

The internal rotational barrier of biphenyl studied with multiconfigurational second-order perturbation theory (CASPT2)

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Summary. A detailed *ab initio* study of the molecular structure and rotational barriers of biphenyl has been performed. First, non-dynamical correlation effects involving the π system are taken into account at the CASSCF level. These wave functions are subsequently employed as reference functions in a multiconfigurational second-order perturbation treatment (CASPT2). The performance single-reference approaches is in addition analysed. The molecular geometries of biphenyl in twisted, coplanar, and perpendicular conformations have been optimized at the CASSCF level. A rotational angle of 44.3° is predicted for the minimum energy conformer in agreement with gas-phase electron diffraction data ($44.4 \pm 1.2^\circ$). The highest level of theory employed yields the values 12.93 (6.0 ± 2.1) and 6.40 (6.5 ± 2.5) kJ/mol for the barrier heights at 0° and 90° , respectively (electron diffraction data within parentheses). In the light of the present findings, the reliability of the available experimental data is discussed.

Key words: Biphenyl – Rotational barrier – Perturbation theory

1. Introduction

One of the main interests in biphenyl arise from its relation to polyparaphenylene (PPP), one of the most studied compounds in the field of conducting polymers. It belongs to the class of non-degenerate ground state polymers that become conducting when exposed to oxidizing or reducing agents (“doping” process) [1]. Studies about the conduction mechanism in such systems have suggested that the conductivity is related to the appearance of states (polaron and/or bipolaron) in the band gap after the doping process [2, 3]. Small oligomers with well-defined structures can be used as models for the polymer in order to provide a better understanding of the structural and electronic changes induced by the charging process [4–6]. We are presently studying the electronic spectrum of biphenyl and ionic systems (cation and anion). The different shape of the internal rotation potential of the excited states with respect to the ground state is of importance to rationalize the excitation energies observed in gas phase as compared to solution or crystalline neutral biphenyl at low temperature. In this context, as a first step towards the theoretical rationalization of the charged-induced defect upon doping,

we focus in this paper on the internal rotation around the interannular bond which the biphenyl shows.

Considerable experimental [7–13] and theoretical efforts [14–22] have been devoted to study the geometry and internal rotational potential of the biphenyl molecule. Some controversy between computed and experimental available data however remains since, as described in detail below, *ab initio* calculations including electron correlation concluded [19] that the experimental value of the energy barrier to the planar conformation may be grossly underestimated. The main aim of this work is the analysis of the requirements for the accurate theoretical determination of the barrier heights to rotation of biphenyl. For this purpose extensive *ab initio* calculations were performed. In particular, two major factors, which were not previously considered, are here analysed: geometry optimization at correlated level and the performance of single-reference approaches with respect to multi-reference methods. The present results support the previous conclusion regarding the underestimation of the experimental estimate for the barrier height to planarity.

The molecular structure of biphenyl is mainly characterized by the twist angle around the inter-ring C–C bond. The equilibrium torsional angle depends strongly on the state of aggregation. Above 40 K, the experimental data in solid state are consistent with a planar structure with large oscillations. On the contrary, in solution, in the crystal below 40 K, and in gas phase, non-planar structures with different twist angles were found (see Ref. [17] for a review of experimental determinations of the molecular structure). The existence of a twisted structure is explained by the balance between two opposite factors: the electron delocalization effect, which favours a coplanar conformation, and the steric repulsion between the hydrogen atoms in ortho positions, which is minimal in the perpendicular conformation. The barrier heights towards coplanar and perpendicular conformations are sensitive to the environment (gas, liquid, or solid phase) [23]. The most recent experimental determination in gas phase [9, 10] has estimated the height of the barriers towards coplanar and perpendicular conformations to be 6.0 ± 2.1 and 6.5 ± 2.0 kJ/mol, respectively. By using electron diffraction techniques [9], a value of $44.4 \pm 1.2^\circ$ has been obtained for the twist angle. Prior determinations (see Ref. [10]) yielded values for the barrier heights within the range 4–8 kJ/mol. For instance, Carreira and Towns [8] predicted equal barrier heights of 5.98 kJ/mol using the rotational potential function obtained from gas-phase Raman spectroscopy assuming a twist angle of 45° .

Biphenyl has been previously studied by using molecular mechanics and semiempirical methods, but no definitive conclusion about the energy ordering and value of the two barriers could be achieved (Ref. [17] provides a summary of theoretical calculations of biphenyl). The first *ab initio* study of biphenyl was performed by Almlöf [14] at the Hartree Fock (HF) level, using a basis set of double-zeta quality. Several *ab initio* calculations were subsequently reported employing a STO-3G basis set [15–17, 21], which differed among them in the approach used (rigid rotor [15], partial optimization [16, 21], or full optimization [17]) to determine the most stable conformer. The computed values [15–17, 21] for the twist angle lie within the range 38.6 – 43.8° . The barrier height at 0° varies between 8.59 and 15.73 kJ/mol, and from 9.2 to 10.5 kJ/mol at 90° . It was concluded that the change of geometry during the twisting is an important factor to be considered in order to obtain reliable values for the rotational barrier heights [17]. Full optimization of the geometry of the three conformers has been carried out at the HF level with the STO-3G, 6-31G, 6-31G*, and 6-31G** basis sets

Table 1. *Ab initio* results and experimental determinations of the twist angle and internal rotational barriers of biphenyl

Method	Reference	Twist angle (°)	ΔE_0 (kJ/mol) ^a	ΔE_{90} (kJ/mol) ^b
HF/double-zeta	14	32	5.02	18.8
HF/STO-3G	15	42	15.73	9.46
HF/STO-3G	21	40	9.6	10.5
HF/STO-3G	16	43.8	13.0	9.2
HF/STO-6G*	22	41.4	14.18	8.66
MP2/STO-6G*	22	38.04	8.41	9.92
HF/STO-3G	17	38.63	11.01	10.33
Full optimization of the geometry of each conformer				
HF/STO-3G	17	38.63	8.59	10.04
HF/6-31G	18	45.40	13.26	6.76
HF/6-31G ^c	18	44.74	13.51	6.91
HF/6-31G*	19	46.13	13.72	6.19
HF/6-31G** ^c	19	45.63	13.97	6.44
HF//6-31G**	19	46.26	13.93	6.32
MP2/6-31G*//	19		16.07	7.20
HF/6-31G*				
MP4(SDQ)/6-31G*//	19		14.52	6.61
HF/6-31G*				
Experiment ^d	9, 10	44.4(1.2)	6.0(2.1)	6.5(2.0)

^a Barrier height at 0°^b Barrier height at 90°^c The planarity restriction of the phenyl rings was removed in the optimization^d Gas-phase electron diffraction data

[17–20]. Extending the one-electron basis set, a better agreement with experiment is achieved for the twist angle and for the rotational barrier to the perpendicular conformation but the opposite effect results for the barrier to the coplanar conformation. Table 1 collects previous *ab initio* results together with the most recent experimental data [9, 10]. From this compilation it is clear that the rotational barrier height calculated for the coplanar conformation (henceforth ΔE_0) is higher than the experimental value. Agreement with experiment is, however, found for the rotational barrier height towards the perpendicular conformation (henceforth ΔE_{90}).

The overestimation of ΔE_0 was firstly ascribed to the lack of inclusion of electron correlation effects, which should differently affect the coplanar and twisted conformations [18, 19]. An increase of the barrier heights was however obtained using Möller–Plesset (MP) perturbation theory [19]. At the highest level of theory employed, fourth-order MP perturbation including singly, doubly, and quadruply excited configurations (MP4(SDQ) results in Table 1), the ΔE_0 and ΔE_{90} values are 14.52 and 6.61 kJ/mol, respectively. Tsuzuki and Tanabe [19] have suggested that the experimental value of ΔE_0 is probably underestimated. Distortions of the phenyl rings from planarity were found to have a minor effect on the computed barrier heights. However, as stated above, the influence of the geometry optimization at correlated level has not been checked. On the other hand, the performance of multi-reference methods to describe the barrier heights has not been analysed. In this contribution, we present a detailed *ab initio* study of the molecular structure and rotational barriers of biphenyl. Multiconfigurational methods are used to

compute the barrier heights. In addition, the performance of single-reference approaches is discussed. The geometry of coplanar, twisted, and perpendicular conformers is optimized at correlated level. In the light of the results obtained in this work, the reliability of the available experimental data is considered.

The details of the calculations are described in the next section. A discussion of the results then follows. Our conclusions are summarized in the last section.

2. Details of calculations

Generally contracted basis sets of atomic natural orbital (ANO) type [24] are used, which are obtained from C(14s, 9p, 4d)/H(8s, 4p) primitive sets [25]. These basis sets were constructed to treat optimally correlation and polarization effects [25]. Five different contraction schemes have been used in the present work: C[2s 1p]/H[1s], C[4s 2p]/H[2s], C[4s 2p 1d]/H[2s], C[4s 2p 1d]/H[2s 1p], and C[4s 3p 1d]/H[2s 1p]. In the geometry optimizations a double-zeta basis set with polarization functions on the carbon and hydrogen atoms (DZP) [26] was employed.

In order to determine the barrier heights to rotation, geometry optimizations of the coplanar D_{2h} , twisted D_2 , and perpendicular D_{2d} conformations were carried out. In the latter, actual calculations were performed with C_{2v} symmetry, imposing D_{2d} constraints. Full geometry optimizations, keeping planar the phenyl rings, have been carried out for the three conformers using the complete active space SCF (CASSCF) method [27]. In order to account for the major differential correlation effects among the different structures, the 12 valence π molecular orbitals (MOs) and electrons were active, keeping the σ -electrons inactive. The σ correlation effects, in addition to the π correlation contributions, were included by using the CASPT2 method [28, 29], in which the CASSCF wave function is used as the reference function. The zeroth-order Hamiltonian generated from the full Fock matrix was used [28, 29]. The CASPT2 method represents a powerful tool to study large molecules with an important multiconfigurational character, as a number of applications have illustrated [30]. For the sake of comparison, single-reference calculations using second-order many-body perturbation theory (MBPT2) were also performed. The 1s MOs were kept in the form determined by the SCF wave function. Unless otherwise stated, the 1s electrons were not correlated.

The calculations have been performed on an IBM 9021/500-2VF computer and on IBM RS/6000 workstations of the University of Valencia using the MOLCAS-2 quantum chemistry software [31]. The geometry optimizations were performed with the recently developed ALASKA and SLAPAF programs [32], implemented in the MOLCAS-3 package [33] of the University of Lund.

3. Results and discussion

We focus first on changes in the computed barrier heights using different theoretical approaches at given fixed molecular geometries [19], in order to analyse the influence of the electron correlation on the ΔE_0 and ΔE_{00} values. Geometry optimization is next performed at the CASSCF level. From the calibration calculation and computed geometries, a final estimation of the barrier heights is then achieved. In the light of the present results, the reliability of the previous experimental and theoretical findings is finally discussed.

Table 2. Rotational barriers (kJ/mol) towards coplanar conformer (ΔE_0) and towards perpendicular conformer (ΔE_{90}) computed with different basis sets and methods^a

Method	E_ϕ ^b	ΔE_0	ΔE_{90}
<i>Basis set: [2s 1p]/[1s]</i>			
HF	-459.318872	7.03	12.59
<i>Basis set: [4s 2p]/[2s]</i>			
HF	-460.152500	11.21	6.94
<i>Basis set: [4s 2p 1d]/[2s]</i>			
HF	-460.324498	11.05	5.52
CASSCF	-460.468703	9.92	5.06
CASPT2	-461.827281	12.13	7.66
MBPT2	-461.833613	12.34	8.24
<i>Basis set: [4s 2p 1d]/[2s 1p]</i>			
HF	-460.362201	12.13	4.56
CASSCF	-460.505481	10.92	4.10
CASPT2	-461.928056	12.22	6.86
MBPT2	-461.933981	12.38	7.36

^a Geometries optimized at the HF/6-31G** level are used in the calculations [19]

^b Total energy of the twisted conformer in a.u

A. Influence of the level of correlation on the barrier heights

We present in this section the results obtained at various theoretical levels in order to analyse the influence of the electron correlation effects on the rotational barrier heights. The HF/6-31G** optimized geometries [19] were employed. The results are collected in Table 2 and are next commented.

The most important change at the HF level occurs from minimal to double-zeta basis set, in agreement with previous experience [17–19]. Thus, ΔE_0 increases 4.18 kJ/mol and ΔE_{90} decreases 5.65 kJ/mol. Further extension of the one-electron basis set, including polarization functions, has a more pronounced effect on the barrier height at 90° than at 0°. As the basis set is enlarged, a progressive decrease of the ΔE_{90} value is noted, yielding 4.56 kJ/mol with the ANO-type basis set [4s 2p 1p]/[2s 1p]. With the same basis set, the ΔE_0 value is computed to be 12.13 kJ/mol. Compared to these values, the HF/6-31G** barriers [19] are somewhat larger, about 1.8 kJ/mol (cf. Table 1). Since the same geometries were employed, such difference can be related to the different type of basis sets. The values of the barrier heights are sensitive to a detailed choice of the one-electron basis set.

Analysis of the valence π - π electron correlation on the barrier heights is achieved by using the CASSCF method, 12 π -orbitals and 12 π -electrons active. The HF configuration has a similar weight, about 79%, for the three conformers. Doubly excited configurations contribute significantly to the ground state wave functions, showing a total weight within the range 13–16%. The natural orbital occupation numbers of the active orbitals, using the [4s 2p 1d]/[2s 1p] basis set, are presented in Table 3. This compilation illustrates the importance of an MCSCF treatment of the electronic structure of biphenyl. All the occupation numbers are different from two and zero. Most of them show a difference larger than 0.05. As far

Table 3. Occupation numbers of the natural orbitals of the π -CASSCF wave functions using the $[4s\ 2p\ 1d]/[2s\ 1p]$ basis set at the HF/6-31G** optimized geometries [19]

State	Occupation number			
D_{2h} coplanar biphenyl (57008 configurations)				
	b_{3u}	b_{1g}	b_{2g}	a_u
1^1A_g	1.9638	1.9061	1.9599	1.9041
	1.9178	0.0983	1.8861	0.0949
	0.1182		0.0807	
	0.0379		0.0322	
D₂ twisted biphenyl (57008 configurations)				
	a	b_3	b_2	b_1
1^1A	1.9059	1.9049	1.9608	1.9632
	0.0968	0.0957	1.8942	1.9137
			0.0853	0.1092
			0.0334	0.0369
D_{2d} perpendicular biphenyl (57168 configurations)				
	a_2	b_1	e	
1^1A_1	1.9069	1.9037	3.9238	
	0.0984	0.0942	3.8083	
			0.1940	
			0.0707	

as our own experience is concerned, the CASSCF wave function should include all orbitals with occupation numbers between ≈ 0.05 and ≈ 1.95 in order to give a balanced treatment of the differential correlation among the corresponding states of interest, computed at the second-order level.

The difference between the barrier heights computed at the HF and the CASSCF levels can be related to the differential correlation effects associated to the π valence electron correlation. Using the $[4s\ 2p\ 1d]/[2s\ 1p]$ basis set, at the CASSCF level the barrier heights decrease 1.21 (ΔE_0) and 0.46 (ΔE_{90}) kJ/mol with respect to the corresponding HF values.

The influence of the electron correlation effects involving both π and σ electrons were accounted for by using perturbative techniques. The CASSCF wave function was first used as reference in the perturbational treatment following the CASPT2 method. The σ and π contributions increase the barrier heights for both the ΔE_0 and ΔE_{90} values. With the largest basis set ($[4s\ 2p\ 1d]/[2s\ 1p]$) employed in these preliminary calculations, the ΔE_0 and ΔE_{90} values computed at the CASPT2 level are 12.22 and 6.86 kJ/mol, respectively. Polarization functions on the hydrogen atoms do not significantly affect the ΔE_0 value but reduce the ΔE_{90} result 0.80 kJ/mol.

The second-order energy computed by using the CASPT2 method can be classified in terms of the σ - σ , σ - π , and π - π electron pairs. The individual contributions to the correlation energy from the different electron pairs, using the $[4s\ 2p\ 1d]/[2s\ 1p]$ basis, are presented in Table 4. The extra-valence π - π electron correlation is small for the three conformers. The major reorganization effects within the π -subsystem are already considered at the CASSCF level. The π - π contributions gathered at the second-order level are similar for the twisted and perpendicular structures and slightly larger with respect to the coplanar form. The

Table 4. Partitioning of the second-order correlation energy computed with the CASPT2 method into σ - σ , σ - π , and π - π contributions for coplanar, twisted, and perpendicular biphenyl^a

Conformer	σ - σ	σ - π	π - π
Coplanar	- 0.771642	- 0.583166	- 0.067258
Twisted	- 0.766233	- 0.588563	- 0.067779
Perpendicular	- 0.762828	- 0.590933	- 0.067757

^a Results from the $[4s\ 2p\ 1d]/[2s\ 1p]$ basis set at the HF/6-31G** optimized geometries [19]. Energies in a.u

σ - σ and σ - π contributions are more significant. On going from the coplanar to the perpendicular conformer, the σ - σ electron correlation contributions decrease, meanwhile the reverse trend is noted for the σ - π total contributions. These findings can be rationalized as follows. In the planar rotamer the σ skeletons of both phenyl rings are located in the same plane, which makes possible a greater coupling between them, resulting in a larger σ - σ contribution. In the perpendicular rotamer, the coupling is more effective in the σ - π interactions, since the σ skeleton of one ring lies parallel to the π -electron plane of the other ring (cf. Table 4). Large differential contributions of both σ - σ and σ - π correlation energies to the barrier heights are found, affecting them in opposite ways. A balanced description of the barrier heights therefore requires to take into account, in addition to the π - π , both σ - σ and σ - π electron energy contributions.

In order to analyse the performance of single-reference methods, second-order MBPT2 many-body perturbation calculations have been also carried out. The largest deviation of the MBPT2 results from the corresponding CASPT2 findings is about 8%. It is therefore not expected that the previous reported [19] discrepancy between theory and experiment for the ΔE_0 value might be due to the use of single-reference methods.

B. Geometry optimization

Previous geometry optimizations [17–19] have been restricted to the HF level. In order to check the influence of electron correlation effects on computed geometries, full geometry optimization at the CASSCF level has been carried out for the three conformers. Table 5 collects the optimal bond distances and bond angles obtained using a DZP basis set [26], (CASSCF/DZP results). For the sake of comparison, the HF values using the 6-31G** basis set (HF/6-31G** results) reported by Tsuzuki and Tanabe [19] along with experimental data [9, 34] are also included.

Inclusion of the π valence electron correlation in the geometry optimization has similar effects in the three structures. At the π -CASSCF level, the C–C distances of the phenyl rings increase (0.012–0.014 Å) compared to the HF values. A slight increase (0.001 Å) also occurs for the C–H distances. In the coplanar and perpendicular conformers, the inter-ring C–C bond distance has, however, a slightly shorter value. For the twisted geometry, a very small change is noted. The π valence electron correlation has a minor effect on the determination of the bond angles for the three conformers, the difference between the π -CASSCF and the HF results being less than 0.2°. It is worth noting, however, the better description of the twist

Table 5. Experimental and computed geometries for coplanar, twisted, and perpendicular biphenyl^a

Bond distances (Å) and angles (deg.)	Coplanar ^b		Twisted ^c		Perpendicular	
	HF/6-31G**d	CASSCF/DZP	HF/6-31G**d	CASSCF/DZP	HF/6-31G**d	CASSCF/DZP
ϕ^e	0.0	0.0	46.26	44.34	90.0	90.0
C ₁ -C ₁ '	1.5012	1.4988	1.4915	1.4920	1.4987	1.4972
C ₁ -C ₂	1.3961	1.4085	1.3925	1.4048	1.3906	1.4033
C ₂ -C ₃	1.3836	1.3974	1.3844	1.3985	1.3855	1.3996
C ₃ -C ₄	1.3834	1.3976	1.3850	1.3991	1.3851	1.3998
C ₂ -H ₂	1.0721	1.0735	1.0755	1.0769	1.0759	1.0773
C ₃ -H ₃	1.0759	1.0772	1.0759	1.0772	1.0760	1.0773
C ₄ -H ₄	1.0756	1.0769	1.0757	1.0770	1.0760	1.0772
H ₂ ...H ₂ '	1.9663	1.9723	2.4989	2.4699	3.5294	3.5498
C ₂ -C ₁ -C ₆	116.805	116.92	118.359	118.35	118.725	118.80
C ₁ -C ₂ -C ₃	121.662	121.64	120.836	120.89	120.660	120.66
C ₂ -C ₃ -C ₄	120.539	120.51	120.247	120.23	120.183	120.14
C ₃ -C ₄ -C ₅	118.792	118.78	119.476	119.41	119.588	119.59
C ₁ -C ₂ -H ₂	120.668	120.69	119.559	119.70	119.423	119.49
C ₂ -C ₃ -H ₃	119.310	119.35	119.675	119.69	119.733	119.78
C ₃ -C ₄ -H ₄	120.604	120.61	120.262	120.30	120.206	120.20

^a Atom numbering is standard (see for instance Ref. [19]).^b X-ray values [34] at 110 K are given within parentheses.^c Values from ED in gas phase [9] are given within parentheses.^d Ref. [19].^e Twist angle.^f Average values.^g The same value was assumed for the three C-H distances, Ref. [9].

angle compared to experiment [9] when the major π -electron correlation effects are accounted for.

Comparison among the geometries of the three conformers illustrates the variation of the molecular geometric parameters upon internal rotation. As expected, the most important changes occur in those interannular parameters mainly involved in determining the distance between the hydrogen atoms in ortho position. Thus, the coplanar structure has the largest value of the C–C distance between the two phenyl rings and the smallest C₂–C₁–C₆ angle. The smallest C₂–H₂ distance and the largest C₁–C₂–H₂ angle are also found for the coplanar conformer. These features favour a large separation between the hydrogen atoms in ortho position. The rotation around the central bond alleviates the steric repulsion between the H₂ and H₂' atoms, allowing the central bond to become shorter, which is also favoured by conjugation. This latter effect precisely explains the increase of the C₁–C₁' distance for the perpendicular conformer. An enlargement of the C₂–H₂ distance and C₂–C₁–C₆ angle is noted on going from the coplanar to the perpendicular structure. Interestingly, the three unique C–C distances of the phenyl ring become progressively more equalized during the twisting process.

X-ray diffraction experiments at 110 and 293 K [34, 35] evidence a planar structure for crystalline biphenyl with large oscillations around the C–C central bond. This fact has to be kept in mind when comparing the experimental data to the optimized coplanar structure. The computed CASSCF C–C distances are somewhat larger than the X-ray values. Certain deviations are also noted in the C–C–C angles. X-ray geometric parameters in which hydrogen atoms are involved have little reliability, and no further comparisons will consequently be performed.

Almenningen et al. [9] have determined the molecular structure of biphenyl in gas phase by electron diffraction techniques. A twist angle of 44.4° (1.2) was found. Jet-cooled biphenyl spectroscopic studies [12, 13] have recently determined the change in the dihedral angle between the two phenyl rings when the molecule is excited to the lowest dipole-allowed excited state. Twist angle values about 40° and 44° have been estimated for the ground state from these two independent studies [12, 13]. The CASSCF optimized geometry for the twisted conformer presents a twist angle of 44.34° in agreement with the electron diffraction data [9]. The C–C bond distances of the phenyl ring agree also with the experimental values [9]. A larger deviation is, however, obtained for the C–C distance of the central bond.

C. Final estimate of the barrier heights and discussion

Using the optimal π -CASSCF geometries, the barrier heights to the coplanar and perpendicular conformers are computed at the HF, π -CASSCF, CASPT2, and MBPT2 levels employing the ANO-type [4s 2p 1d]/[2s], [4s 2p 1d]/[2s 1p], and [4s 3p 1d]/[2s 1p] basis sets. The results are listed in Table 6. The first remarkable aspect is the similarity of the ΔE_0 and ΔE_{90} values compared to the corresponding results of Table 2, where the HF/6-31G** geometries were employed. It is clearly seen that the use of different geometries affects the barrier heights by less than 0.20 kJ/mol. Using, if possible, a higher level of calculation for the full geometry optimization of the three conformers, small effects on the barrier heights to rotation are therefore expected. The same conclusion was achieved by Raghavachari [36] in a study of the rotational potential surface of *n*-butane. Minor corrections coming from the geometries were also found in the calculation of rotational barriers of substituted ethylenes [37].

Table 6. Barrier heights (kJ/mol) computed using the geometries optimized at CASSCF/DZP level

Method	E_{ϕ}^a	ΔE_0	ΔE_{90}
<i>Basis set: [4s 2p 1d]/[2s]</i>			
HF	-460.323006	11.05	5.52
CASSCF	-460.470300	9.87	4.98
CASPT2	-461.832161	11.97	7.53
MBPT2	-461.838282	12.22	8.12
<i>Basis set: [4s 2p 1d]/[2s 1p]</i>			
HF	-460.360654	12.05	4.52
CASSCF	-460.506993	10.79	3.93
CASPT2	-461.932569	12.05	6.69
MBPT2	-461.938277	12.26	7.20
<i>Basis set: [4s 3p 1d]/[2s 1p]</i>			
HF	-460.383833	12.71	4.69
CASSCF	-460.529902	11.41	3.99
CASPT2	-462.024987	12.93	6.40
MBPT2	-462.030308	13.34	6.75

^a Total energy of the twisted conformer in a.u

The π valence electron correlation effects decrease both barrier heights with respect to the HF results. The remaining electron correlation contributions calculated at the second-order level are particularly important for the ΔE_{90} barrier which is increased by a factor of 1.5–1.7 with respect to the CASSCF values. Inclusion of polarization functions on the hydrogen atoms affects mainly the barrier height at 90° , which decreases 0.84 kJ/mol at the CASPT2 level. Enlargement of the number of contracted p -type functions on the carbon atoms affects mainly the ΔE_0 value, which increases 0.88 kJ/mol. The best estimates, calculated at the CASPT2 level using the [4s 3p 1d]/[2s 1p] basis set and the optimized π -CASSCF geometries, yield 12.93 and 6.40 kJ/mol for the ΔE_0 and ΔE_{90} barrier heights, respectively. The value obtained for ΔE_{90} matches the experimental predictions. On the contrary, the value computed for the barrier at 0° , which indeed is close to the best previous theoretical result (MP4(SDQ) level) of 14.52 kJ/mol [19] (cf. Table 1), still doubles the gas-phase electron diffraction estimate of 6.0 ± 2.1 kJ/mol reported by Almenningen et al. [9].

In order to estimate the influence of the remaining correlation effects on the theoretical prediction of the barrier heights, the core–core (c–c) and core–valence (c–v) contributions were computed at the MBPT2 level using the [4s 2p 1d]/[2s 1p] basis set. Inclusion of the c–c and c–v correlation decreases 0.25 and 0.21 kJ/mol the barrier height at 0° and 90° , respectively. The c–c and c–v electron correlation have therefore a minor effect on the rotational barriers of biphenyl and do not account for the large difference found for ΔE_0 between theoretical predictions and experimental results.

As has been pointed out in the introduction and in spite of the numerous investigations concerning to the molecular structure of biphenyl, few experimental data about the internal rotation barriers are available. In addition, only results obtained from gas-phase experiments are strictly comparable to the theoretical

calculations. As mentioned above there is a strong dependence of the equilibrium conformation of biphenyl on the state of aggregation. The most relevant gas-phase determinations of the rotational barrier heights of biphenyl are those reported by Carreira and Towns [8] and by Bastiansen and Samdal [10]. It is important to note that these determinations are not exempt from assumptions.

Carreira and Towns [8] observed only one overtone for the torsional mode in the vibrational spectra measured by Raman spectroscopy. They used the simple sinusoidal potential function $V(\Phi) = \frac{1}{2} V_2(1 - \cos 2\Phi) + \frac{1}{2} V_4(1 - \cos 4\Phi)$ to analyse the torsional mode. To determine V_2 and V_4 they had to fix a value for the equilibrium torsional angle and afterwards vary V_2 and V_4 to fit the experimentally determined torsional frequency of $\nu(2 \leftarrow 0) = 55.4 \text{ cm}^{-1}$. Varying the equilibrium angle from 35° to 55° they obtained deviations for the torsional frequency of only 0.4 cm^{-1} , while the barrier heights oscillate between 249.6 cm^{-1} (2.99 kJ/mol) and 1039.6 cm^{-1} (12.44 kJ/mol). For a rotational angle of 45° , the barrier heights are both equal to 500 cm^{-1} (5.98 kJ/mol). Using qualitative arguments they finally proposed a torsional angle of about 50° and barrier heights of about 700 and 350 cm^{-1} (8.37 and 4.19 kJ/mol) at 0° and 90° , respectively. It should be noted that recent determinations of the fundamental frequency for the torsional motion of biphenyl yield values of about $50\text{--}60 \text{ cm}^{-1}$ [12, 13], i.e., of the same order of the value assigned by Carreira and Towns to the $2 \leftarrow 0$ transition.

Bastiansen et al. [9, 10] adopted the two-term Fourier expansion proposed by Carreira and Towns [8] for the potential energy function to internal rotation in the least-square treatment of their gas-phase electron diffraction data. The values reported for the equilibrium twist angle ($\Phi = 44.4 \pm 1.2^\circ$) and for the barrier heights ($\Delta E_0 = 6.0 \pm 2.1 \text{ kJ/mol}$ and $\Delta E_{90} = 6.5 \pm 2.0 \text{ kJ/mol}$) were then estimated from the potential function obtained in the fitting. However, as Bastiansen and Samdal [10] remarked, the electron diffraction data come essentially from Φ -value areas where the population is high, i.e., around the minimum. Using their own words: "This means that the curvature at the minimum is determined with some degree of accuracy, while the barrier heights are to a great extent dependent on the mathematical expression selected to describe the potential energy function". Tsuzuki and Tanabe [19] have recently corroborated this dependence. These authors argue that a two-term Fourier expansion is inappropriate to describe the internal rotational potential of biphenyl. Following previous suggestions [16], they show that the third term (V_6 -term) in the Fourier expansion has a non-negligible contribution to the potential. They finally concluded that the use of the two-term Fourier expansion to analyse the experimental data would underestimate the value of ΔE_0 if the shape of the experimental rotational potential is close to the potential shape obtained from *ab initio* calculations.

To summarize, there are no reasons to attribute the large discrepancy between the experimental ΔE_0 value and the theoretical estimate to an insufficient calculation level. In this sense, the present theoretical results suggest that this discrepancy should be then due to the underestimation of ΔE_0 from experimental data, supporting the conclusions of Tsuzuki and Tanabe [19]. On the other hand, a comprehensive analysis of the diffraction data oligophenyls has been recently reported by Baudour [38]. It was concluded that the intramolecular potential between two adjacent phenyl rings cannot be described by a simple sinusoidal function but exhibits a steeper gradient near the planar conformation. This supports the fact that the two-term Fourier expansion used in gas-phase experiments has not enough flexibility to analyse the rotational potential of biphenyl.

4. Summary and conclusions

A detailed *ab initio* study of the internal rotational barrier of biphenyl has been performed. The influence of the correlation level on the barrier heights has been analysed using different correlation approaches and basis sets. Full optimization of the geometry of coplanar, twisted, and perpendicular conformers has been carried out at the π -CASSCF/DZP level. The twist angle resulting from the optimization is in excellent agreement with that determined from the electron diffraction data in gas phase [9]. The computed barrier heights are affected by less than 0.20 kJ/mol when geometries optimized at different levels (HF and π -CASSCF) are used.

The multiconfigurational CASPT2 method has been employed to compute the barrier heights to rotation in biphenyl. The performance of the single-reference MBPT2 method to describe the barrier heights has also been analysed. The computed barrier heights at the MBPT2 level have been found to be only ≈ 0.5 kJ/mol larger than the CASPT2 results. The computed ΔE_0 and ΔE_{90} values at the CASPT2 level, using the $[4s3p1d]/[2s1p]$ basis set and π -CASSCF/DZP optimized geometries, are 12.93 and 6.40 kJ/mol, respectively. Agreement with the experimental estimation [8–10] has been thus obtained for the barrier height at 90° , but a deviation of ≈ 7 kJ/mol is noted for the ΔE_0 value. The present theoretical results of the barrier heights ought to be nearly (within ≈ 1 kJ/mol) converged with respect to both one-electron basis set and treatment of the major differential correlation effects. They therefore support that the corresponding experimental values, which are not free of assumptions [9, 10], should be revisited.

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