-bifuran, (g) *n*-butane, and (h) 1-butene.

Method of Calculation

All quantum chemical calculations were performed with the Gaussian 94 suite of programs.[87] As calculational methods, the SCF approach, the MP2 method,[88] and several DFT variants[89−91] were applied. As exchange functionals, the Slater exchange (S),[87,92,93] the gradient-corrected Becke exchange (B),[94] and Becke's hybrid exchange B3[95] were used. As correlation functionals, the local spin density functional of Vosko, Wilk, and Nusair (VWN),[96] the local functional of Perdew (PL),[97] Perdew's gradient-corrected (P86)[98] functional, the Lee−Yang−Parr nonlocal functional (LYP),[99,100] and the more recently developed gradient-corrected functional of Perdew and Wang (PW91)[101] were selected. The BLYP and B3LYP exchange correlation functionals were applied to the entire series of molecules. The combinations SVWN, BPL, BP86, B3P86, and B3PW91 were used for 1,3-butadiene and 2,2′-bithiophene only.

For consistency, the 6-31G(d) basis set has been chosen for all eight molecules at all levels of description considered. As far as the computational resources allowed that, a few larger basis sets were applied as well, however, not for all molecules and methods. The 6-311++G(d,p) basis was used for SCF, B3LYP, and MP2 calculations on all eight molecules; the 6-311G(2d,2p) basis was selected for SCF, MP2, B3LYP, B3PW91, and B3P86 investigations on 1,3-butadiene and 2,2′-bithiophene.

Fully relaxed single-bond torsional potentials were calculated; i.e., for each fixed torsional angle around the central single-bond, all remaining internal degrees of freedom were optimized for each of the methods and each of the basis sets chosen. A rather tight, regular 10° grid of points was applied in most cases. For some of the more expensive, larger basis set MP2 calculations a wider 30° grid was calculated only. The energies thus obtained were subsequently least-squares-fitted to a simple analytical form, which has been used by most workers in the field:

$$V(\phi) = \sum_{n=1}^{m} {}^{1}\!/_{2} V_n (1 - \cos n\phi) \qquad (1)$$

with *m* varying from 4 to 8 in order to check the convergence of this series. In the case of 1,3-butadiene, *n*-butane, 2,2′-bithiophene, 2,2′-bipyrrole, and 2,2′-bifuran ϕ is defined as $180 - \theta$, where θ is the torsional angle and $\theta = 0$ corresponds to the syn or s-cis structure. For 1-butene $\phi = \theta$. For the remaining two molecules, styrene and biphenyl, the potential is symmetric around $\phi = 90°$.

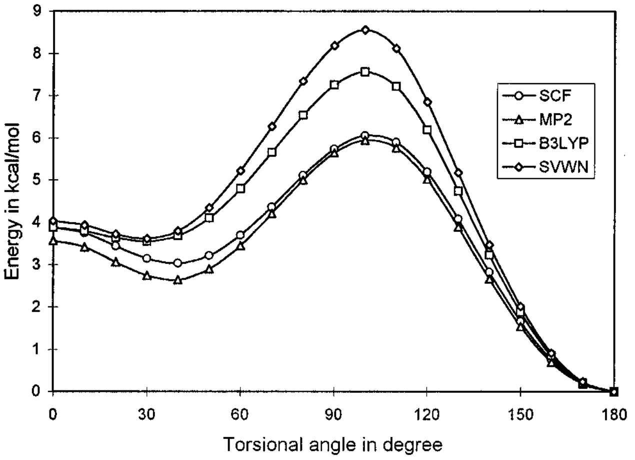

Figure 2. Torsional potential of 1,3-butadiene as obtained with SCF, MP2, B3LYP, and SVWN methods using the 6-31G(d) basis.

At this stage, we did not take into account any zero-point or thermal corrections to the energies. More detailed information on the optimized structures and on the vibrational spectra of these molecules will be given elsewhere. Here, we emphasize the performance of the various methods for calculating the single-bond torsional potentials.

Results and Discussion

A. Conjugated Hydrocarbons. *1,3-Butadiene.* From all the conjugated systems considered in this work, 1,3-butadiene is certainly the most frequently studied molecule. All the ab initio SCF calculations and all of the various post-Hartree−Fock studies performed so far agree about the qualitative shape of the torsional potential. The most stable structure corresponds to the anti conformation, separated by a large barrier from the gauche conformation, which in turn is separated from the syn saddle point by a small barrier. The vapor-phase Raman data[23,25] equally point in the direction of a gauche minimum and a syn saddle, whereas UV and infrared investigations in cryogenic, inert matrixes were interpreted in favor of a syn minimum for the second, minor conformer. Evidence that the influence of an argon matrix could in principle reverse the relative stabilities of syn and gauche conformations was given in a molecular dynamics simulation.[24]

The computed single-bond torsional potentials of 1,3-butadiene as obtained within the framework of the SCF and MP2 methods and with SVWN and B3LYP as representative examples for the DFT approaches are displayed in Figure 2. Only the results as obtained with the 6-31G(d) basis set are shown. In Table 1, we compiled the energies of the different stationary points relative to the energy of the global anti minimum for a larger set of methods and basis sets. Already the visual inspection of Figure 2 shows a clear separation between the group formed by the SCF and MP2 results on one side and the group of density functional results (B3LYP and SVWN) on the other. The relative energies of the anti minimum and of the syn saddle as obtained with the SCF, DFT, and MP2 methods range from 3.7 to 4.3 kcal mol^{-1}, the SCF results lying on the higher side; the corresponding MP2 energy differences are about 0.3 kcal mol^{-1} smaller than their DFT counterparts. However, much larger discrepancies are observed for the energy difference between anti and gauche structures and much more so for the barrier separating these two minima. Whereas the SCF and MP2 anti−gauche energy differences are in the region

TABLE 1: Energetics of Stationary Points in 1,3-Butadiene Relative to the Global Anti Minimum[a]

basis set	method	syn	gauche	TS
6-31G(d)	SCF	3.9	3.0 (40)[b]	6.1 (102)[b]
	MP2	3.6	2.6 (39)	5.9 (101)
	B3LYP	3.9	3.6 (31)	7.5 (99)
	BLYP	4.0	3.8 (26)	8.1 (99)
	B3PW91	3.9	3.5 (32)	7.4 (100)
	B3P86	3.9	3.5 (32)	7.5 (100)
	SVWN	4.0	3.6 (28)	8.6 (99)
	BPL	3.9	3.7 (25)	7.8 (98)
	BP86	4.0	3.7 (28)	8.0 (99)
6-311++G(d,p)	SCF	4.1	3.2 (44)	6.0 (102)
	MP2	3.7	2.4 (40)	5.5 (101)
	B3LYP	4.0	3.5 (31)	7.0 (100)
	BLYP	4.0	3.7 (29)	7.3 (99)
	B3PW91	4.0	3.5 (35)	6.9 (100)
	B3P86	4.0	3.5 (35)	7.0 (100)
6-311G(2d,2p)	SCF	4.3	3.3 (42)	6.1 (103)
	MP2	3.7	2.8 (39)	6.3 (102)
	B3LYP	4.0	3.6 (34)	7.1 (100)
	BLYP	4.0	3.7 (32)	7.4 (99)
	B3PW91	4.0	3.5 (35)	7.0 (100)
	B3P86	4.0	3.5 (35)	7.1 (100)
CBS-Q[c]		3.4	3.2 (38)	6.0 (102)
G2[c]		3.5	2.9 (38)	5.7 (102)

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses, in degrees. [c] Taken from ref 27.

of 3.0−3.3 and 2.4−2.8 kcal mol^{-1}, respectively, the corresponding DFT values range from 3.5 to 3.8 kcal mol^{-1}. Consequently, the DFT gauche−syn energy differences (the gauche−gauche barrier) are significantly smaller (0.2−0.5 kcal mol^{-1}) than their SCF (0.9−1.0) or MP2 (0.9−1.3) counterparts. Therefore, the optimal torsional angles for the gauche minimum as obtained with the DFT methods are much smaller (25−35°) than the computed SCF (40−44°) or MP2 (39−40°) values. Whereas the computed anti−gauche barrier amounts to about 6.0−6.1 and to 5.5−6.3 kcal mol^{-1} for SCF and MP2, respectively, significantly larger values ranging from 6.9 to 8.6 kcal mol^{-1} are predicted with the DFT approaches. Excluding all the DFT results not obtained with the hybrid B3 exchange, i.e., SVWN, BLYP, BP86, and BPL, the energy range for the anti−gauche barrier is narrowed to 6.9−7.5 kcal mol^{-1}, still about 1 kcal mol^{-1} above the SCF and MP2 values. The three variants with the hybrid B3 exchange, B3LYP, B3PW91, and B3P86, produce almost identical potential curves, implying that these values are more strongly dependent on the exchange functionals and incorporating exact exchange is important to improve the results.

One might compare these findings with the very similar *spectroscopically fitted* torsional potentials of Durig et al.,[6] Panchenko et al.,[11] and Engeln et al.,[25] who report values of about 5.9−6.0 kcal mol^{-1} for the anti−gauche barrier, about 2.7−2.9 kcal mol^{-1} for the anti−gauche energy difference, and about 1.0−1.2 kcal mol^{-1} for the gauche−gauche barrier. These values have been considered as the most reliable ones also by other theorists.[15,21,26,27] From the group of DFT approaches under investigation here, the B3LYP, B3PW91, and B3P86 torsional potentials are always closest to the SCF and MP2 results, irrespective of the basis set applied, and they lead essentially to identical descriptions of the torsional potential. The largest deviation occurs for the SVWN variant with an anti−gauche barrier of 8.6 kcal mol^{-1}. While the SCF anti−gauche barrier is essentially independent from changing the basis set from 6-31G(d) to 6-311++G(d,p) or to 6-311G(2d,2p), the corresponding DFT barrier heights are reduced by 0.5−0.7 kcal mol^{-1}. Relative to the 6-31G(d) value, the MP2 barrier is lowered by 0.4 kcal mol^{-1} applying the 6-311++G(d,p) and raised by about 0.4 kcal mol^{-1} using the 6-311G(2d,2p) basis. This observation indicates that the basis set limit of the MP2 theory has not yet been attained.

TABLE 2: Fitted Potential Parameters for the Single-Bond Torsional Potential of 1,3-Butadiene[a]

method	basis set	V_1	V_2	V_3	V_4	V_5	V_6
SCF	6-31G(d)	1.66	3.90	2.30	−0.56	−0.08	−0.09
	6-311++G(d,p)	1.87	3.73	2.30	−0.53	−0.09	−0.09
	6-311G(2d,2p)	1.97	3.67	2.45	−0.50	−0.10	−0.10
MP2	6-31G(d)	1.34	3.98	2.24	−0.71	−0.05	−0.10
	6-311++G(d,p)	1.49	3.52	2.19	−0.84	−0.03	−0.14
	6-311G(2d,2p)	1.39	4.16	2.41	−0.66	−0.08	−0.11
B3LYP	6-31G(d)	1.81	5.41	2.24	−0.68	−0.19	−0.07
	6-311++G(d,p)	1.90	4.85	2.20	−0.63	−0.16	−0.06
	6-311G(2d,2p)	1.93	4.91	2.24	−0.64	−0.17	−0.07
exp[b]		1.41	3.59	2.59	−0.51	−0.007	−0.06

[a] All values in kcal mol^{-1}. [b] Data from ref 25.

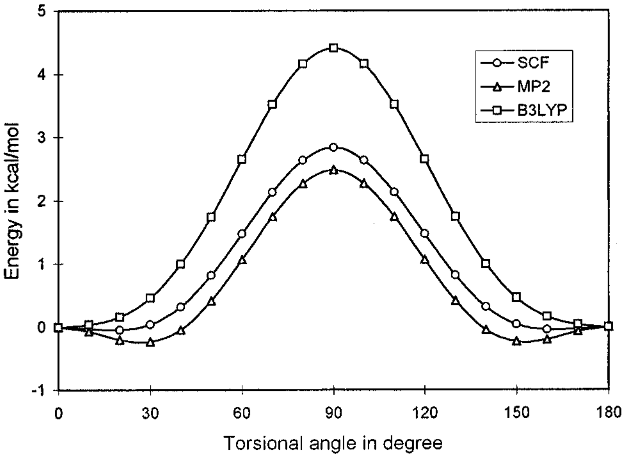

Figure 3. Torsional potential of styrene as obtained with SCF, MP2, and B3LYP methods using the 6-31G(d) basis.

TABLE 3: Energetics of Stationary Points in Styrene Relative to the Planar Conformation[a]

basis set	method	gauche	TS (90°)
6-31G(d)	SCF	−0.04 (19)[b]	2.8
	MP2	−0.24 (27)	2.5
	B3LYP	*c*	4.4
	BLYP	*c*	4.8
6-311++G(d,p)	SCF	−0.02 (15)	2.8
	MP2	−0.60 (33)	2.0
	B3LYP	*c*	3.9

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses. [c] Calculated minimum is planar.

In all cases, the simple Fourier representation (see eq 1) of the torsional potential is sufficiently accurate when using a six-term expansion. As representative examples, the fitted parameters V_1 to V_6 as obtained from SCF, MP2, and B3LYP energies are compiled in Table 2. Apparently, V_2 followed by V_1 shows the largest variations upon changing the calculational method or the basis set. Both are substantially larger within the DFT framework than those originating from the MP2 potential. Actually, a four-parameter representation is already quite accurate considering the small values of V_5 and V_6, which are certainly much smaller than the methodological uncertainties.

Styrene. The computed torsional potentials of styrene are shown in Figure 3. The conformational energies relative to the planar configuration are collected in Table 3. Whereas in agreement with previous ab initio investigations, SCF produces a very shallow, possibly energetically insignificant minimum for a gauche conformation; a distinctly deeper minimum is observed for the MP2 optimized gauche conformation, particu-

TABLE 4: Fitted Potential Parameters for the Single-Bond Torsional Potential of Styrene[a]

method	basis set	V_2	V_4	V_6
SCF	6-31G(d)	2.85	−0.88	−0.01
	6-311++G(d,p)	2.77	−0.81	0
MP2	6-31G(d)	2.51	−1.12	−0.04
	6-311++G(d,p)	2.07	−1.40	−0.09
B3LYP	6-31G(d)	4.41	−0.86	0.1
	6-311++G(d,p)	3.89	−0.79	0.02
exp[b]		3.06	−0.79	0.02

[a] All values in kcal mol^{-1}. [b] Data from ref 34.

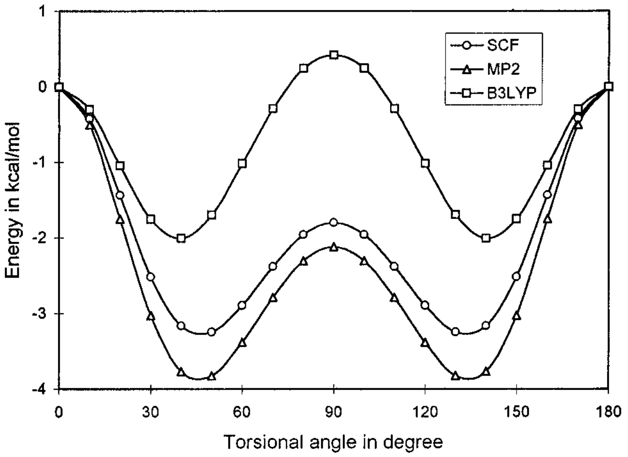

Figure 4. Torsional potential of biphenyl as obtained with SCF, MP2, and B3LYP methods using the 6-31G(d) basis.

larly when applying the larger basis set. Both SCF and MP2 thus render the planar structure formally as a saddle point, whereas the DFT methods predict a minimum for the planar structure. More importantly, however, and in complete analogy to the previously discussed case of butadiene, the barrier at the orthogonal conformation is significantly larger with the DFT approaches than with either SCF or MP2. B3LYP and BLYP barriers amount to 4.4 (3.9 with the larger basis) and 4.8 kcal mol^{-1}, respectively; the SCF and MP2 barriers with 2.8 and 2.5 (2.0 with the larger basis) kcal mol^{-1} are considerably smaller. For the experimental barrier gas-phase and liquid-phase values have been reported,[37] ranging from 1.6 to 4.0 kcal mol^{-1}. The most recent gas-phase values reported are 3.0[34] and 3.3 kcal mol^{-1},[33,38] respectively, and appear to lie midway between MP2 and B3LYP, with the SCF value being fortuitously close to experiment. The fitted potential parameters collected in Table 4 show the expected trends with comparable V_2 parameters from SCF and MP2 and distinctly larger values from B3LYP. In line with the trends in the computed barrier heights, the SCF values of V_2 and V_4 agree best with the experimentally fitted values of Hollas et al.[34] V_6 is already negligible in all cases. According to our recent vibrational studies,[102] the actual conformation of styrene is planar or near-planar in the solution phase, indicating that the effect of the medium can change the equilibrium conformation if the energy difference between the two conformers is small.

Biphenyl. The computed torsional potentials of biphenyl are shown in Figure 4. The conformational energies, again measured relative to the energy of the planar saddle point, are compiled in Table 5. Qualitatively and quantitatively, the difference in the behavior of the torsional potential curves as obtained with different methods is in complete analogy to the previously discussed two cases. Again, the gauche minima turn out to be considerably deeper and somewhat displaced to larger torsional angles (close to 45/135°) within the SCF and MP2 schemes, and the barrier at the orthogonal conformation is obtained much higher with the DFT methods, thus resulting in conflicting predictions as to the relative energies of planar and orthogonal saddle points. Although the experimental electron diffraction investigations on the torsional barrier of biphenyl[47] have been interpreted in terms of a more symmetrical potential curve, i.e., about equal barrier heights for planar and orthogonal saddles, all the previous ab initio calculations performed with and without electron correlation contributions result in distinctly different barrier heigths for the planar and the orthogonal conformations, the former being about twice as large. In agreement with earlier calculations, we obtain barriers between 3.1 and 3.9 kcal mol^{-1} for the planar saddle and 1.2−1.8 kcal mol^{-1} for the orthogonal saddle from SCF and MP2 calculations, whereas the corresponding DFT values range from 1.8 to 2.0 kcal mol^{-1} for the planar saddle and from 1.8 to 2.5 kcal mol^{-1} for the orthogonal saddle, thus inverting the relative energies of the transition points. The larger basis set MP2 calculation has been omitted in that case. However, we may compare with MBPT2 calculations with a large ANO-type basis set by Rubio et al.,[55] who reported 3.2 and 1.6 kcal mol^{-1} for planar and orthogonal saddles, respectively. The fitted torsional parameters are listed in Table 6. We note only a small difference to the parameters obtained from MP2, MP3, and MP4 6-31G(d) calculations performed at SCF optimized geometries reported by Tsuzuki and Tanabe.[53]

TABLE 5: Energetics of Stationary Points in Biphenyl Relative to the Planar Conformation[a]

basis set	method	gauche	TS (90°)
6-31G(d)	SCF	−3.3 (46)[b]	−1.8
	MP2	−3.9 (46)	−2.1
	B3LYP	−2.0 (39)	0.4
	BLYP	−1.8 (39)	0.7
6-311++G(d,p)	SCF	−3.1 (48)	−1.9
	B3LYP	−2.0 (42)	−0.2

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses.

TABLE 6: Fitted Potential Parameters for the Single-Bond Torsional Potential of Biphenyl[a]

method	basis set	V_2	V_4	V_6
SCF	6-31G(d)	−1.46	−2.38	−0.36
	6-311++G(d,p)	−1.64	−2.12	−0.30
MP2	6-31G(d)	−1.67	−2.82	−0.48
B3LYP	6-31G(d)	0.77	−2.13	−0.35
	6-311++G(d,p)	0.10	−1.90	−0.27

[a] All values in kcal mol^{-1}.

B. Heteroaromatic Dimers. *2,2′-Bithiophene.* Among the three dimeric heteroaromatic ring systems discussed in the following, 2,2′-bithiophene may be the most frequently investigated species. Several ab initio SCF[61−64,70] studies of the single-bond torsional potential have already been reported. Additionally, an MP2/6-31G(d)[70] flexible rotor investigation and DFT calculations[73] have already been presented. Despite these efforts, uncertainties in the torsional potential of 2,2′-bithiophene still remain and as we shall see cannot be completely resolved in our investigation.

Selected theoretical flexible rotor torsional potentials as obtained with SCF, MP2, and B3LYP approaches applying 6-31G(d), 6-311++G(d,p), and 6-311G(2d,2p) basis sets are depicted in Figure 5. The corresponding energetic characterization of the stationary points including data from larger sets of DFT calculations is reported in Table 7. Fitted torsional parameters as obtained with SCF, MP2, and B3LYP energies are presented in Table 8. The quantitative and qualitative differences between the torsional potential curves as obtained

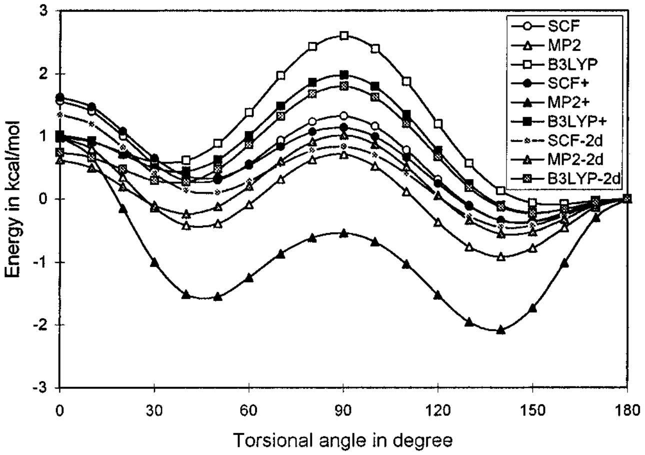

Figure 5. Torsional potential of 2,2′-bithiophene as obtained with various methods and basis sets; open symbols, 6-31G(d); black-filled symbols, 6-311++G(d,p); gray symbols, 6-311G(2d,2p).

TABLE 7: Energetics of Stationary Points in 2,2′-Bithiophene Relative to the Planar Anti Conformation[a]

basis set	method	anti−gauche	TS	syn−gauche	syn
6-31G(d)	SCF	−0.4 (146)[a]	1.3 (89)[b]	0.3 (45)[b]	1.6
	MP2	−0.9 (141)	0.7 (88)	−0.4 (43)	1.0
	B3LYP	−0.1 (157)	2.6 (90)	0.6 (34)	1.0
	BLYP	−0.04 (163)	2.9 (90)	0.6 (31)	0.9
	B3PW91	−0.1 (154)	2.4 (89)	0.5 (35)	1.0
	B3P86	−0.1 (155)	2.6 (89)	0.5 (34)	1.0
	SVWN		4.0 (89)	0.8 (22)	0.9
	BPL	−0.1 (161)	2.5 (90)	0.6 (33)	0.9
	BP86	−0.1 (161)	2.8 (89)	0.6 (32)	1.0
6-311++G(d,p)	SCF	−0.4 (146)	1.1 (88)	0.3 (46)	1.6
	MP2	−2.1 (138)	−0.5 (88)	−1.6 (46)	1.0
	B3LYP	−0.2 (152)	2.0 (89)	0.4 (38)	1.0
	B3PW91	−0.2 (150)	2.0 (89)	0.4 (37)	1.0
	B3P86	−0.2 (150)	2.1 (89)	0.4 (36)	1.0
6-311G(2d,2p)	SCF	−0.4 (144)	0.8 (89)	0.1 (46)	1.3
	MP2	−0.6 (144)	1.0 (89)	−0.2 (40)	0.6
	B3LYP	−0.2 (152)	1.8 (89)	0.3 (35)	0.7
	B3PW91	−0.2 (150)	1.8 (89)	0.2 (36)	0.7
	B3P86	−0.2 (150)	1.9 (89)	0.2 (35)	0.7

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses

TABLE 8: Fitted Potential Parameters for the Single-Bond Torsional Potential of 2,2′-Bithiophene[a]

method	basis set	V_1	V_2	V_3	V_4	V_5	V_6
SCF	6-31G(d)	1.14	0.58	0.34	−1.01	0.06	−0.05
	6-31G(d)[b]	1.17	0.61	0.35	−0.94	0.05	−0.07
	6-311++G(d,p)	1.22	0.38	0.35	−0.94	0.06	−0.05
	6-311G(2d,2p)	1.01	0.22	0.28	−0.90	0.05	−0.06
MP2	6-31G(d)	0.77	0.30	0.12	−1.19	0.03	−0.10
	6-31G(d)[b]	0.80	0.34	0.15	−1.11	0.02	−0.12
	6-311++G(d,p)	0.84	−0.70	0.15	−1.80	0.00	−0.34
	6-311G(2d,2p)	0.50	0.77	0.11	−1.01	0.01	−0.06
B3LYP	6-31G(d)	0.76	2.08	0.19	−1.00	0.01	0.01
	6-311++G(d,p)	0.83	1.48	0.18	−0.97	0.01	−0.01
	6-311G(2d,2p)	0.62	1.44	0.12	−0.91	0.01	−0.01

[a] All values in kcal mol^{-1}. [b] Values reported in ref 68.

from the different methods are again very similar to the cases of the pure hydrocarbons discussed in the previous sections. The qualitative nature of the torsional potentials with syn−gauche and anti−gauche minima, the latter being somewhat more stable, and with syn, anti, and orthogonal transition states is correctly described at all levels of approximation, and this characterization appears to be in agreement with gas-phase[63,67] and liquid-phase[58−60] spectroscopic data.

The energy differences between the planar anti and syn saddles as computed with the different DFT variants and with the MP2 method are essentially identical and do not depend too sensitively on the basis sets applied. We obtain about 1 kcal mol^{-1} with the 6-31G(d) and 6-311++G(d,p) basis sets and 0.6−0.7 kcal mol^{-1} for the 6-311G(2d,2p) basis. The corresponding SCF energy difference is slightly larger (1.3−1.6 kcal mol^{-1}).

However, the minima at the anti−gauche and syn−gauche conformations are significantly deeper within MP2 and SCF schemes, and the energies at the orthogonal transitions state are substantially larger when computed with the DFT methods. The SCF and MP2 results as obtained with the 6-31G(d) basis are in complete agreement with earlier SCF[61,62,64,68,70,71] and MP2[70] calculations. Similarly, our 6-31G(d) DFT calculations agree with the most recent DFT investigations by Viruela et al.,[73] who already noticed the DFT overestimation of rotational barriers.

Turning to the results as obtained with the two larger basis sets, we notice quite substantial modifications with respect to the corresponding 6-31G(d) potential curves. Similar to the butadiene case, each of the three approaches, SCF, B3LYP, and MP2, reacts quite differently upon basis set extension. A particularly strong change is observed with the MP2/6-311++G(d,p) result. The syn−gauche and anti−gauche minima and the barrier between them are lowered by about 1.2 kcal mol^{-1} relative to the MP2/6-31G(d) torsional curve. In contrast, the MP2/6-311G(2d,2p) torsional curve is shifted to higher energies, with the exception of the syn configuration. Overall, the shift is, however, much smaller. For both larger basis sets, the B3LYP barrier at the orthogonal transition state is shifted to lower energies by about 0.6−0.8 kcal mol^{-1}. These comparatively large effects indicate that 2,2′-bithiophene is probably a more complicated case and that still further investigations are necessary to arrive at a sufficiently reliable torsional potential that is useful for spectroscopic predictions.

From the fit parameters collected in Table 8 we observe that a four-parameter representation is sufficient in most cases. Our values for 6-31G SCF and MP2 potentials agree very well with that of Ortí et al.[70] The small differences are attributed to the use of a 10° grid in our case rather than a 30° grid. The strong quantitative changes of the MP2 potential curve upon adding diffuse functions result, however, in large negative V_2 and V_4 parameters. Regrettably, sufficiently refined vapor-phase Raman studies which probe some features of the torsional potential in greater detail and which could result in experimental estimates for V_n are not available for 2,2′-bithiophene.

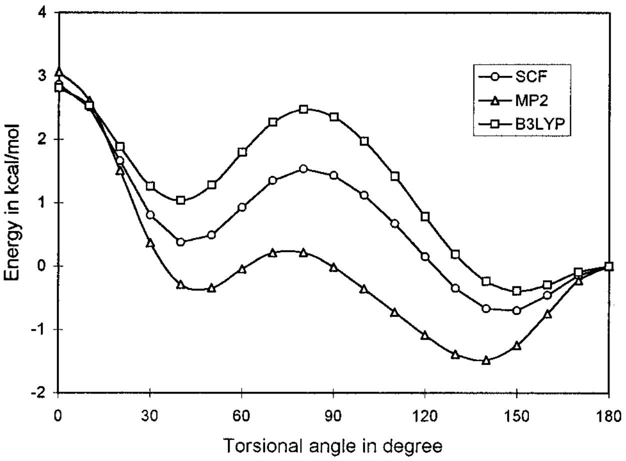

Figure 6. Torsional potential of 2,2′-bipyrrole as obtained with SCF, MP2, and B3LYP methods using the 6-31G(d) basis.

2,2′-Bipyrrole. The computed 6-31G(d) SCF, MP2, and B3LYP torsional potentials are drawn in Figure 6. Stationary point energies relative to the anti saddle are given in Table 9.

TABLE 9: Energetics of Stationary Points in 2,2′-Bipyrrole Relative to the Planar Anti Conformation[a]

basis set	method	anti−gauche	TS	syn−gauche	syn
6-31G(d)	SCF	−0.7 (146)[b]	1.5 (81)[b]	0.4 (42)[b]	2.9
	MP2	−1.4 (138)	0.2 (75)	−0.4 (51)	3.1
	B3LYP	−0.4 (150)	2.5 (81)	1.0 (40)	2.8
	BLYP	−0.3 (152)	2.7 (82)	1.1 (39)	2.7
6-311++G(d,p)	SCF	−0.6 (147)	1.4 (80)	0.6 (44)	3.0
	MP2	−1.8 (137)	−0.3 (74)	−0.8 (47)	3.1
	B3LYP	−0.3 (153)	2.1 (80)	1.1 (41)	2.7

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses.

TABLE 10: Fitted Potential Parameters for the Single-Bond Torsional Potential of 2,2′-Bipyrrole[a]

method	basis set	V_1	V_2	V_3	V_4	V_5	V_6
SCF	6-31G(d)	2.08	0.32	0.44	−1.51	0.35	−0.33
	6-311++G(d,p)	2.22	0.08	0.52	−1.27	0.29	−0.29
MP2	6-31G(d)	2.30	−1.11	0.33	−1.68	0.44	−0.43
	6-311++G(d,p)	2.26	−1.59	0.37	−1.74	0.41	−0.56
B3LYP	6-31G(d)	2.23	1.20	0.26	−1.36	0.32	−0.25
	6-311++G(d,p)	2.19	0.87	0.30	−1.12	0.24	−0.23

[a] All values in kcal mol^{-1}.

In contrast to the previous case, extension of the basis set from 6-31G(d) to 6-311++G(d,p) results in comparatively modest modifications of the computed torsional potentials. MP2 and B3LYP potential curves are shifted to slightly lower energies. At all levels of description and in agreement with previous ab initio investigations,[75,76] the anti−gauche conformation is the energetically preferred structure of 2,2′-bipyrrole. The full geometry optimizations performed in this work lead to substantial energy lowerings for the nonplanar structures, i.e., in the region around the syn−gauche and anti−gauche minima and for the barrier between them. As with the bithiophene case discussed above, with the exception of the planar configurations the MP2 torsional potential is considerably below the SCF curve, whereas the B3LYP torsional potential is always above.

The fit parameters are collected in Table 10. The analytic representation in the vicinity (±20°) of the high-lying syn saddle is actually not very good. Bipyrrole is the only molecule in this study for which such fitting problems occurred. The deviations amount to a few tenths of a kcal mol^{-1}. This behavior is due to a strong coupling of the single-bond torsion to an out-of-plane movement (about 15°) of the hydrogen atoms connected to the N−H groups, which in turn is caused either by too close steric contact and/or repulsive electrostatic contributions. The flexible rotor curve with full geometry optimization is thus not well represented by a pure 1D torsion. An indication for that can also be found in the comparatively large values for V_5 and V_6.

2,2′-Bifuran. The theoretical torsional potentials are depicted in Figure 7; the corresponding energetic characterization of the stationary points and the fit parameters are reported in Tables 11 and 12. The SCF results are in good agreement with the only previous ab initio investigation available.[77] With all methods and basis sets considered the planar anti conformation is the global minimum. Compared to the previous five cases, bifuran behaves differently insofar as the SCF and DFT curves are largely identical over a wide range and differ only in the region close to the syn configuration. The MP2 energies agree with the DFT energies at the planar configurations only, whereas the MP2 barrier at the orthogonal configuration is considerably lower (by about 2.5 kcal mol^{-1}). Hence, the entire torsional potential is more flat in the MP2 case. Only with MP2 a distinct minimum is obtained for the syn−gauche structure, reminiscent of the styrene case discussed above. With the 6-311++G(d,p) basis the MP2 barrier at the orthogonal transition state and the energy of the syn−gauche conformation are lowered, whereas in the B3LYP case only the barrier is lowered. As with bipyrrole and bithiophene, there are no detailed vapor-phase spectroscopic investigations available which could give hints to the shape of the torsional potential.

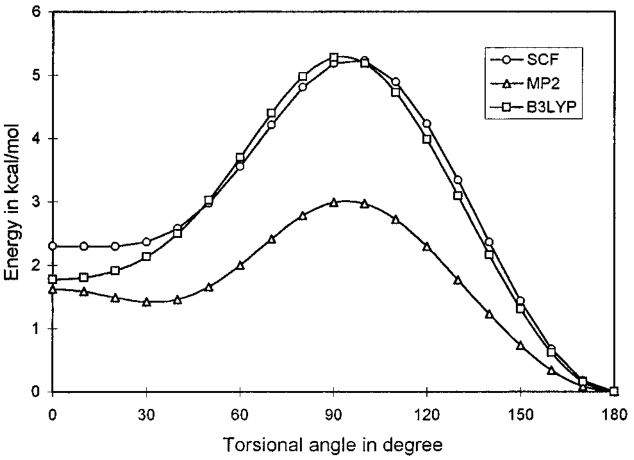

Figure 7. Torsional potential of 2,2′-bifuran as obtained with SCF, MP2, and B3LYP methods using the 6-31G(d) basis.

TABLE 11: Energetics of Stationary Points in 2,2′-Bifuran Relative to the Planar Anti Conformation[a]

basis set	method	TS	syn−gauche	syn
6-31G(d)	SCF	5.2 (98)[b]		2.3
	MP2	3.0 (94)	1.4 (30)[b]	1.6
	B3LYP	5.3 (92)		1.8
	BLYP	5.2 (91)		1.7
6-311++G(d,p)	SCF	5.1 (98)		2.5
	MP2	2.4 (95)	1.0 (37)	1.6
	B3LYP	4.8 (94)		1.8

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses.

TABLE 12: Fitted Potential Parameters for the Single-Bond Torsional Potential of 2,2′-Bifuran[a]

method	basis set	V_1	V_2	V_3	V_4	V_5	V_6
SCF	6-31G(d)	1.08	4.02	1.22	−0.37	0.01	0.02
	6-311++G(d,p)	1.09	3.76	1.36	−0.24	0.01	0.01
MP2	6-31G(d)	0.84	2.16	0.74	−0.38	0.04	0.01
	6-311++G(d,p)	0.82	1.64	0.73	−0.48	0.07	−0.09
B3LYP	6-31G(d)	0.97	4.34	0.78	−0.40	0.02	0.05
	6-311++G(d,p)	0.90	3.87	0.85	−0.28	0.02	0.04

[a] All values in kcal mol^{-1}.

C. Nonconjugated Systems. *n-Butane and 1-Butene.* These two molecules and 1,3-butadiene have repeatedly been used to discuss the characteristic differences in the torsional potentials of conjugated and nonconjugated systems.[20,27] We have included *n*-butane and 1-butene in our study merely to show that in the case of typical nonconjugated systems one does not encounter such large differences between conventional ab initio and DFT torsional potentials. We show our computed torsional potentials for these two molecules in Figures 8 and 9. The detailed stationary point energetics is shown in Tables 13 and 14. It is immediately visible that contrary to previously discussed cases with conjugated molecules all the theoretical torsional potentials are qualitatively and even quantitatively very similar, indeed. For both molecules the DFT curves are very close to the SCF and MP2 data, the differences between MP2 and B3LYP not exceeding 0.4 kcal mol^{-1}. These observations probably imply that the discrepancies in describing the partial double-bond breaking of conjugated single-bond by internal

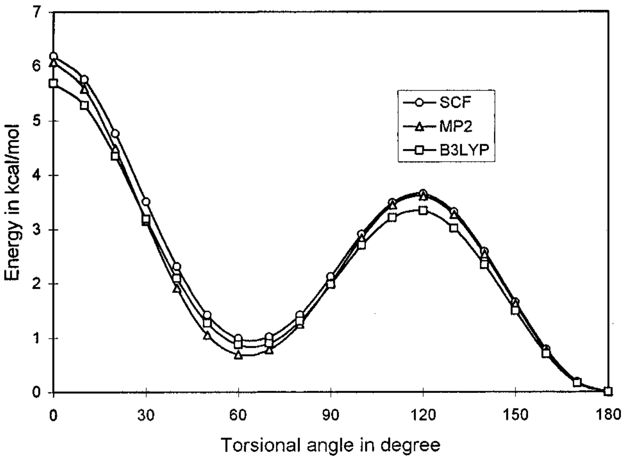

Figure 8. Torsional potential of *n*-butane as obtained with SCF, MP2, and B3LYP methods using the 6-31G(d) basis.

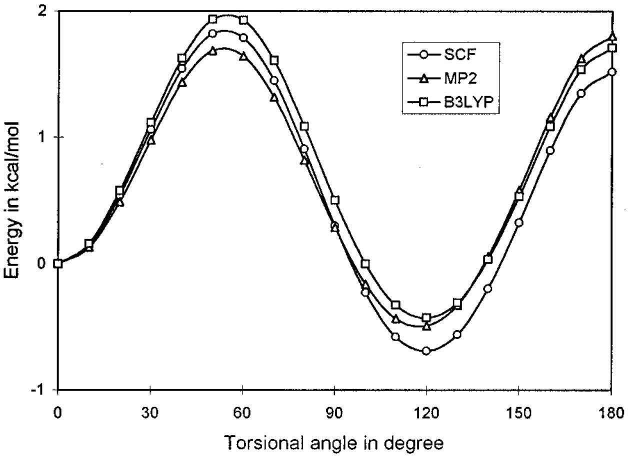

Figure 9. Torsional potential of 1-butene as obtained with SCF, MP2, and B3LYP methods using the 6-31G(d) basis.

TABLE 13: Energetics of Stationary Points in Butane Relative to the Anti Conformation[a]

basis set	method	TS	gauche	syn
6-31G(d)	SCF	3.7 (119)[b]	1.0 (65)[b]	6.2
	MP2	3.6 (119)	0.7 (63)	6.1
	B3LYP	3.3 (118)	0.9 (64)	5.7
	BLYP	3.2 (118)	0.9 (64)	5.6
6-311++G(d,p)	SCF	3.6 (119)	1.0 (66)	6.3
	MP2	3.4 (120)	0.5 (63)	6.0
	B3LYP	3.2 (119)	0.9 (65)	5.7
	BLYP	3.1 (119)	0.9 (66)	5.6

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses.

TABLE 14: Energetics of Stationary Points in 1-Butene Relative to the Syn Conformation[a]

basis set	method	gauche	skew	anti
6-31G(d)	SCF	1.8 (52)[b]	−0.7 (120)[b]	1.5
	MP2	1.7 (53)	−0.5 (118)	1.8
	B3LYP	1.9 (54)	−0.4 (119)	1.7
	BLYP	1.8 (52)	−0.5 (120)	1.6
6-311++G(d,p)	SCF	2.0 (55)	−0.7 (121)	1.5
	MP2	1.6 (54)	−0.5 (117)	1.9
	B3LYP	2.0 (55)	−0.4 (121)	1.6

[a] All values in kcal mol^{-1}. [b] Optimized torsional angle in parentheses.

rotation between DFT and MP2 results are mainly due to differences in describing the effects of conjugation rather than those of the van der Waals repulsions between nonbonded hydrogens.

Summary and Conclusions

We have presented a large-scale systematic study of the single-bond torsional potentials in comparatively simple conjugated systems which represent also the dimeric building blocks of conjugated polymers forming an important class of compounds: organic metals. We have also investigated the influence of basis set extension beyond basis set sizes previously used for these molecules and have analyzed the performance of some of the recently developed DFT methods in comparison with the more conventional SCF and MP2 techniques.

The main issue of this investigation is that, irrespective of the system considered and quite independent of the basis sets applied, the electron correlation corrections to the torsional potential curve as obtained with either the DFT methods or within the framework of MP2 have *different signs*. The MP2 torsional potential curves ran mostly distinctly below the corresponding SCF curves, whereas the DFT curves are almost always above.

Adding diffuse functions consistently lowers most of the torsional potential curves. The effect is strongest for the barriers around the orthogonal configurations, and classified by systems, the most sensitive case is 2,2′-bithiophene. The relative energetics of the planar syn and anti configurations, however, is hardly modified for all systems considered. For these planar configurations the energy predictions of MP2 and DFT methods agree quite well. The still sizable basis set effects, however, point to the need for still more extended calculations, particularly also probing the effects beyond MP2.

Among the different types of DFT variants, B3LYP and the closely related B3P86 and B3PW91 approaches yield the best and, moreover, also almost identical results, whereas SVWN shows the largest deviations. These observations imply that the gradient corrected exchange-correlation functionals, especially incorporated with the exact exchange, are more accurate than local density approximations for total energy calculations.

Besides diagnosing the different behavior of the MP2 and DFT methods, we have also compared our computed torsional potentials to experimental data, where available: for butadiene and styrene. MP2 and even the uncorrelated SCF proved to be superior to all variants of DFT studied here.

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