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Anchoring the Torsional Potential of Biphenyl at the ab Initio Level: The Role of Basis Set versus Correlation Effects

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Abstract: The torsional profile of biphenyl has been calculated by means of quantum-chemical perturbations and coupled-cluster methods of increasing accuracy. The performance of the various theoretical approaches has been assessed through a critical comparison with experimental barrier heights. The theoretical data indicate that the basis set effects become more critical than the correlation effects beyond the perturbational MP4 or variational CCSD(T) levels of theory to obtain the most accurate results. We also discuss the various additional corrections that would be required beyond the scope of our study to provide the best match to the experimental results.

1. Introduction

Considerable efforts have been devoted in recent years to the determination of the torsional potential of biphenyl at various levels of theory.[1−8] Biphenyl is an attractive model compound to study both the conformational changes induced by the interplay between π-conjugation and steric effects and by extension the relationship between conformations and electronic and optical properties. Torsions between conjugated rings dictate the nature of the emission and absorption spectra of many organic conjugated oligomers and polymers;[9,10] a planarization of the backbone, induced for instance by packing effects in the solid state, typically shifts the spectra to the red due to the increased overlap between the π-electronic clouds of the neighboring monomer units. Such torsions also play a significant role in determining the fluorescence quantum yield of conjugated chains[11] and the occurrence of intersystem crossing processes[12] as well as the shape of vibronic progressions in absorption and emission spectra.[13] The torsional potentials obtained by different quantum-chemical approaches may vary significantly de-

pending on the choice of the basis set and the correlation treatment. Severe deviations from experimental data can further be encountered in force fields used for molecular mechanics and molecular dynamics simulations. The torsional terms in current force fields are usually derived from experiment for model systems; the transferability assumption underlying the development of a force field might however fail for related systems, in particular in the presence of small torsional barriers; this has been illustrated in the case of biphenyl.[14,15] The development of a torsional profile for biphenyl fitted from accurate quantum-chemical calculations is thus highly desirable for force field simulations in order to reduce the uncertainties inherent to a large number of modern molecular modeling tools.

It is well-established experimentally[16−18] that the gas-phase barriers (ΔE) separating the global minimum ($\phi = 44.4° \pm 1.2°$) from the planar ($\phi = 0°$) and perpendicular ($\phi = 90°$) conformations are very similar and are on the order of 1−2 kcal/mol. The widely used "chemical accuracy" criterion (defined as ± 1 kcal/mol of uncertainty with respect to the experimental results) is clearly not relevant for such small energy barriers. A more stringent "calibration accuracy" (± 1 kJ/mol $= 0.24$ kcal/mol) will thus be sought here by using a well-defined hierarchy of correlated ab initio methods

together with a carefully selected molecular orbital expansion that converges systematically toward the infinite basis set limit. The computational strategy that we have adopted relates somehow to the composite methods recently introduced to provide highly accurate results in the subchemical accuracy range: (i) the Gaussian-n (G-n) family of methods;[19,20] (ii) the focal point analysis (FPA);[21-25] (iii) the Weizmann-n (W-n) protocols;[26-28] and (iv) the HEAT method.[29] The main features of our alternative approach are as follows: (i) the absence of empirical corrections; (ii) the use of extrapolation techniques to reach both the asymptotic basis set and the correlation energy limits; and (iii) the applicability to medium-size conjugated systems without significant loss in accuracy. Density Functional Theory (DFT)[30-33] is known to behave erratically when high accuracy is required for conjugated systems[34-36] due to the fact that current exchange functionals overstabilize π-conjugation in planar conformers and hence provide overestimated energy barriers. A systematic study is thus always recommended when DFT is chosen in view of its reduced computational cost. It is the goal of this contribution to define, on the basis of our previous experience,[37-42] a generally applicable model to calculate accurately the torsional potential of biphenyl. This model could then be applied to other archetypal systems which constitute the building blocks of widely studied conjugated polymers.

2. Theoretical Methods

We have first performed a full optimization of the structure of each conformer for a wide range of dihedral angles, thus dealing explicitly with $3N - 7$ degrees of freedom. A regular and rather tight grid (step of $10°$ between $0°$ and $180°$) has been considered for the torsion angle ϕ between the two phenyl rings. Hartree−Fock (HF) and Møller−Plesset perturbation theory methods (up to the second order, MP2) involving large basis sets (several hundreds of basis functions) have been employed for these geometry optimizations. The energy of each conformer has been further corrected by applying higher-order valence correlation schemes at the MP4 (Møller−Plesset up to the fourth order), CCSD (Coupled Cluster method with Single and Double excitations), and CCSD(T) (with perturbatively estimated triple excitations) levels with the largest possible basis set. The energy difference E_{CC} between the full configuration interaction limit (FCI) and our most accurate results can be estimated by means of a continued fraction (cf) extrapolation as[43]

$$E_{CC} = \cfrac{\delta_1}{1 - \cfrac{\delta_2}{1 - \cfrac{\delta_3}{\delta_2}}} \qquad (1)$$

where $\delta_1 = E_{HF}$, $\delta_2 = E_{CCSD} - E_{HF}$, and $\delta_3 = E_{CCSD(T)} - E_{CCSD}$. CC-based multiplicative approaches[44] are not used here since torsional barriers are derived from energy differences that are better described with continued fractions. The use of MP and CC correlated techniques, although computationally very demanding and strongly basis set dependent, is the only way to ensure the targeted high accuracy.

The infinite basis set limit can be estimated by using the n-tuple cc-pVnZ basis sets[45] which systematically approaches completeness as n grows. The extrapolation of the cc-pVnZ sequence ($n =$ double, triple, quadruple, ...) is done with the function

$$E(n) = E(\infty) + Af(n) \qquad (2)$$

where $f(n)$ is written as n^{-5} [46,47] or n^{-3} [48] for the HF and for the MP2 correlation energy, respectively; $E(\infty)$ is the corresponding extrapolated energy, and A is the parameter to be fitted. Note that the use of power expansions is nowadays preferred to exponential ones.[49] When the pair of cc-pVnZ/cc-pV(n+1)Z results required to eliminate A from eq 2 is not available for computationally demanding systems, the extrapolation can still be applied in the framework of a method-dependent slightly modified model[50]

$$E_c(n) = E_c(\infty)\{1 - 2.4n^{-3}[a + be^{-2.4b} + c]n^{-1}\} \qquad (3)$$

where a new set of optimal parameters (a, b, and c) is included; their values can be extracted from ref 50.

Since the zero-point vibrational energies (ZPVE) are different going from the global minimum to the planar or to the perpendicular conformations,[51] such corrections must be explicitly taken into account to estimate the energy barriers. We have thus computed here ZPVE-corrected barriers to allow for the most relevant comparison with the experimental results. Other contributions such as the explicit coupling of vibrational modes, scalar relativistic effects, spin−orbit coupling, or diagonal corrections to the Born−Oppenheimer approximation are not considered in the present work since their impact on the torsional potentials is expected to be negligible.[21,52]

Perturbative approaches or truncated CC methods can fail in producing highly accurate results if the starting single determinant HF wave function is not reliable for the system under study. For the whole range of torsions, the CCSD/cc-pVDZ-calculated low value (0.01) of the T_1 diagnostic,[53-55] which was specifically designed to provide an indication of the quality of the results, did not advise us to use more than a single determinant to generate the manifold of excitations; multireference versions of the CC theory[56] are thus not needed. Moreover, a previous study including nondynamical correlation effects[57] through a multiconfigurational second-order perturbation treatment (CASPT2) provided barrier heights comparable to the monoconfigurational treatment, thus indicating that a single-reference wave function is also an adequate starting point for MP2 calculations. All the results described in this manuscript have been obtained with the Gaussian98[58] and Gaussian03[59] packages.

3. Results and Discussion

3.1. Geometry Optimizations and Zero-Point Vibrational Energy Corrections. Each of the stationary points (i.e., the global twisted minimum as well as the planar and perpendicular conformations) of the torsional profile has been optimized using the HF, MP2, and the B3LYP-based DFT

Table 1. Calculated Bond Lengths (in Å) and Bond Angles (in deg) for Biphenyl[a] as Obtained at Different Levels of Theory and with Different Basis Sets
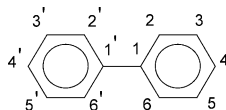
		cc-pVDZ			cc-pVTZ		
	exp[b]	HF	B3LYP	MP2	HF	B3LYP	MP2
$C_1-C_{1'}$	1.507	1.493	1.482	1.485	1.489	1.482	1.473
C_1-C_2	1.404	1.395	1.407	1.413	1.389	1.399	1.400
C_2-C_3	1.395	1.387	1.396	1.404	1.381	1.388	1.392
C_3-C_4	1.396	1.388	1.398	1.406	1.382	1.390	1.394
C–H	1.102	1.082	1.092	1.095	1.073	1.082	1.082
$C_2-C_1-C_6$	119.4	118.3	118.0	118.7	118.3	118.0	118.5
$C_1-C_2-C_3$	119.9	120.9	121.0	120.7	120.9	121.0	120.8
$C_2-C_3-C_4$	120.9	120.3	120.3	120.2	120.3	120.3	120.2
$C_3-C_4-C_5$	119.0	119.4	119.4	119.6	119.4	119.4	119.6
$C_{2'}-C_{1'}-C_1-C_2$	44.4	46.3	39.3	42.1	45.0	39.6	39.7

[a] See chemical structure on top for site labeling. [b] Taken from ref 17.

method[60] with the cc-pVDZ and cc-pVTZ basis sets. The cc-pVQZ basis set could be applied only at the HF level. Table 1 shows the comparison between the geometric parameters experimentally derived from gas-phase electron diffraction data[17] and the corresponding calculated values for the global twisted minimum. Systematic deviations between the vibrationally averaged experimental bond lengths (r_g) and the calculated equilibrium values (r_e) have always to be considered for a detailed comparison: r_g values are about 0.004−0.009 Å and 0.014−0.018 Å longer than r_e for C−C and C−H bonds, respectively.[61] Differences in bond angles are assumed to be negligible. In general, we find that the bond lengths decrease with the extension of the basis set and increase when electron correlation is introduced. This is not the case for the $C_1-C_{1'}$ bond length for which the largest error is found, as previously reported;[62,63] the experimental uncertainty on this parameter is, however, expected to be large. Very small differences are found for the bond angles among the different methods. All together, the MP2 results can be judged as slightly more accurate than the B3LYP values. Whereas a cc-pVTZ basis set is considered to be converged for a DFT calculation,[64−68] this does not hold true for the MP2 method. A practical scheme for extrapolating the geometric parameters calculated with a sequence of cc-pVnZ basis sets has been proposed[69] though being severely questioned.[70] Accordingly, no attempt has been made here to account for this basis set effect, and the MP2/cc-pVTZ-optimized geometries have been used as a starting point for the subsequent energetic corrections. Extrapolated torsional angles are obtained when needed by means of a splines treatment.

In our study, B3LYP was the only affordable technique to calculate with a cc-pVTZ basis set the frequencies of the stationary points and the resulting ZPVE correction. The assignment of the fundamental vibrational frequencies of biphenyl has been, however, repeatedly studied in the literature[71] and will not be discussed here. We have accounted for anharmonic corrections to the harmonic zero-point

vibrational energies by scaling them by a factor of 0.985, as suggested in ref 26. The scaled values of the ZPVE for the global minimum and the planar and perpendicular conformations are 112.09, 112.08, and 111.85 kcal/mol, respectively, at the B3LYP-cc-pVTZ level; this leaves almost unaltered the barrier ΔE^0 between the global minimum and the planar conformation and decreases the barrier ΔE^{90} by roughly 0.2 kcal/mol with respect to the ZPVE-uncorrected value. All curves presented in the following will be corrected with this B3LYP/cc-pVTZ-derived values. Note that this correction will also slightly modify the torsion angles with respect to the optimized values listed in Table 1.

3.2. Electron Correlation Effects. One open question in view of the scarcity of literature results is to elucidate whether treatments of the electron correlation beyond the MP2 level may substantially change the barrier heights for a given basis set. We have collected in Table 2 the HF, MP, and CC barriers calculated with the cc-pVDZ basis sets. The MP2 method slightly decreases the ΔE^0 value compared to the uncorrelated HF level (by about 0.1 kcal/mol) but, most importantly, largely increases ΔE^{90} by 0.5 kcal/mol to make it more consistent with the experimental value. MP4 calculations further point to the role of electron correlation effects for the ΔE^0 barrier; the difference between the MP2 and HF values is a few times smaller than between the MP4 and MP2 results. The impact is less pronounced for ΔE^{90} which is very similar at the MP2 and MP4 levels. The CCSD and CCSD(T) calculations provide consistent numbers, with the CCSD(T) value lying close to that obtained with MP4. This nicely reflects the parallel convergence of the two sequences of methods [HF → MP2 → MP4 versus HF → CCSD → and CCSD(T)] toward the exact solution.

The use of the continued fraction technique further demonstrates this convergence process, as illustrated in Table 3. This approach has been recently applied to both thermochemical data[72−76] and rotational barriers[77] but not without warnings about a possible erratic behavior.[28,72] Although the formula given in eq 1 was originally derived to assess the

Table 2. ZPVE-Corrected Relative Energies (in kcal/mol) between the Global Twisted Minimum (Characterized by the Torsion Angle ϕ) and the Planar (ΔE^0) and Perpendicular (ΔE^{90}) Conformations in Biphenyl, as Calculated with Different Approaches

method	ϕ	ΔE^0	ΔE^{90}
HF/cc-pVDZ	48.7	3.10	1.15
HF/cc-pVTZ	47.5	2.97	1.24
HF/cc-pVQZ	47.5	2.99	1.25
HF/cc-pV∞Z	47.5	2.99	1.26
MP2/cc-pVDZ	45.5	3.02	1.63
MP2/cc-pVTZ	41.2	2.39	2.04
MP2/cc-pV∞Z	39.8	2.19	2.26
CCSD/cc-pVDZ[a]	46.6	2.76	1.35
CCSD/cc-pV∞Z[a]	44.3	2.61	1.62
MP4/cc-pVDZ[a]	45.1	2.70	1.59
MP4/cc-pV∞Z[a]	42.1	2.56	1.97
CCSD(T)/cc-pVDZ[a]	45.5	2.67	1.51
CCSD(T)/cc-pV∞Z[a]	42.6	2.51	1.85
exp[b]	44.4 ± 1.2	1.4 ± 0.5	1.6 ± 0.5

[a] From the MP2/cc-pVTZ optimized geometry. [b] Taken from ref 17.

Table 3. ZPVE-Corrected Relative Energies (in kcal/mol) between the Global Twisted Minimum (Characterized by the Torsion Angle ϕ) and the Planar (ΔE^0) and Perpendicular (ΔE^{90}) Conformations in Biphenyl, as Calculated at Different Levels of Theory with the cc-pVDZ Basis Set

method	ϕ	ΔE^0	ΔE^{90}
HF	48.7	3.10	1.15
MP2	45.5	3.02	1.63
MP4	45.1	2.70	1.59
MP-cf	45.0	2.63	1.58
CCSD	46.6	2.76	1.35
CCSD(T)	45.5	2.67	1.51
CC-cf	45.4	2.66	1.53
exp[a]	44.4 ± 1.2	1.4 ± 0.5	1.6 ± 0.5

[a] Taken from ref 17.

difference between CCSD(T) and the full CI limit, it has been also used here to extrapolate the MP4 energies since the MP and CC sequences of methods have much in common. Quadratic approximants of MP series[78] have not been investigated. Moreover, no attempt has been made to justify the validity of eq 1 for the MP sequence; its use appears to be justified on an empirical basis by observing the smooth convergence of the calculated barrier heights. We stress, however, that the prerequisites for a coherent evolution ($\delta_1 \gg \delta_2 + \delta_3$, and $\delta_2 \gg \delta_3$; where $\delta_1 = E_{HF}$, $\delta_2 = E_{MP2} - E_{HF}$, and $\delta_3 = E_{MP4} - E_{MP2}$) are fulfilled by the MP series. Analysis of Table 3 reveals that the impact of the approximations made in our methods on the barrier heights is very small. The approximate FCI/cc-pVDZ values are estimated to be 2.6–2.7 kcal/mol and 1.5–1.6 kcal/mol for ΔE^0 and ΔE^{90}, respectively, while the corresponding experimental values are around 1.4 and 1.6 kcal/mol. Basis set effects thus appear to be the root of the well-documented problem of obtaining highly accurate barrier heights with ab initio methods.

3.3. Basis Set Effects. The previous section suggests that augmenting the size of the basis set is more crucial than going beyond MP4 or CCSD(T) for the correlation treatment. However, the computational limits are easily reached if no restrictions are imposed on the number of unoccupied orbitals involved to generate the manifold of excitations (N_u). Since the MP4 and CCSD(T) methods scale as $N_o^3 \times N_u^4$ (with N_o being the number of occupied orbitals), the extension of the basis set size typically leads to a strong increase in N_u and hence to unaffordable computational requirements. Accordingly, we will exploit in the following the systematic convergence of correlation consistent basis sets with the help of eqs 2 and 3 to overcome this problem. Other extrapolation schemes have been proposed[79–81] but usually yield marginal improvements in the torsional potentials and energy barriers.[40,41]

The corresponding extrapolated results are reported in Table 2 where cc-pV∞Z refers to HF, MP, or CC results after estimation of the basis set limit. The extrapolated energy associated with a given correlation treatment has been added here to the separately extrapolated HF/cc-pV∞Z energy. The ΔE^0 and ΔE^{90} barriers calculated at the HF level do not largely depend on the basis set; the cc-pVTZ results can be actually be considered as nearly converged. The well-known slower convergence of correlated electronic structure calculations is clearly observed at the MP2 level where both energy barriers markedly evolve with the size of the basis set; ΔE^0 decreases from 2.39 to 2.19 kcal/mol, whereas ΔE^{90} increases from 2.04 to 2.25 kcal/mol going from cc-pVTZ to the basis set limit. These results are in good agreement with those previously reported by Tsuzuki et al.[2] The same trends are also observed with the MP4, CCSD, and CCSD(T) results; this gives us confidence in the fitting procedure done in eq 2 and shows uniformly the slightly larger dependence of ΔE^{90} with respect to the size of the basis set. Considering the residual effects associated with the truncation of the MP or CC series, as detailed in the previous section, optimal FCI/cc-pV∞Z values of 2.5 kcal/mol and 1.9–2.0 kcal/mol are obtained for the ΔE^0 and ΔE^{90} barriers, respectively. Unexpectedly, the "calibration accuracy" is still not matched for the ΔE^0 barrier. Additional possible contributions to the torsional potentials will thus be carefully explored in the next section to try and solve this discrepancy. Figures 1 and 2 display the CC and MP torsional energy profiles obtained when the above-mentioned corrections (continued fraction extrapolation to the FCI limit and basis set extrapolation to the infinite basis set limit) are included. The cc-pVDZ curves are also illustrated for sake of completeness.

3.4. Additional Factors. The MP and CC calculations described so far have been routinely performed within the frozen-core approximation, i.e., the lower lying 1s orbitals of carbon were not correlated. Although core correlation effects are expected to modify the barriers by less than 0.1 kcal/mol, it is necessary to account for both core–core (intrashell 1s) and core-valence (intershell 1s – 2s2p) correlation effects to attain a definitive set of results. We have thus investigated the impact of the highly computationally expensive inner-shell correlation effects at the MP2 level by using the recently introduced weighted core-valence
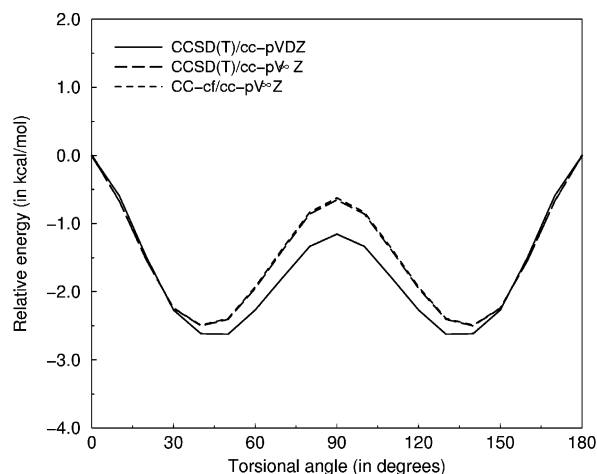
Torsional Potential of Biphenyl

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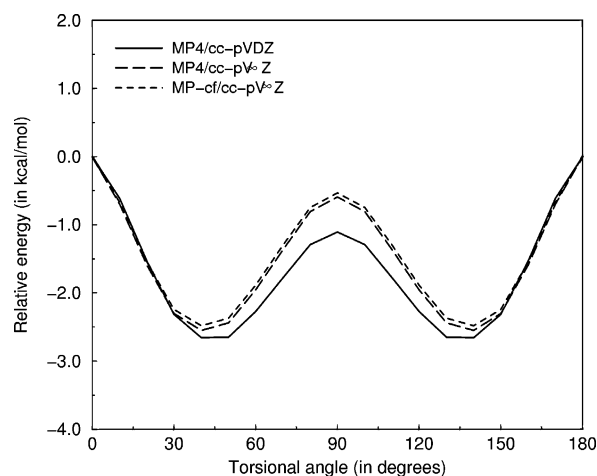**Figure 1.** Torsion potential of biphenyl calculated at different levels of CC theory.

Figure 2. Torsion potential of biphenyl calculated at different levels of MP theory.

Table 4. ZPVE-Corrected Relative Energies (in kcal/mol) between the Global Twisted Minimum (Characterized by the Torsion Angle ϕ) and the Planar (ΔE^0) and Perpendicular (ΔE^{90}) Conformations in Biphenyl, as Calculated at the MP2 Level with Different Basis Sets

method	ϕ	ΔE^0	ΔE^{90}
MP2/cc-pVDZ	45.5	3.02	1.63
MP2/cc-pwCVDZ	45.8	3.10	1.60
MP2/aug-cc-pVDZ	46.4	2.46	1.52
MP2/cc-pVTZ	41.2	2.39	2.04
exp[a]	44.4 ± 1.2	1.4 ± 0.5	1.6 ± 0.5

[a] Taken from ref 17.

basis set (cc-pwCVDZ[82] compared to the former cc-pCVDZ[83]). Table 4 reports the corresponding results. The difference between the all-electron (cc-pwCVDZ) and valence-only (cc-pwCVDZ) energy barriers provides an estimate of the amplitude of the core correlation effects for a given basis set. The extrapolation of these results provides barrier heights that are negligibly modified compared to the extrapolated frozen core value: both barriers are increased by less than 0.01 kcal/mol. When this correction is taken into account,
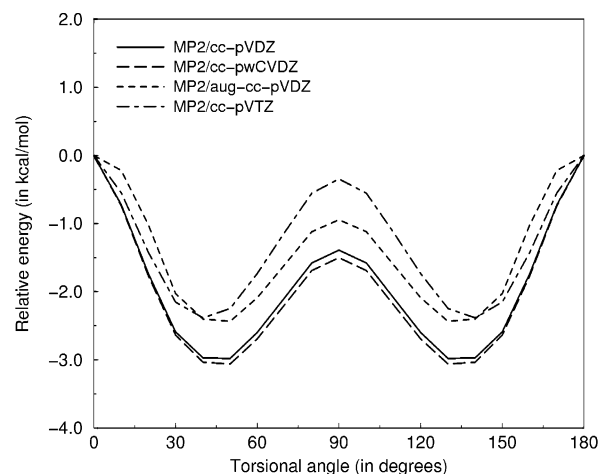

Figure 3. Torsion potential of biphenyl calculated at the MP2 level with different basis sets.

all-electrons FCI/cc-pV∞Z barrier heights of 2.5 kcal/mol and 1.9−2.0 kcal/mol are still obtained for ΔE^0 and ΔE^{90}, respectively.

On the other hand, the use of diffuse functions (aug-cc-pVDZ) helps the ΔE^0 barrier to converge toward the higher levels of the hierarchy, as evidenced in Table 4. However, the dihedral angle is found to increase and the ΔE^{90} barrier to be reduced in this case, in marked contrast with the trends found when a complete set of polarization functions is added (going for instance from cc-pVDZ to cc-pVTZ). The $C_1-C_1{}'$ distances in the 90° conformer (1.4915, 1.4924, and 1.4802 Å for the cc-pVDZ, aug-cc-pVDZ, and cc-pVTZ basis set, respectively) demonstrate that the underestimation of the π-conjugation effects by the aug-cc-pVDZ basis set is at the origin of this discrepancy, in agreement with the results obtained for other conjugated molecules.[41] The aug-cc-pVTZ basis set should probably improve the description of these effects; however, the requested compromise between accuracy and computational cost precludes the use of the aug-cc-pVnZ extension, thus favoring the cc-pVnZ sequence in conjunction with the extrapolation scheme. The deviations between these various approaches are further illustrated through the corresponding torsional profiles depicted in Figure 3.

It has also been suggested that the cc-pVDZ basis set underestimates the dispersion interactions and hence the stability of the coplanar conformer of biphenyl;[2] this translates into an overestimation of ΔE^0 compared to ΔE^{90}. The employed extrapolation technique can hardly overcome this intrinsic deficiency of the cc-pVDZ basis functions. To evaluate the amplitude of this effect, the impact of an additional set of polarization d-type functions on the hydrogen atoms[84] has been analyzed; the imposed contraction [C/H] scheme thus becomes at this stage [3s2p/2s1p1d] instead of the standard one. As expected, multiple polarization functions on the hydrogen atoms reduce ΔE^0 (ΔE^{90}) by 0.4 (0.2) kcal/mol, while the dihedral angle increases by a few degrees due to the exaltation of nonbonding interactions. All-electrons hydrogen d-polarized FCI/cc-pV∞Z values of 2.1−2.2 kcal/mol and 1.7−1.8 kcal/mol are obtained for the

Table 5. Expansion Coefficients (in kcal/mol) for the Analytical Torsional Potential of Biphenyl Fitted from the Extrapolated HF/cc-pV∞Z and the Most Accurate MP and CC Results[a]

method	V_2	V_4	V_6	V_8	V_{10}	V_{12}
HF	−1.301	−2.096	−0.3760	−0.1575	−0.0464	−0.0251
MP[b]	0.0332	−2.142	−0.3938	−0.2462	−0.1193	−0.0945
CC[c]	−0.0923	−2.112	−0.3916	−0.2428	−0.1174	−0.0931

[a] The odd terms are zero for symmetry reasons. [b] All-electrons MP-cf/cc-pV∞Z results. [c] All-eleectrs CC-cf/cc-pV∞Z results.

ΔE^0 and ΔE^{90} barriers. This basis set engineering should be treated however with much caution.[85]

3.5. Analytical Torsional Functions. The point-wise calculated torsion energies can be fitted to a Fourier-like expansion of the form

$$V(\phi) = \frac{1}{2}\sum_{n=1}^{m} V_n[1 - \cos n(180 - \phi)] \qquad (4)$$

where V_n are the expansion coefficients to be determined. Since such a potential energy function $V(\phi)$ is virtually included in all current force fields, it is of interest to determine the coefficients required to best match our ab initio results. This has been done for an expansion up to the sixth order from HF/cc-pV∞Z and all-electrons basis set extrapolated MP-cf and CC-cf results (see Table 5).

4. Summary and Perspectives

A thorough study of the gas-phase torsional potential of biphenyl has been performed at the ab initio level to determine the role of correlation versus basis set effects in the search of the most accurate results. Our approach involves primarily hierarchical calculations at the MP or CC levels, followed by an extrapolation procedure of the results to the infinite basis set limit and the highest order of MP or CC, and finally a set of small but non-negligible additive corrections to the energy (among them, core correlation effects and the impact of including an additional set of polarization functions on the hydrogen atoms were explicitly evaluated). The degree of sophistication of the most advanced theoretical approaches used here fulfills the constraints of "calibration accuracy". The best predictions achieved in our work for ΔE^0 (ΔE^{90}) amount to 2.1 (1.7) and 2.2 (1.8) kcal/mol at the corrected CC and MP doubly extrapolated levels, respectively.

Ingredients are still missing in the protocol to predict with higher accuracy the torsional potentials of medium-size conjugated molecules. We discuss below some of these factors and their possible impact at a quantitative level:

(a) Improved extrapolation to the infinite basis set limit. Although modern extrapolation techniques[50] allow for the use of only one basis set from the cc-pVnZ sequence, they might provide in some cases a rough estimate of the extrapolated energies if the lowest cc-pVDZ level is used. In this context, the application of the dual-level scheme of Halkier et al.[48] or Schwenke[86] relying on the cc-pVDZ and cc-pVTZ basis sets could shed light on the quality of the extrapolation schemes performed at the MP or CC level. This

is expected to be the main source of error in our approach. A separate extrapolation of the singlet-coupled and triplet-coupled CCSD pair correlation energies has also been proposed based on the fact that their convergence appears to be different.[87] Moreover, the (T) contribution is known to converge more rapidly with the basis set than the CCSD correlation energy;[88] particular attention should therefore be paid to the extrapolation of CCSD energies. Nevertheless, it is generally accepted that an extrapolated value obtained with the cc-pVnZ member of the hierarchy usually compares qualitatively with at least a cc-pV(n+2)Z result. Moreover, since the number of paired electrons remain unchanged during the rotation, the basis set convergence is expected to be very fast;[89] previously published nonextrapolated results can thus hardly compete in terms of accuracy with the CC extrapolated values presented in this work.

(b) Iterative treatment of T_3 contributions at the CCSDT level. The explicit treatment of triple excitations is not expected to significantly change barrier heights with respect to the CCSD(T) values, as suggested by the results of the continued-fraction approximation and by previous studies.[90] The error introduced in the CCSD(T) perturbed method is relatively large (about 10% of the full contribution arising from triple excitations)[91] but is partly canceled by the neglect of quadruple excitations; thus, the CCSDT method might only account for the possibly remaining nondynamical correlation effects,[92] which are expected to affect the barrier by less than 0.01 kcal/mol.

(c) Improved core correlation contribution. The use of all-electron CCSD(T) instead of MP2 should also be tested to evaluate the inner-shell correlation effects and their extrapolation to the asymptotic limit. Since the basis set incompleteness errors are expected to be much larger than the core-valence effects,[93] this correction is expected to be also negligible.

(d) The impact of performing the geometry optimizations beyond the MP2/cc-pVTZ level employed here may also be explored; the correction is, however, expected to be very small.[40,94]

We do not know at this stage to which extent these different factors might fill the gap between the experimental and theoretical value obtained for the ΔE^0 barrier. Both barriers were experimentally estimated from the analysis of Raman spectra of the torsional mode[16] or from electron diffraction measurements.[17,18] The periodic potential function extracted from the experimental analysis is essentially accurate in the region around the potential minimum. However, the barrier heights might be affected to a large extent[18] by the severely truncated mathematical expression which was selected to describe the potential. Further confirmations of the experimental number reported in the literature are seen as a prerequisite to solve this apparent discrepancy since the aforesaid corrections are expected to be very small and possibly of different signs.

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