

## Ab initio study of the structures and dynamic stereochemistry of biaryls

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### Abstract

The static and dynamic stereochemistry of biphenyl (**1**), 1-phenylnaphthalene (**2**), 1-phenylanthracene (**3**), 9-phenylanthracene (**4**), 1,1'-binaphthyl (**5**), 1,1'-naphthylanthracene (**6**), 1,9'-naphthylanthracene (**7**), 1,1'-bianthryl (**8**), 9,9'-bianthryl (**9**) and 1,9'-bianthryl (**10**) were examined using ab initio molecular orbital (MO) and the Becke, Lee, Yong and Parr density functional (B3LYP) methods. The structure of the ground states, the activation energies for rotation about the  $\sigma$ -bonds of compounds **1–10** and the nature of deformation of aromatic rings in the equilibrium structures and saddle point geometries were also investigated. Studies on the HF/6-31G\*\*//Hf/3-21G, MP2/6-31G\*\*//HF/3-21G and B3LYP/6-31G\*\*//HF/3-21G levels of theory confirm that compounds **5**, **6** and **8** should racemize preferably the *anti* path, (with about 9 kcal mol<sup>-1</sup> lower energy than the *syn* path). However, the resulted racemization energy for compound **5** through the *syn* path is found to contradict the previously reported semi-empirical calculations.

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### 1. Introduction

Extensive research has been performed on the static and dynamic stereochemistry of organic molecules containing aryl groups [1]. The classical examples of such molecules are the biaryls, which have non-coplanar structure, and further, some of them were of interest in research on charge transfer (CT) complexes [2]. Suitably substituted biaryls are optically active and their racemization via a fairly planar transition state is possible [2–4].

The internal rotation of gaseous biphenyl (**1**) presents one energy minimum having non-planar geometry [5] with a torsional angle ( $\phi$ ) between both phenyl rings of 44.6°, as well as two energy maxima at  $\phi=0$  and 90° (1.43 and 1.55 kcal mol<sup>-1</sup> relative to the minimum geometry,

respectively). Moreover, X-ray diffraction results show a planar structure for crystalline biphenyl (**1**) is [6]. The rotational barriers of biphenyl (**1**) have been reproduced by empirical force field (EFF) calculations using a modified MM2' program (MM2-V4) [7]. Gas electron diffraction (GED) studies have shown for the pivot bond length for biphenyl (**1**) a value of 1.505 Å [5], whereas X-ray diffraction results have shown a value of 1.493 Å [6]. Therefore, there is no dependency of the pivot bond length on the system planarity for biphenyl (**1**). This long C<sub>sp2</sub>–C<sub>sp2</sub> bond in gas phase suggests little overlapping of  $\pi$ -electron clouds across this bond.

Internal rotational barrier heights of *peri*-substituted diarylnaphthalenes has been estimated [8,9], determined experimentally [10–12] and investigated computationally [13–18]. However, in the computational calculations only molecular mechanics and semi-empirical methods have been employed.

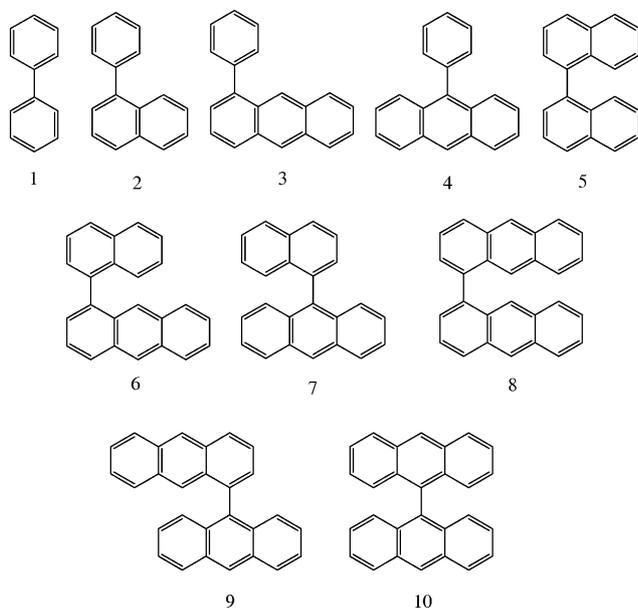
1,1'-Binaphthyl is chiral and racemization can proceed via *syn* and *anti* transition states. Molecular mechanics and

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semi-empirical calculation studies have indicated non-planar rings in the transition state structure of 1,1'-binaphthyl (**5**). MMDO, AM1 and PM3 semi-empirical calculation results for racemization of 1,1'-binaphthyl (**5**) via *syn* and *anti* transition state geometries, were reported previously [18]. Also, except for compounds **1**, **2** and **5**, there is not significant published data on the dynamic behaviours of compounds **6–10**.

Successful applications of density functional theory (DFT) based methods have broadened the applicability of the computational methods and now represent an interesting approach for determining activation barrier and molecular energies [19,20,22]. The B3LYP functional method combines Becke's, three-parameter exchange function with the correlation function of Lee et al. [19,20]. Therefore, in this work, we report the results of a detailed theoretical investigation of the structural and dynamic properties of compounds **1–10**, performed by ab initio molecular orbital (MO) and density functional methods (DFT), using the GAUSSIAN 98 package of programs [19–23]. Based on the more efficient ab initio and DFT calculations, the reported results show different energetic results concerning the height of the *syn* and *anti* racemization paths for 1,1'-binaphthyl (**5**), compared to the previously reported semi-empirical results (specially to the AM1 results).



## 2. Calculations

Ab initio calculations were carried out using HF/6-31G\*\*/HF/3-21G, MP2/6-31G\*\*/HF/3-21G and B3LYP/6-31G\*\*/HF/3-21G levels of theory with the GAUSSIAN 98 package of programs [23], implemented on a Pentium-PC computer with 500 MHz processor. Initial structural geometries of the compounds **1–10** were obtained by

a molecular mechanic program PCMODEL (88.0) [24] and for reoptimizing of geometries, the AM1 method of MOPAC 6.0 computer program [25,26] was used. Energy-minimum structures were located by minimizing the energy with respect to all geometrical coordinates and without imposing any symmetry constraints.

The GAUSSIAN 98 program was finally used to perform ab initio calculations at the HF/3-21G level in order to obtain the energy-minimum structures, and MP2/6-31G\*\*/HF/3-21G and B3LYP/6-31G\*\*/HF/3-21G methods for the single point energy calculations.

The nature of the stationary points for compounds **1–10** has been fixed by means of the number of imaginary frequencies. For minimum state structures, only real frequency values, and in the transition state only single imaginary frequency values were accepted. The structure of the transition state geometries was located using the optimized geometries of the equilibrium structure according to the procedure of Dewar et al. (keyword SADDLE) [27]. These geometry structures were then reoptimized by the TS option at the HF/3-21G level. The vibrational frequency of ground states and transition states were calculated by the FREQ subroutine.

It has to be noted that, the use of HF/6-31G\* and HF/3-21G methods, generated nearly the same structural parameters for the ground state and transition state structures of compound **5**, however, from energetic point of view, the obtained energetic results using medium basis set (6-31G\*), were closer to the experimental data. Therefore, in this work, in order to use less time consuming methods HF/6-31G\*\*/HF/3-21G, MP2/6-31G\*\*/HF/3-21G and B3LYP/6-31G\*\*/HF/3-21G levels of theory were used for the investigation of the ground state structures and dynamic behaviours (rotation about pivot bands) of compounds **1–10**.

## 3. Results and discussion

### 3.1. Phenylaryls: biphenyl (**1**), 1-phenylnaphthalene (**2**), 1-phenylanthracene (**3**) and 9-phenylanthracene (**4**)

The total electronic ( $E_{el}$ ) energies for compounds **1–10**, as calculated by the ab initio HF/6-31G\*\*/HF/3-21G, MP2/6-31G\*\*/HF/3-21G MO and DFT methods (B3LYP/6-31G\*\*/HF/3-21G) are given in Table 1.

HF/3-21G results show that the minimum structure of biphenyl (**1**) is chiral with twist angle between the two phenyl ring of 50.9°, which is in good agreement with the experimental GED structure data of compound **1** ( $\phi = 44.4^\circ$ ) [6]. Degenerate interconversion of the twist conformation of compound **1** with its mirror-image geometry can take place by rotation of the phenyl group around the pivot bond. There is two distinct maxima geometries for compound **1**: (a) perpendicular geometry with  $\phi = 90^\circ$ , and (b) coplanar geometry with  $\phi = 0^\circ$ . The calculated barrier

Table 1  
Calculated energies (in Hartree) for minima and transition state structures of compounds **1–10**

Method Geometry	HF/6-31G**/HF/3-21G		MP2/6-31G**/HF/3-21G		B3LYP/6-31G**/HF/3-21G		Previous compu- tational data	Experimental data
	$E_c$	$\Delta E^a$	$E_{el}$	$\Delta E^a$	$E_{el}$	$\Delta E^a$		
<b>1</b> (Min, $D_2$ )	−460.253603	0.000000 (0.000000) <sup>b</sup>	−461.765350	0.000000 (0.000000) <sup>b</sup>	−463.302042	0.000000 (0.000000) <sup>b</sup>	(0.00)	(0.00)
<b>1</b> (TS, $D_{2h}$ )	−460.248438	0.005166 (3.241528)	−461.759207	0.006143 (3.854731)	−463.299468	0.002733 (1.711530)	(MM2-V4: 1.58) <sup>c</sup>	(1.55) <sup>c</sup>
<b>1</b> (TS, $D_{2d}$ )	−460.2514464	0.002157 (1.353476)	−461.762555	0.002795 (1.753828)	−463.300049	0.001997 (1.250502)	(MM2-V4: 1.32) <sup>c</sup>	(1.43) <sup>c</sup>
<b>2</b> (Min, $C_1$ )	−612.901471	0.000189 (0.1189131)	−614.919388	0.000348 (0.218562)	−616.940176	0.000383 (0.240073)	–	–
<b>2</b> (Min, $C_s$ )	−612.901661	0.000000 (0.000000)	−614.919736	0.000000 (0.000000)	−616.940559	0.000000 (0.000000)	–	–
<b>2</b> (TS, $C_1$ )	−612.87587	0.025596 (16.061683)	−614.894936	0.024452 (15.343623)	−616.921300	0.018876 (11.845004)	(MM2-V4: 12.4) <sup>c</sup>	–
<b>3</b> (Min, $C_1$ )	−765.545653	0.000000 (0.000000)	−768.069116	0.000008 (0.004957)	−770.5770911	0.000006 (0.003765)	–	–
<b>3</b> (Min, $C_s$ )	−765.545652	0.000001 (0.000878)	−768.069124	0.000000 (0.000000)	−770.577097	0.000000 (0.000000)	–	–
<b>3</b> (TS, $C_1$ )	−765.520023	0.025630 (16.083207)	−768.036730	0.0323948 (20.328067)	−770.557808	0.019288 (12.103914)	–	–
<b>4</b> (Min, $C_2$ )	−765.542565	0.000000 (0.000000)	−768.069840	0.000000 (0.000000)	−770.574784	0.000000 (0.000000)	–	–
<b>4</b> (Min, $C_{2v}$ )	−765.542564	0.000001 (0.000375)	−768.069830	0.000010 (0.006212)	−770.574775	0.000010 (0.006024)	–	–
<b>4</b> (TS, $C_s$ )	−765.499366	0.043199 (27.107553)	−768.036729	0.033111 (20.777484)	−770.542613	0.032172 (20.188063)	–	–
<b>5</b> (Min, $C_2$ )	−765.551651	0.000000 (0.000000)	−768.076847	0.000000 (0.000000)	−770.581716	0.000000 (0.000000)	(0.00)	(0.00)
<b>5</b> (TS <sub>syn</sub> , $C_2$ )	−765.488010	0.063641 (39.935677)	−768.037183	0.052969 (33.238389)	−770.530167	0.051550 (32.347952)	(AM1: 29.80), <sup>d</sup> (AM1: 29.18), <sup>c</sup> (MNDO: 34.80), <sup>d</sup> (PM3: 27.20) <sup>d</sup>	–
(TS <sub>anti</sub> , $C_i$ )	−765.503264	0.0483864 (30.362950)	−768.023880	0.039665 (24.890060)	−770.544370	0.037347 (23.435428)	(MM2': 24.8), <sup>c</sup> (AM1: 29.5), <sup>d</sup> (AM1: 20.06), <sup>c</sup> (MNDO: 33.80), <sup>d</sup> (PM3: 23.10) <sup>d</sup>	(21.5–22.7) <sup>c</sup>
<b>6</b> (Min, $C_1$ )	−918.195670	0.000000 (0.000000)	−921.2263710	0.000000 (0.000000)	−924.217903	0.000000 (0.000000)	–	–
<b>6</b> (TS <sub>syn</sub> , $C_1$ )	−918.132810	0.062860 (39.44483934)	−921.174121	0.0522500 (32.787711)	−924.167135	0.050768 (31.857490)	–	–
<b>6</b> (TS <sub>anti</sub> , $C_1$ )	−918.147926	0.047743 (29.959524)	−921.187362	0.039009 (24.478537)	−924.181411	0.036492 (22.899346)	–	–
<b>7</b> (Min, $C_s$ )	−918.192643	0.000000 (0.000000)	−921.227784	0.000000 (0.000000)	−924.215883	0.000000 (0.000000)	–	–
<b>7</b> (TS, $C_1$ )	−918.116623	0.076020 (47.703373)	−921.168399	0.059386 (37.265058)	−924.155198	0.060685 (38.080319)	–	–
<b>8</b> (Min, $C_2$ )	−1070.839592	0.000000 (0.000000)	−1074.375930	0.000000 (0.000000)	−1077.854756	0.000000 (0.000000)	–	–
<b>8</b> (TS <sub>syn</sub> , $C_2$ )	−1070.777507	0.062085 (38.959272)	−1074.324731	0.0511986 (32.127633)	−1077.803817	0.050940 (31.964983)	–	–
<b>8</b> (TS <sub>anti</sub> , $C_i$ )	−1070.792599	0.046994 (29.48901669)	−1074.337593	0.038336 (24.056349)	−1077.818372	0.036384 (22.831198)	–	–
<b>9</b> (Min, $C_s$ )	−1070.836644	0.000000 (0.000000)	−1074.377326	0.000000 (0.000000)	−1077.852343	0.000000 (0.000000)	–	–
<b>9</b> (TS, $C_1$ )	−1070.761738	0.074906 (47.004452)	−1074.318822	0.058504 (36.711657)	−1077.792109	0.060233 (37.797186)	–	–
<b>10</b> (Min, $D_{2d}$ )	−1070.833876	0.000000 (0.000000)	−1074.379963	0.000000 (0.000000)	−1077.851177	0.000000 (0.000000)	–	–
<b>10</b> (TS, $C_2$ )	−1070.741777	0.092099 (57.793232)	−1074.316665	0.063299 (39.720567)	−1077.779118.	0.072059 (45.217806)	–	–

<sup>a</sup> Relative to the most stable form.

<sup>b</sup> Numbers in the parenthesis are the corresponding  $\Delta E$  values in kcal mol<sup>−1</sup>.

<sup>c</sup> This work.

<sup>d</sup> See Ref. [18].

<sup>e</sup> See Ref. [17].

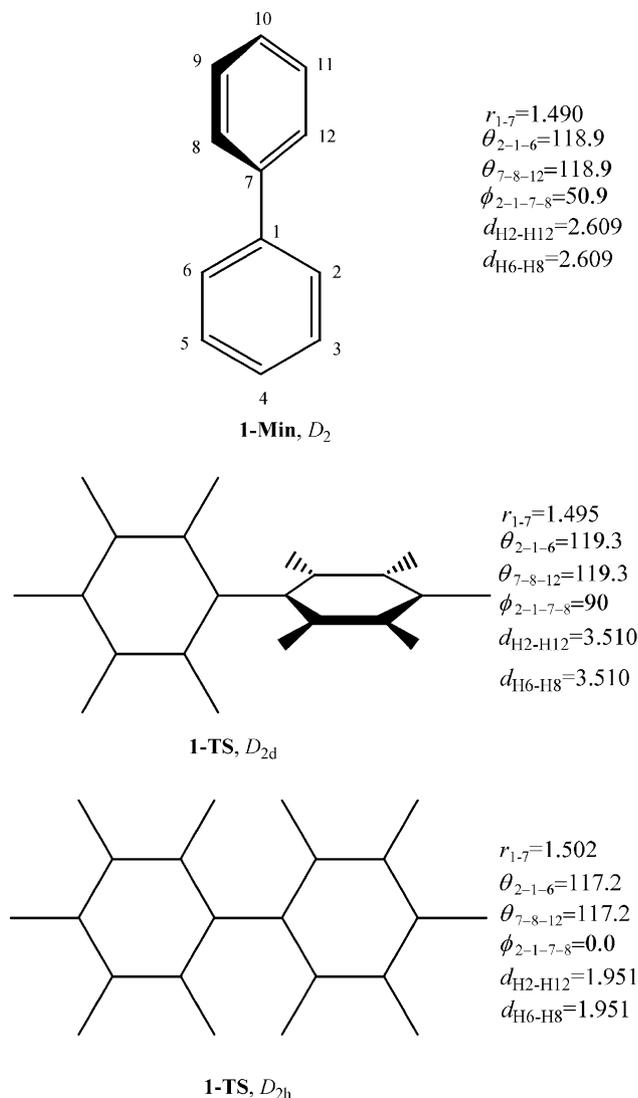


Fig. 1. HF/3-21G calculated structural parameters of minima and transition state structures of biphenyl (**1**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

height for the perpendicular maxima for compound **1** is 1.25, 1.75 and 1.35 kcal mol<sup>-1</sup>, as calculated by B3LYP/6-31G\*\*//HF/3-21G, MP2/6-31G\*\*//HF/3-21G and HF/6-31G\*\*//HF/3-21G methods, respectively. On the other hand, the calculated energy barrier, by B3LYP/6-31G\*\*//HF/3-21G, MP2/6-31G\*\*//HF/3-21G and HF/6-31G\*\*//HF/3-21G methods, for coplanar geometry of compound **1** is 1.71, 3.85 and 3.24 kcal mol<sup>-1</sup>, respectively. The energy difference between the coplanar and perpendicular maxima geometries can be explained in terms of strong H/H non-bonded contacts across the pivot bond. Among these three methods, the calculated barrier height by HF/6-31G\*\*//HF/3-21G method is the closest to the experimental perpendicular form (HF: 1.35 kcal mol<sup>-1</sup>, Exp.: 1.43 kcal mol<sup>-1</sup>), but the calculated barrier height for the planar form is much too high compared to the experimental value (HF: 3.24 kcal mol<sup>-1</sup>, Exp.: 1.55 kcal mol<sup>-1</sup>). B3LYP/6-31G\*\*//HF/3-21G results for planar structure of compound

**1** is also close to the experimental value (B3LYP: 1.71 kcal mol<sup>-1</sup>, Exp.: 1.55 kcal mol<sup>-1</sup>) [5].

In 1-phenylnaphthalene (**2**), the equilibrium torsion angle between the phenyl and naphthalene rings have been reported to be 50° in non-polar media by measurement of the Kerr constant [28] and 66° in CCl<sub>4</sub> by the measurement of magnetic anisotropy [29]. The equilibrium torsion angle is 66.5° [17], as calculated by MM2' molecular mechanics method [30]. HF/6-31G\*\*//HF/3-21G, MP2/6-31G\*\*//HF/3-21G and B3LYP/6-31G\*\*//HF/3-21G results show that the internal rotational potential of the phenyl ring of compound **2** would be very shallow over a wide range. In the saddle point structure of compound **2**, the steric repulsion between the hydrogen atoms attached to C8 and C12 carbons causes in-plane deformation of benzene and out-of-plane deformation of naphthalene rings.

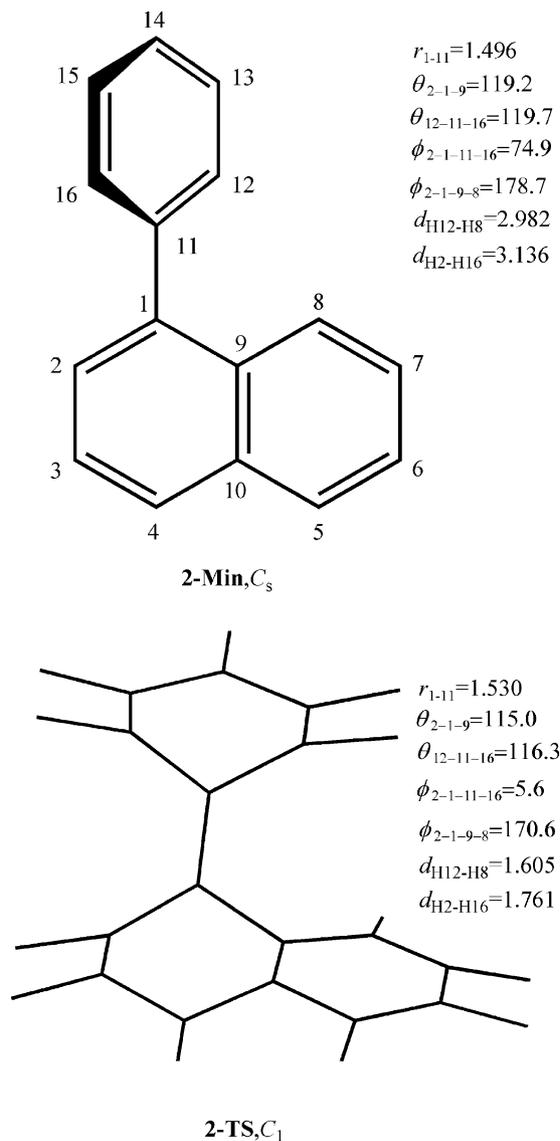


Fig. 2. HF/3-21G calculated structural parameters of minima and transition state structures of 1-phenylnaphthalene (**2**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

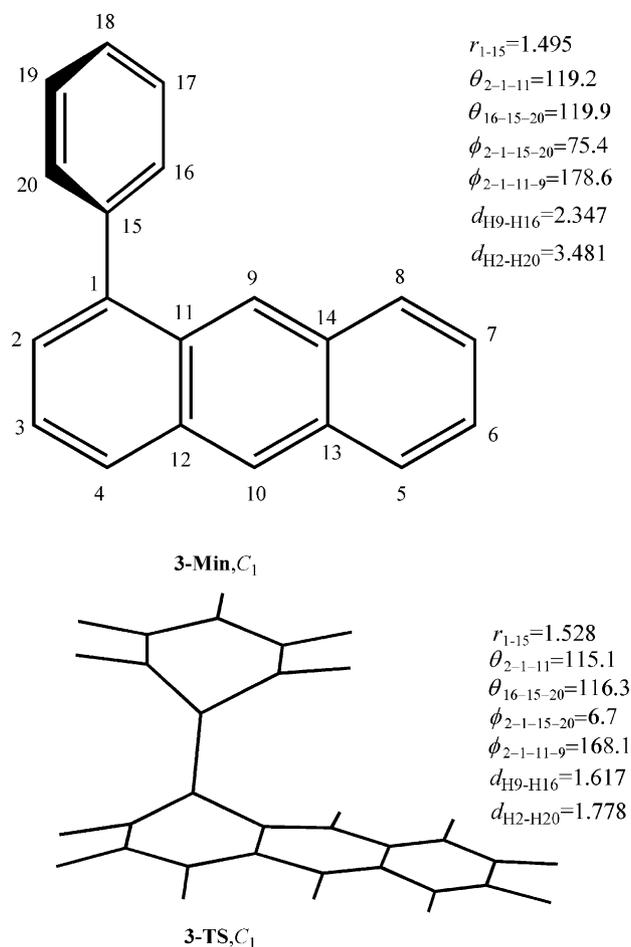


Fig. 3. HF/3-21G calculated structural parameters of minima and transition state structures of 1-phenylanthracene (**3**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

The deformation of valence angles of the naphthalene ring are observed not only in the region near the substituted *peri* positions, but also in the region far away from the substituent positions. The internal rotational barrier height of compound **2** is 11.85, 15.34 and 16.06 kcal mol<sup>-1</sup>, as calculated by B3LYP/6-31G\*//HF/3-21G, MP2/6-31G\*//HF/3-21G and HF/6-31G\*//HF/3-21G, respectively. It has to be noted that the calculated barrier height by B3LYP/6-31G\*//HF/3-21G level of theory is close to the MM2' result (12.4 kcal mol<sup>-1</sup>) (Figs. 1–4) [17].

Like for compound **2**, B3LYP/6-31G\*//HF/3-21G, MP2/6-31G\*//HF/3-21G and HF/6-31G\*//HF/3-21G results show that the internal rotational potential of phenyl ring of 1-phenylanthracene (**3**), would be very shallow over a wide range. The barrier height for internal rotation of compound **3** is 12.10, 20.32 and 16.06 kcal mol<sup>-1</sup>, as calculated by B3LYP/6-31G\*//HF/3-21G, MP2/6-31G\*//HF/3-21G and HF/6-31G\*//HF/3-21G, respectively.

Similar to compounds **2** and **3**, the internal rotational potential of phenyl ring of 9-phenylanthracene (**4**) would also be very shallow over a wide range, as calculated by all the three methods. The barrier height for internal

rotation of compound **4** is 20.19, 20.78 and 17.11 kcal mol<sup>-1</sup>, as calculated by B3LYP/6-31G\*//HF/3-21G, MP2/6-31G\*//HF/3-21G and HF/6-31G\*//HF/3-21G, respectively. The results show that the barrier height for internal rotation of compound **4** is higher than in compound **3**.

This fact may be explained by the greater steric repulsions between the hydrogens attached to C1 and C8 carbon atoms of anthracene ring and C16 and C20 carbon atoms of phenyl ring in compound **4** than the steric repulsions between the hydrogen atoms attached to C2 and C9 carbons of anthracene ring and C16 and C20 carbons of phenyl ring in compound **3**.

### 3.2. Naphthylaryls: 1,1'-binaphthyl (**5**), 1,1'-naphthylanthracene (**6**) and 1,9'-naphthylanthracene (**7**)

Representative structural parameters for compounds **5**–**10**, as calculated by HF/3-21G level and total electronic ( $E_{el}$ ) energies as calculated by B3LYP/6-31G\*//HF/3-21G, MP2/6-31G\*//HF/3-21G and HF/6-31G\*//HF/3-21G levels, are given in Figs. 5–10 and Table 1, respectively.

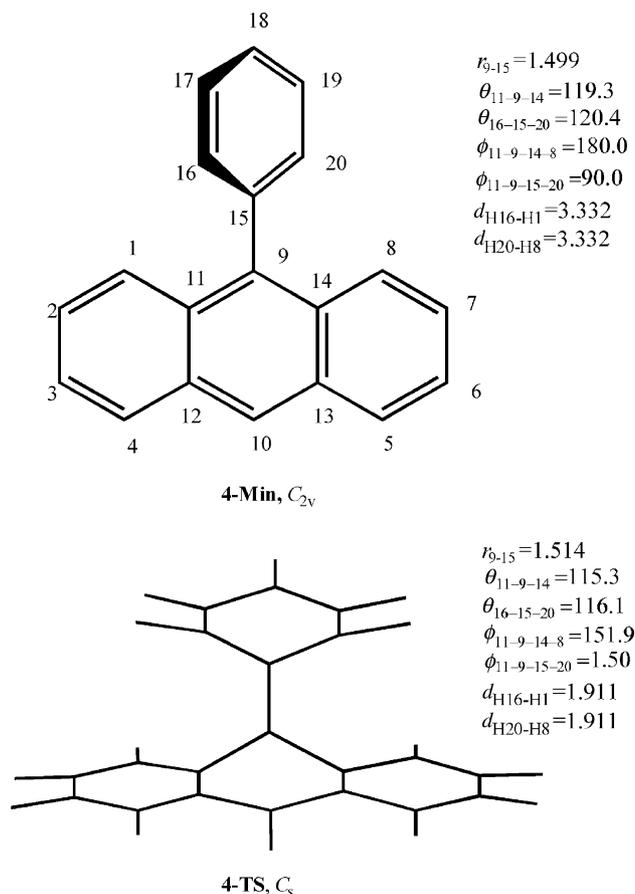


Fig. 4. HF/3-21G calculated structural parameters of minima and transition state structures of 9-phenylanthracene (**4**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

X-ray crystallographic studies of compound **5** have shown that the twist angles between the two naphthalene rings are 103.1 and 68.6° [31–33]. The experimental twist angle between the two naphthalene rings, in benzene as solvent, has been reported to be 48° from the Kerr constant measurement [34]. In the most stable conformation of compounds **5** and **6**, the two aromatic moieties are nearly perpendicular, with torsion angle of about 83° for the pivot bond. Both compounds are chiral and racemization can proceed via *syn* and *anti* transition state paths (see Figs. 5 and 6). B3LYP/6-31G\*\*//HF/3-21G calculated barrier height for the *anti* pathway in compound **5** is 23.43 kcal mol<sup>-1</sup>,

which is in good agreement with the experimentally determined values of 21.5–22.7 kcal mol<sup>-1</sup>. The barrier height for the *syn* pathway in compound **5** is 32.35 kcal mol<sup>-1</sup>, as calculated by B3LYP/6-31G\*\*//HF/3-21G, which is about 9 kcal mol<sup>-1</sup> higher than the *anti* mechanism (see Table 1).

For compound **5**, a value of 24.8 kcal mol<sup>-1</sup> is obtained for racemization via *anti* mechanism by MM2/ EFF calculations [17]. The reported AM1, MNDO and PM3 semi-empirical SCF-MO results for the barrier height of rotation about pivot bond via *anti* path in compound **5** are: 29.5, 33.8 and 23.1 kcal mol<sup>-1</sup>,

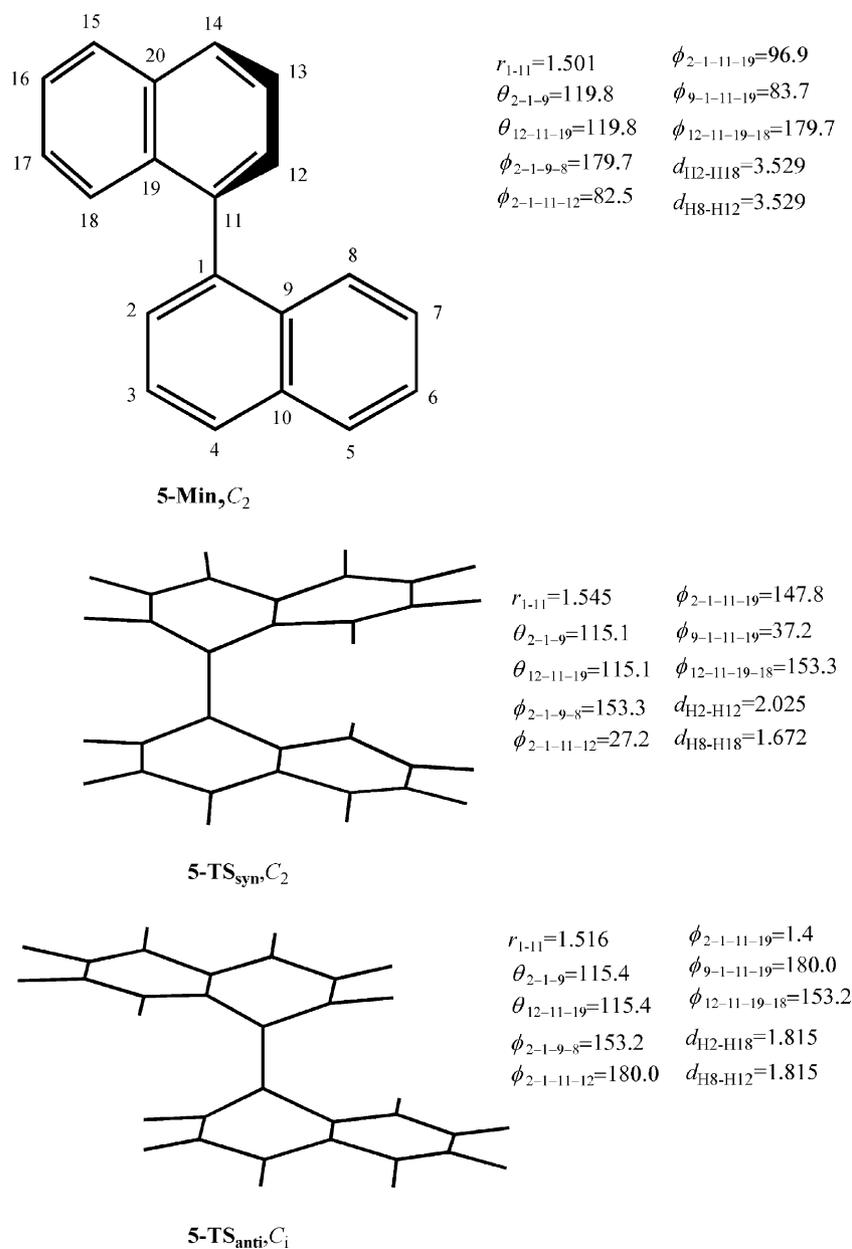


Fig. 5. HF/3-21G calculated structural parameters of minima and transition state structures of 1,1'-binaphthyl (**5**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

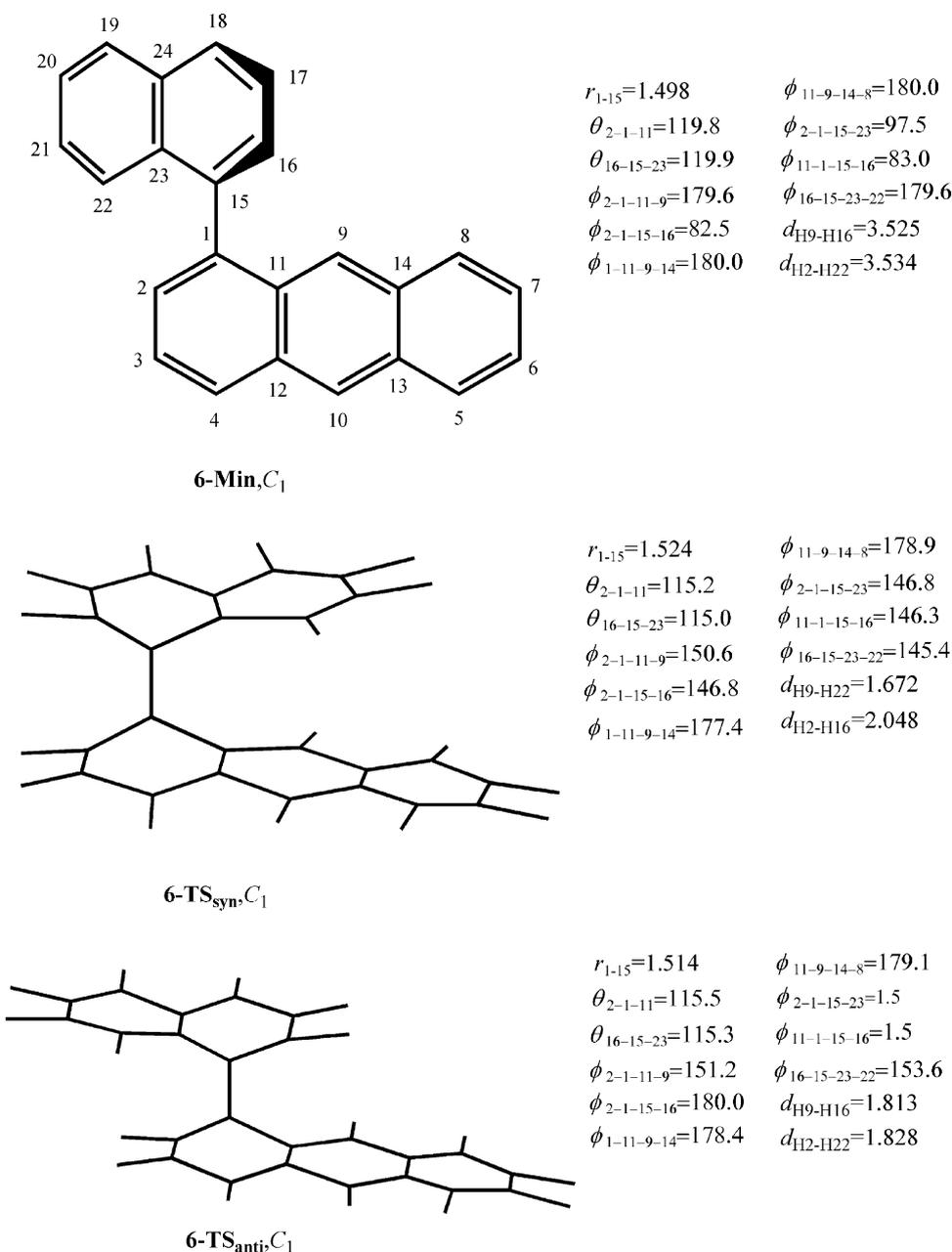


Fig. 6. HF/3-21G calculated structural parameters of minima and transition state structures of 1,1'-naphthylanthracene (**6**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

respectively, while the reported values by these methods for *syn* mechanism are: 29.80, 34.80 and 27.20 kcal mol<sup>-1</sup>. AM1 and MNDO reported results do not predict any significant differences between the barrier heights of the *syn* and *anti* mechanisms, while PM3 reported results predict about 4 kcal mol<sup>-1</sup> higher energy for *syn* mechanism [18].

It has to be noted that for the barrier heights of the *syn* and *anti* mechanisms in compound **5**, our AM1 results show values about 29.18 and 20.06 kcal mol<sup>-1</sup>, respectively, in disagreement with the previously reported data [18]. However, the results of B3LYP/6-31G\*\*//HF/3-21G, MP2/6-31G\*\*//HF/3-21G and HF/6-31G\*\*//HF/3-21G

methods confirm the energy barriers reported in our work (e.g. B3LYP/6-31G\*\*//HF/3-21G: 32.35 and 23.44 kcal mol<sup>-1</sup>; MP2/6-31G\*\*//HF/3-21G: 32.24 and 24.89 kcal mol<sup>-1</sup> and HF/6-31G\*\*//HF/3-21G: 39.94 and 30.36 kcal mol<sup>-1</sup>). It can be concluded that a significant difference should exist between *syn* and *anti* mechanisms, in agreement with our AM1, B3LYP, MP2 and HF results and in contrast to the previously reported semi-empirical SCF-MO results, specially AM1 and MNDO values [18].

As shown in Figs. 5 and 6, the transition geometries of compounds **5** and **6** have fairly twisted naphthalene and anthracene moieties. In 1,1'-binaphthyl

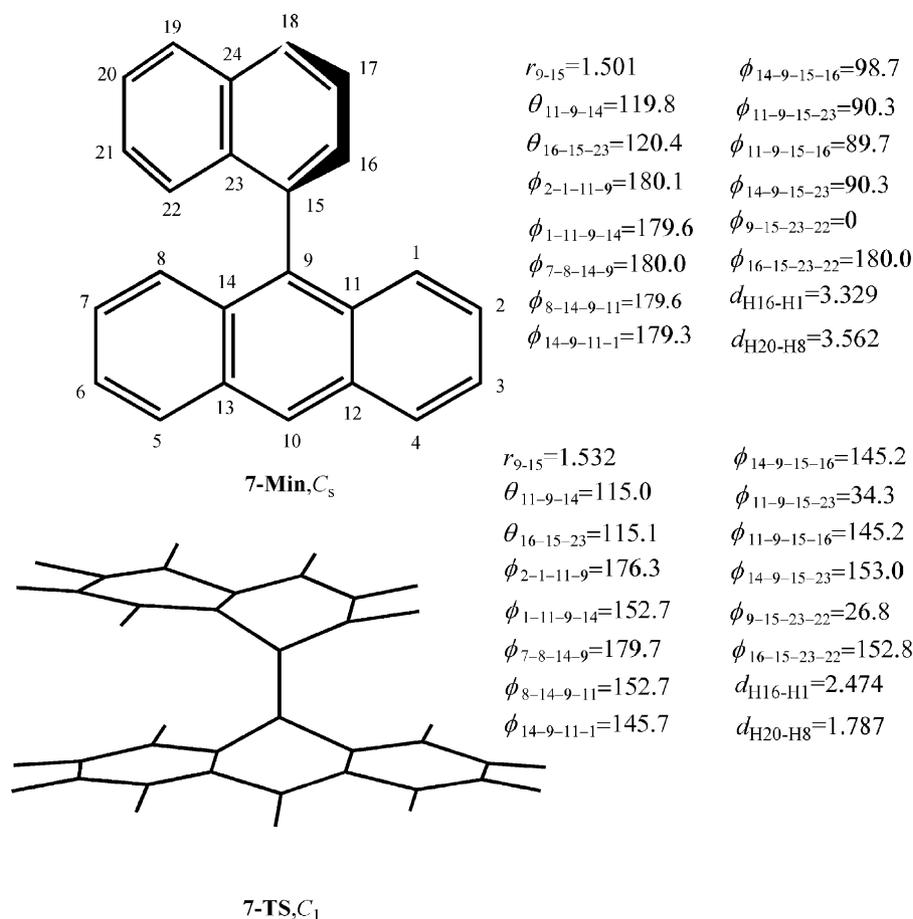


Fig. 7. HF/3-21G calculated structural parameters of minima and transition state structures of 1,9'-naphthylanthracene (**7**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

(**5**), C2–C1–C9–C8 torsion is used as a criterion for ring deformation. The value of this torsion angle in *syn* and *anti* transition state geometries is 153.3 and 153.2°, respectively.

The most stable conformation of 1,9'-naphthylanthracene (**7**) has  $C_s$  symmetry. In this geometry, the naphthalene and anthracene moieties are perpendicular. Rotation about the pivot bond in compound **7** requires about 38.08 kcal mol<sup>-1</sup>, as calculated by B3LYP/6-31G\*//HF/3-21G method. In the transition state structure of compound **7**, both naphthalene and anthracene systems (present in **7**) are fairly twisted (see Fig. 7).

### 3.3. Bianthrils: 1,1'-bianthrill (**8**), 1,9'-bianthrill (**9**) and 9,9'-bianthrill (**10**)

The conformational properties of 1,1'-bianthrill (**8**) are similar to that of 1,1'-binaphthyl (**5**). The most stable conformation of compound **8** has  $C_2$  symmetry. Conformational interconversion in **8** can take place by *syn* and *anti* transition state geometries, as shown in Fig. 8. The barrier height of *syn* and *anti* pathways for compound **8** are 31.96 and 22.83 kcal mol<sup>-1</sup>, respectively, as calculated by B3LYP/6-31G\*//HF/3-21G method (see Table 1).

The *anti* pathway in **8** is calculated to be 9 kcal mol<sup>-1</sup> lower than that in the *syn* mechanism.

The ground state structure of compound **9** has  $C_s$  symmetry and anthracene rings are perpendicular, as calculated by HF/3-21G\* method. B3LYP/6-31G\*//HF/3-21G method shows that the rotation about the pivot bond in compound **9** require 37.80 kcal mol<sup>-1</sup>. Similar to compound **8**, in the transition state structure of compound **9**, both anthryl moieties are also fairly twisted (see Fig. 9).

9,9'-Bianthrill (**10**) has been a favourite molecule in research on CT complexes since Schneider and Lippert [35] found the emission from its intramolecular CT state. From previous theoretical and experimental works on 9,9'-bianthrill (**10**) [36–39], it is known that the two anthryl moieties are perpendicular in the electronic ground state and twisted by an angle of about 70–78° in the first excited singlet state [40–42]. These experimental results show the balance between the non-bonding repulsion of the hydrogen atoms and the resonance stabilization of the two parts of molecular structure of compound **10**.

The ground state conformation of 9,9'-bianthrill (**10**) has  $D_{2d}$  symmetry, as calculated by HF/3-21G method, in which both anthryl moieties are perpendicular to each other in

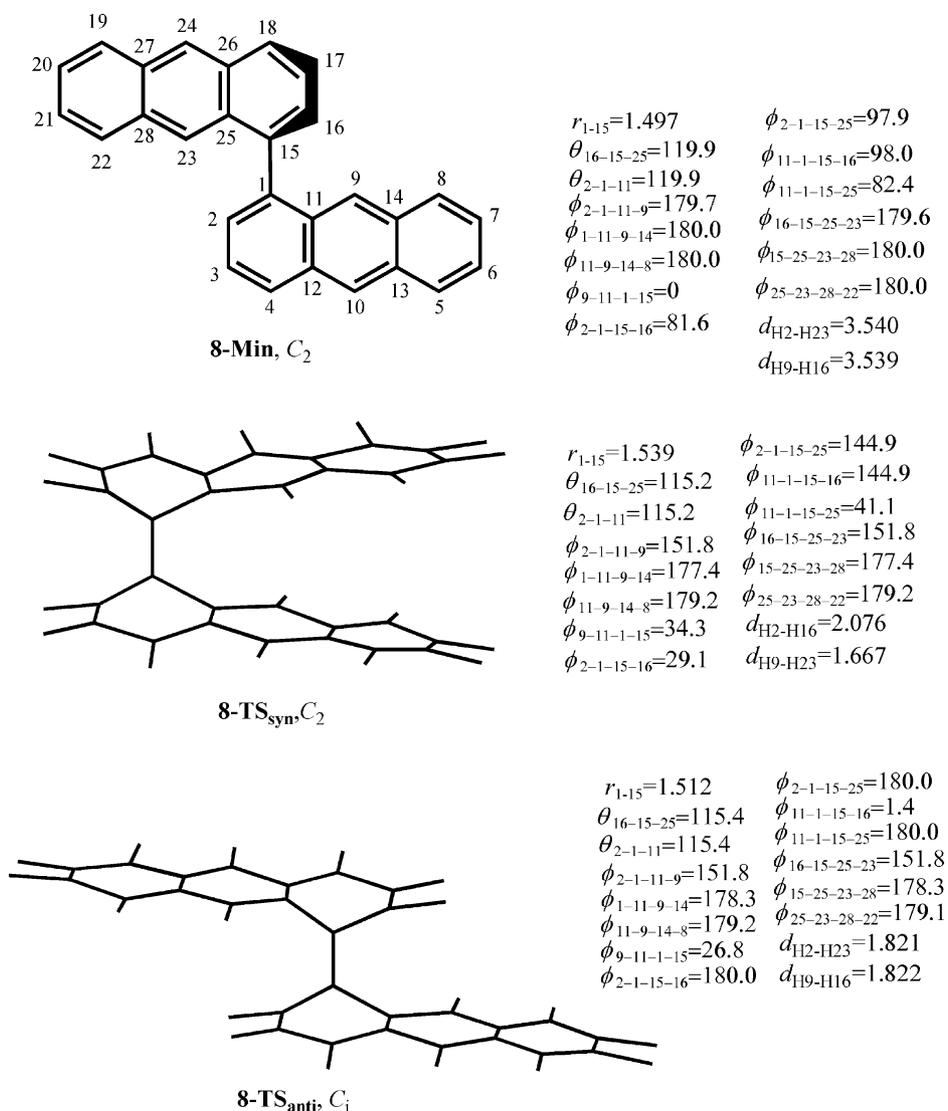


Fig. 8. HF/3-21G calculated structural parameters of minima and transition state structures of 1,1'-bianthryl (**8**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

agreement with the above mentioned experimental results [36–39]. B3LYP/6-31G\*\*//HF/3-21G method reveals that the rotation about the pivot bond require  $45.2 \text{ kcal mol}^{-1}$ . In the transition state structure of compound **10** (with  $C_2$  symmetry), both anthryl moieties are fairly twisted ( $\phi_{1,11,9,14}=142.4^\circ$ ) from its ground state structure ( $\phi_{1,11,9,14}=180.0^\circ$ , see Figs. 8–10).

#### 4. Conclusion

B3LYP, MP2 and HF calculations support the non-coplanar geometry for biaryls of **1–10**. The ground state geometries of compounds **1**, **5**, **6** and **8** are chiral with twist angle of about  $50\text{--}90^\circ$ . The two aromatic moieties in **5** and **6** are nearly perpendicular and conformational racemization is predicted to take place via *anti* transition state. The calculated barrier heights for the *syn* pathways in

compounds **5**, **6** and **8** is  $9 \text{ kcal mol}^{-1}$  higher than the *anti* mechanism. For compound **5**, our calculated AM1, B3LYP, MP2 and HF results showed, particularly, that a significant difference should exist between *syn* and *anti* mechanisms, in contrast to the previously reported semi-empirical SCF-MO data, specially AM1 and MNDO values [18]. Compound **7** has  $C_s$  symmetry and rotation about its pivot bond required about  $38.08 \text{ kcal mol}^{-1}$ , as calculated by B3LYP/6-31G\*\*//HF/3-21G method. The most stable conformation of bianthryls **8** and **9** has  $C_2$  and  $C_s$  symmetry, respectively. The *anti* pathways for conformational interconversion in compound **8**, require about  $9 \text{ kcal mol}^{-1}$  less energy than the *syn* mechanism. The bianthryl **10** has  $D_2$  symmetry and rotation about its pivot bond requires  $45.2 \text{ kcal mol}^{-1}$ , as calculated by B3LYP/6-31G\*\*//HF/3-21G method. In the transition state structure of compounds **2–10**, the benzene, naphthalene and anthracene moieties are fairly twisted.

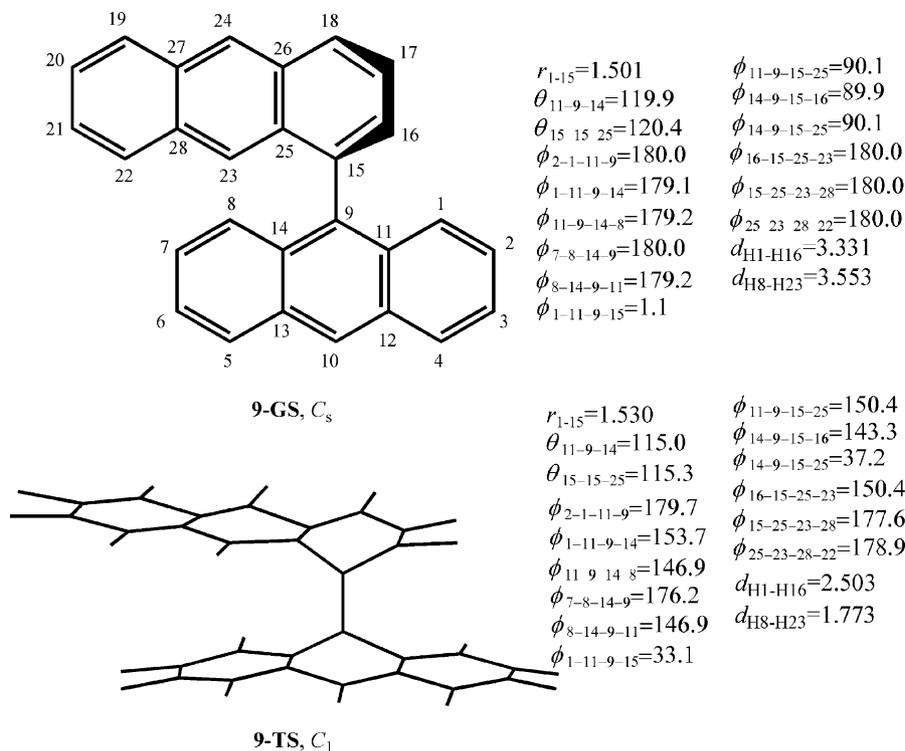


Fig. 9. HF/3-21G calculated structural parameters of minima and transition state structures of 1,9'-bianthryl (**9**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

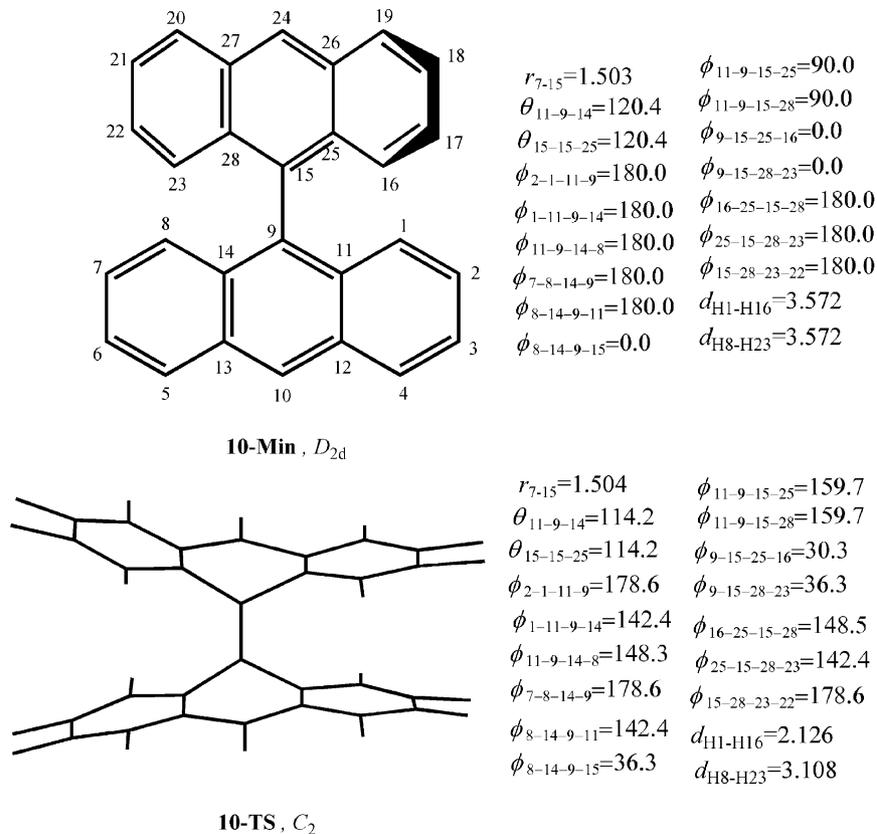


Fig. 10. HF/3-21G calculated structural parameters of minima and transition state structures of 9,9'-bianthryl (**10**). Bond lengths ( $r$ ) are in Angstrom and bond angles and torsion angles ( $\theta$ ,  $\phi$ ) in degrees.

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