RESULTS AND DISCUSSION

The Torsional Potential for Bicarbazole and Bifluorene at High-Level *ab initio* and DFT Results

1. Conformational Analysis

All calculations have been performed with the Gaussian 03 package (Frisch *et al.*, 2004). Non-rigid calculations of torsional potentials require full optimization of the geometric structure of all conformers at the *ab initio*, Hartree-Fock (HF), and DFT levels for each fixed value of the torsional angle(ϕ). A regular grid was imposed for ϕ from 0^o to 180^o in steps of 10^o. A general expression to systematically tune the mixing of exchange-correlation functionals with exact Hartree-Fock (HF) exchange (E_x^{HF}) may be defined as follows:

$$E_{xc}[\rho] = a_x E_x^{HF} + (1 - a_x) E_x[\rho] + E_c[\rho],$$

where $E_i[\rho]$ is one of the most employed exchange (i=x) or correlation (i=c) functionals. The coefficient a_x has been introduced to probe in a systematic way the influence of the exact exchange,which indeed primarily governs the torsional energy profiles of π-conjugated systems. We have selected two categories of density-functional methods, the Generalized Gradient Approximation (GGA) and the so-called m-GGA extension which includes new variables of the density in addition to its gradient $\Delta\rho(r)$. Among the former, the well-known B (Becke, 1988, 1993, 1996, 1997) and PW91 (Adamo and Barone, 1998) expressions were selected and, respectively, coupled to the LYP (Lee *et al.*, 1988) and PW91 (Perdew *et al.*, 1996) correlation counter-parts. The hybrid versions resulting from the variation of a_x in Eq. (2) are termed BLYP and PW1 (a_x=0.25) and BH&HLYP (a_x=0.5). B3LYP-based (Becke, 1993, 1996, 1997) results are also included since these functionals are often used as reference. The present study broadly expands the set of applied exchange-correlation functionals and thus the assessment of the theory. All the HF and DFT results were obtained with the 6-31G and 6-31G(d) basis sets, which ensure a large coverage of the one-particle space. As a matter of fact, an additional set of polarization functions (6-31G(d)) only marginally affected the results, and thus the results are not expected to significantly vary upon further basis sets extension.

The performance of the large set of assessed exchange-correlation functionals is shown in Figure 22. This figure displays the torsional potential for a set of representative GGA results. The analysis of the results allows us to conclude that all the DFT methods show an amazingly difference range of values for the energy barriers, independent of the exchange-correlation kernel being used. A larger percentage of HF exchange helps the *syn-gauche/anti-gauch* barrier to converge towards the reference value but, contrarily to what is observed in other systems (Sancho-Garcia and Karpfen, 2005, 2006), progressively deteriorates the results in the 30^o–150^o range. The recently devised, and closely related, B3LYP and BH&HLYP schemes behave almost similarly in the calculation of torsional potentials, as is actually expected (Sancho-Garcia and Cornil, 2004) for highly parameterized specific purposes functionals that operate out of their fitting range. However, in spite of the aforesaid features, the most striking conclusion seems to be the general inability shown by all the hybrid and non-hybrid functionals to predict the shallow minimum for the *syn*-gauche structure.

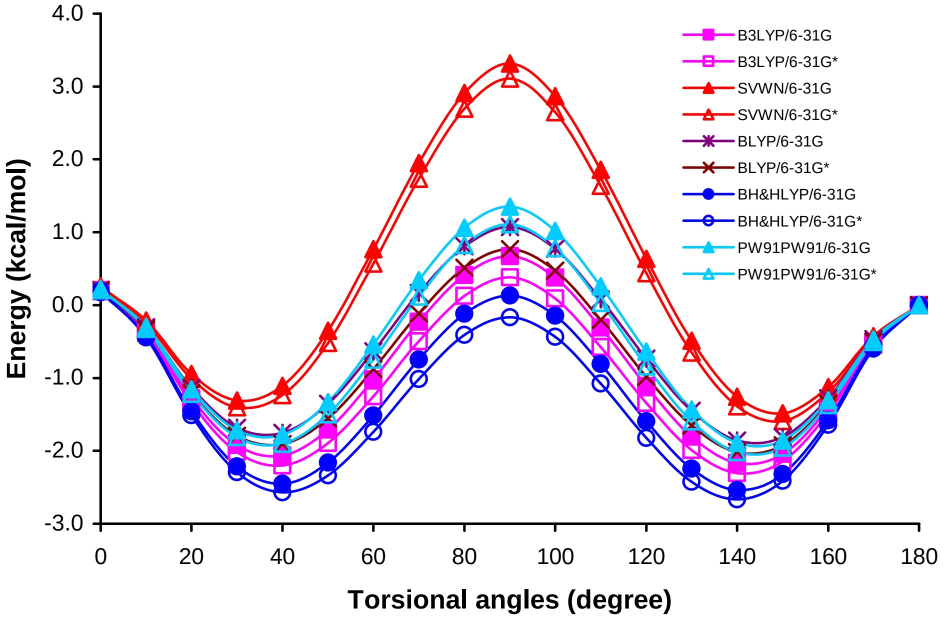


Figure 22 Torsional potential of bicarbazole, as calculated at various GGA levels with the 6-31G and 6-31G(d) basis sets.

The conformations of bicarbazole (Belletete *et al.*, 2004) and bifluorene (Poolmee *et al.*, 2005; Sriwichitkamol *et al.*, 2006) have been extensively investigated both experimentally and theoretically and can be used as a model to obtain information about the structure of polycarbazole and polyfluorene chains. Recently a number of theoretical studies have been reported addressing the torsional potential of bicarbazole and bifluorene. HF and DFT methods have been employed, using, in most of the cases, the split-valence 6-31G* basis sets, which contain polarization function only on the heavy atoms. These features have motivated the investigation performed here. Although several preliminary studies are found in the literature the question still remains open since torsional potential are largely dependent on the theoretical method chosen. This elusive character clearly deserves systematic application of *ab initio* methods in order to firmly establish a set of benchmark results to be further exploited; cost-effective and widely used density-functional methods are then carefully applied in a second step. Since some weaknesses of this theory have been recently detected for closely related systems, the present study will also analyze the way these functionals describe, not only the torsional barrier heights, but also the entire torsional potential of bicarbazole and bifluorene.

The most accurate point-wise calculated energies were subsequently used to obtain the corresponding Fourier expansion of the torsional potentials according to the form

$$V(\phi) = \sum_{n=1}^{m} \frac{1}{2} V_n (1 - \cos n\phi)$$

where V_n are the coefficients to be fitted and φ the inter-ring torsional angle. Such a potential energy function is almost universally included in all current force fields and, consequently, it is of much interest to determine these expansion coefficients as accurate as possible. Fits extended here up to the eight order yield a sufficiently negligible difference between calculated and fitted values.

The polymers based on the molecules of carbazole and fluorene all possess the sequence of bonded benzene rings characteristic of the geometry of poly(para-phynylene, PPP) (see in Figure 19). The similarity in the atomic structure of the polymers and molecules suggests a resemblance in their electronic and optical properties. Therefore, this procedure has been tested methods for studies the potential energy surface of biphenyl molecule and showed that this process can use for validate methods for conformational analysis. Aiming to assess the role played by both correlation effects and the size of the basis set for the determination of the equilibrium and transition state structures located on the torsional potential energy.

1.1 Biphenyl

The fully optimized torsional dihedral angle values for each stationary point located on the torsional potential for the biphenyl molecule are given in Table 1, along with the relative energy values, calculated at the HF, B3LYP, BH&HLYP and MP2 levels of theory employing different basis sets. The torsional potential of biphenyl has been the subject of a number of previous *ab initio* and DFT studies (McLean, 1980; Dunning, 1989; Woon, 1993; Helio, 2003; Karpfen, 1997). Therefore, the comparison between own results and previous *ab initio* and DFT studies were determined in this section. In Table 1, it can be seen from Table 1 that the gauche minima turn out to be considerably deeper and somewhat displaced to larger torsional angles (close to $40^o/140^o$) within the HF, DFT and MP2 schemes. It is well established experimentally that the barrier separating the global minimum, typically located around 40^o-50^o. The results obtain barriers between 1.7-2.1 kcal/mol for the planar saddle and 1.9-2.3 kcal/mol for the orthogonal saddle from DFT calculations, whereas the corresponding HF and MP2 values range from 3.1-3.2 and 2.3-4.1 kcal/mol for the planar saddle and from 1.1-1.6 and 1.5-2.2 kcal/mol for the perpendicular saddle, respectively. The HF barrier and MP2 barrier of the syn conformation are obtained much difference with the DFT methods. A while the barriers of the perpendicular conformation are in agreement with DFT methods. In Table 1, it shows experimental electron diffraction investigations on the torsional barrier of biphenyl and the previous *ab initio* calculations (Sancho-Garcia and Karpfen, 2005), MP2/cc-pV∞Z, MP4/cc-pV∞Z, CCSD/cc-pV∞Z and CCSD(T)/cc-pV∞Z. It can see that the B3LYP and BH&HLYP energy barriers agree with agreement with earlier calculations and experimental data. In addition to, the MP2 energy barriers at large basis sets, aug-cc-pVDZ and aug-cc-pVDZ basis sets, agree. It is indicated that the performance by B3LYP and BH&HLYP methods can use to predict the torsional potentials for hetero-aromatic dimers. In addition the B3LYP and BH&HLYP energy barriers from several basis sets were consider. It can see that the energy barrier predictions are sensitive both to the functional and basis sets used. Basis set effects are important. Therefore, in next type of methods would like to concentrates on the effect of methods and the basis set on the torsional energy by using Fourier expansion.

The relative energies of the rotamers were fitted to a six-term truncated Fourier expansion. The energies thus obtained were subsequently least-squares-fitted to a simple analytical form, which has been used by most workers in the field. The quality of the methods and basis sets are interesting for the calculation of torsional potential analysis. By using all methods to assess the quality of a given basis set and the relative torsional energy values are indistinguishable. The relative energies of the rotamers were then fitted to a six-term truncated Fourier expansion and the results are shown in Table 2. In Table 2, the fitted parameters V_1 to V_6 as obtained from HF, B3LYP, BH&HLYP and MP2 using several basis set were analyzed. V_1, V_3, and V_5 were negligible because these coefficients are zero. It was found that V_2 and V_4 show that largest variations with the different calculation methods and basis sets, but V_6 coefficients did not change much with different basis sets. The parameters from B3LYP and BH&HLYP using several basis set were considered because the B3LYP and BH&HLYP results agree with experimental data (see in Table 1). Figure 23 shows the fitted parameters as obtained from B3LYP, BH&HLYP using several basis set and MP2/aug-cc-pVTZ level of theory.

Table 1 Energetic (in kcal/mol) of stationary points in biphenyl relative to the planar anti conformers. (Values in parentheses are torsional angles in degrees at the local minimum).

Methods	syn	syn-gauche	perpendicular
HF/6-31G	3.24	0.0 (44.7)	1.66
HF/6-31G(d)	3.34	0.0 (45.5)	1.54
HF/6-311G(d,p)	3.19	0.0 (46.3)	1.22
HF/6-311++G(2d,2p)	3.06	0.0 (46.5)	1.18
B3LYP/6-31G	1.96	0.0 (37.6)	2.65
B3LYP/6-31G(d)	2.09	0.0 (38.4)	2.51
B3LYP/6-311G(d,p)	2.16	0.0 (40.5)	1.99
B3LYP/6-311++G(2d,2p)	1.93	0.0 (40.1)	1.92
B3LYP/cc-pVDZ	1.73	0.0 (39.0)	2.18
B3LYP/cc-pVTZ	1.93	0.0 (39.2)	2.14
B3LYP/aug-cc-pVDZ	1.45	0.0 (38.9)	2.14
B3LYP/aug-cc-pVTZ	1.86	0.0 (38.7)	2.15
BH&HLYP/6-31G	2.25	0.0 (39.0)	2.50
BH&HLYP/6-31G(d)	2.38	0.0 (39.8)	2.35
BH&HLYP/6-311G(d,p)	2.35	0.0 (41.2)	1.95
BH&HLYP/6-311++G(2d,2p)	2.14	0.0 (40.8)	1.88
BH&HLYP/cc-pVDZ	1.99	0.0 (40.0)	2.06
BH&HLYP/cc-pVTZ	1.93	0.0 (39.2)	2.14
BH&HLYP/aug-cc-pVDZ	1.72	0.0 (39.7)	2.02
BH&HLYP/aug-cc-pVTZ	2.06	0.0 (39.7)	2.14
MP2/6-31G	4.15	0.0 (46.3)	1.57
MP2/6-31G(d)	3.96	0.0 (44.6)	1.54
MP2/6-311G(d,p)	3.78	0.0 (45.4)	1.57
MP2/6-311++G(2d,2p)	2.79	0.0 (42.2)	1.78
MP2/cc-pVDZ	3.00	0.0 (43.1)	1.84
MP2/cc-pVTZ	2.44	0.0 (39.8)	2.23
MP2/aug-cc-pVDZ	2.33	0.0 (42.7)	1.66
MP2/cc-pV∞Z[a,b]	2.19	0.0 (39.8)	2.26
MP4/ cc-pV∞Z[b]	2.56	0.0 (42.1)	1.97
CCSD/cc-pV∞Z[b]	2.61	0.0 (44.3)	1.62
CCSD(T)/cc-pV∞Z[b]	2.51	0.0 (42.6)	1.85
Experimental[c]	1.4±0.5	44.4±1.2	1.6±0.5

[a]From the MP2/cc-pVTZ optimized geometry, [b](Almenningen, 1985), [c](Marchese *et al.*, 1980).

Table 2 Fitted potential parameters for single-bond torsional potential of biphenyl.

Methods	Basis set	V_1	V_2	V_3	V_4	V_5	V_6
HF	6-31G	0.0	-1.224	0.0	-2.409	0.0	-0.354
	6-31G(d)	0.0	-1.452	0.0	-2.405	0.0	-0.349
	6-311G(d,p)	0.0	-1.568	0.0	-2.207	0.0	-0.326
	6-311++G(2d,2p)	0.0	-1.557	0.0	-2.085	0.0	-0.321
B3LYP	6-31G	0.0	1.035	0.0	-2.094	0.0	-0.348
	6-31G(d)	0.0	0.764	0.0	-2.129	0.0	-0.348
	6-311G(d,p)	0.0	0.129	0.0	-1.977	0.0	-0.304
	6-311++G(2d,2p)	0.0	0.276	0.0	-1.818	0.0	-0.286
	cc-pVDZ	0.0	0.768	0.0	-1.727	0.0	-0.203
	aug-cc-pVDZ	0.0	0.801	0.0	-1.796	0.0	-0.285
	cc-pVTZ	0.0	0.511	0.0	-1.921	0.0	-0.303
	aug-cc-pVTZ	0.0	0.616	0.0	-1.961	0.0	-0.337
BH&HLYP	6-31G	0.0	0.614	0.0	-2.231	0.0	-0.363
	6-31G(d)	0.0	0.339	0.0	-2.249	0.0	-0.362
	6-311G(d,p)	0.0	0.070	0.0	-2.075	0.0	-0.324
	6-311++G(2d,2p)	0.0	0.055	0.0	-1.932	0.0	-0.313
	cc-pVDZ	0.0	0.342	0.0	-1.919	0.0	-0.271
	aug-cc-pVDZ	0.0	0.576	0.0	-2.001	0.0	-0.316
	cc-pVTZ	0.0	0.341	0.0	-2.010	0.0	-0.328
	aug-cc-pVTZ	0.0	0.382	0.0	-2.001	0.0	-0.316
MP2	6-31G	0.0	-2.152	0.0	-2.799	0.0	-0.435
	6-31G(d)	0.0	-1.659	0.0	-2.858	0.0	-0.467
	6-311G(d,p)	0.0	-1.746	0.0	-2.645	0.0	-0.459
	cc-pVDZ	0.0	-0.789	0.0	-2.373	0.0	-0.371
	aug-cc-pVDZ	0.0	-0.377	0.0	-2.014	0.0	-0.256
	cc-pVTZ	0.0	0.220	0.0	-2.322	0.0	-0.472
	aug-cc-pVTZ	0.0	0.145	0.0	-2.309	0.0	-0.335

In Figure 23 is show the effect of electron correlation and quality of the basis set on the potential energy curve are shown. It can be seen that the MP2/aug-cc-pVTZ energy values are always in agreement with the B3LYP and BH&HLYP values for the Fourier fit coefficients. The B3LYP and BH&HLYP at 6-311G(d,p) and 6-311++G(2d,2p) basis sets tend to predict the parameters agree with MP2/aug-cc-pVTZ parameter. V_2 and V_6 have both the same trend, whereas V_4 behave slightly different. These results are in agreement with those given in Table 1 that the B3LYP and BH&HLYP both 6-311G(d,p) and 6-311++G(2d,2p) basis sets have been predicted relative energy of the syn, anti-syn and perpendicular conformations. Taking this into account, it can be concluded that the Fourier least-squares-fitted method is appropriate to validate various methods. Therefore, it can be used for bicarbazole and bifluorene molecule. Due to the structure for bicarbazole and bifluorene show the same behavior as the biphenyl molecule.

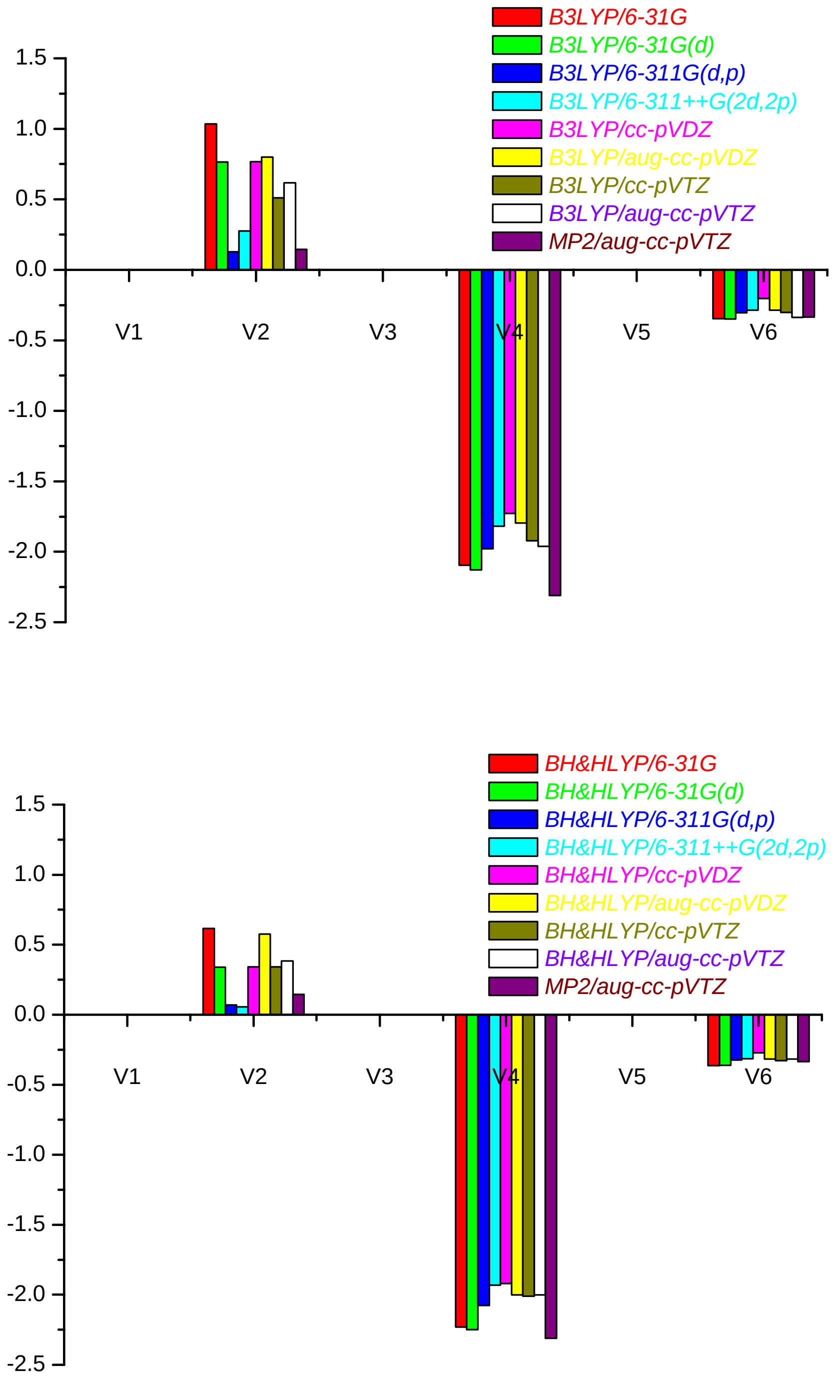


Figure 23 Fourier potential parameters for biphenyl calculated by B3LYP, BH&HLYP at several basis sets and MP2/aug-cc-pVTZ basis set.

1.2 Bicarbazole and Bifluorene

For last section, it can be concluded that the Fourier least-squares-fitted method is appropriate to validate various methods. Therefore, Fourier least-squares-fitted method was used for study with bicarbazole and bifluorene molecules. Due to the structure for bicarbazole and bifluorene show the same behavior as the biphenyl molecule. Evidently, the molecules of bicarbazole and bifluorene are bigger than biphenyl, but the torsional potential can be calculated at some basis sets. Type of methods should consider which level of calculations is the most appropriate method for bicarbazole and bifluorene molecules. The relative energies of the stationary points, including data from HF, B3LYP, BH&HLYP and MP2 calculations with several basis sets are reported in Table 3. It found that the relative energies of bicarbazole and bifluorene have similar trend as biphenyl. The torsional energies are close to that obtained for biphenyl by using the same level of calculations. The sensitivity of the relative energy to the level of the theory and the size of the basis set is easily seen and the HF and MP2 energy values of syn and anti energy barrier are always higher than the B3LYP and BH&HLYP for the energy barrier. Whereas perpendicular energy barrier are lower. The results show that exchange-correlation of density functional theory effects seem to decrease the planar (0^{o} and 180^{o}) barriers and the perpendicular barrier. This is indicated that higher exchange-correlation methods of theory energy barriers are accurate than low exchange-correlation methods. This conclusion a definitive direction of the exchange-correlation effects on the torsional potential energy, which certainly is a satisfied result. Therefore, the effect of exchange correlation, B3LYP (20% of HF exchange) and BH&HLYP (50% of HF exchange), of density functional theory and quality of the basis set were concentrated on the study of the potential energy curve. The quality of the basis sets is interesting with in regard to the Pople and Dunning basis set for the calculation. By using all methods to assess the quality of a given basis set and the relative torsional energy values are indistinguishable. The fitted parameters V_1 to V_6 as obtained from B3LYP, BH&HLYP and MP2 coefficients are compiled in Table 4. One point that may call our attention is which level of calculation can be considered to be the best.

The parameters obtained from B3LYP and BH&HLYP using by several basis sets and MP2 calculations were analyzed.

These fitted parameters for bifluorene show the same behavior as the biphenyl molecule (Karpfen, 1997 and Almenningen, 1985). V_1, V_3 and V_5 were negligible because these coefficients are small about 0.1 with different basis sets. It was found that V_2, V_4 and V_6, show that largest variations with the different calculation methods and basis sets. The coefficients of bicarbazole V_1, V_2, V_4 and V_6 were considered and V_3 and V_5 coefficients were neglected.

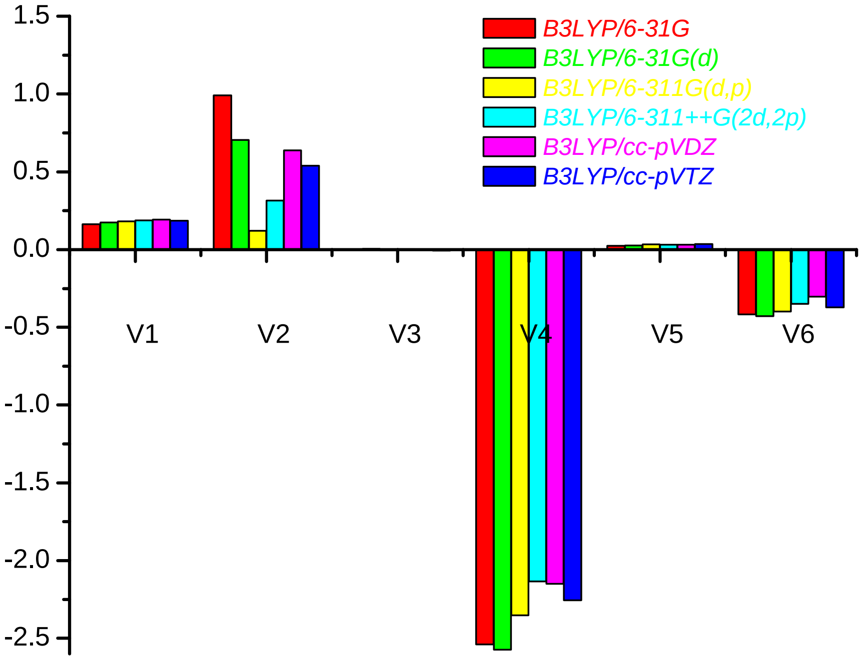
For Figure 24 and 25 show variations of parameter coefficients from the different calculation methods and basis sets of bicarbazole molecules. The parameter coefficients of bicarbazole were calculated at B3LYP and BH&HLYP levels of theory using the 6-31G, 6-31G(d), 6-311G(d,p), 6-311++G(2d,2p), cc-pVDZ and cc-pVTZ basis sets. From Figure 24 and 25 it can be seen that the coefficients V_1, V_2, V_4 and V_6 vary in the range about 0.2, 1.5, -2.5 and -0.5 respectively for all basis sets. In addition to, the coefficients from Dunning's basis sets, cc-pVDZ and cc-pVTZ basis set, are in agreement with the coefficients from Pople's basis sets. The fitted torsional parameters show the expected trends with comparable V_1, V_2, V_4 and V_6 parameters from MP2 and both functional. It can be seen that the MP2/cc-pVDZ energy values are always in agreement with the B3LYP/and BH&HLYP from 6-311G(d,p) 6-311++G(2d,2p) basis sets, whereas the 6-31G basis set overestimates. Thus the basis set size affects the calculation of the torsional energy, with the larger sets giving more realistic results. Similar results were observed for bifluorene molecule. It is noted that the B3LYP and BH&HLYP calculations predicted relative energies of the carbazole-based conformations in good agreement with MP2/cc-pVDZ methods. It can be concluded that the B3LYP and BH&HLYP method is appropriate, in terms of both accuracy and computing time, for the ground state geometry optimization. Therefore, B3LYP and BH&HLYP optimized geometries were test to answer which optimizations are appropriate to calculate the vertical excitation energies in next section.

Table 3 Energetic (in kcal/mol) of stationary points in bicarbazole and bifluorene relative to all conformers. (Values in parentheses are torsional angles in degrees at the local minimum).

Methods	syn	syn-gauche	Perpen-dicular	anti-gauche	anti
Bicarbazole					
HF/6-31G	3.79	0.14	1.74	0.0 (134.9)	3.65
HF/6-31G(d)	3.94	0.10	1.61	0.0 (134.0)	3.77
HF/6-311G(d,p)	3.79	0.09	1.31	0.0 (132.9)	3.60
HF/6-311++G(2d,2p)	4.00	0.47	1.59	0.0 (134.7)	3.80
B3LYP/6-31G	2.37	0.12	2.85	0.0 (142.7)	2.18
B3LYP/6-31G(d)	2.51	0.11	2.68	0.0 (142.0)	2.31
B3LYP/6-311G(d,p)	2.53	0.11	2.15	0.0 (140.1)	2.32
B3LYP/6-311++G(2d,2p)	2.24	0.11	2.09	0.0 (141.0)	2.02
B3LYP/cc-pVDZ	2.10	0.12	2.33	0.0 (141.4)	1.88
B3LYP/ cc-pVTZ	2.27	0.12	2.33	0.0 (141.6)	2.06
BH&HLYP/6-31G	2.72	0.09	2.68	0.0 (141.0)	2.54
BH&HLYP/6-31G(d)	2.86	0.10	2.50	0.0 (140.2)	2.67
BH&HLYP/6-311G(d,p)	2.80	0.11	2.06	0.0 (138.9)	2.60
BH&HLYP/6-311++G(2d,2p)	2.54	0.11	1.99	0.0 (139.6)	2.32
BH&HLYP/cc-pVDZ	2.43	0.11	2.16	0.0 (139.9)	2.21
BH&HLYP/cc-pVTZ	2.52	0.11	2.26	0.0 (140.5)	2.31
MP2/6-31G	5.10	0.10	1.89	0.0 (133.8)	4.90
MP2/6-31G(d)	4.72	0.11	2.11	0.0 (135.2)	4.47
MP2/6-311G(d,p)	4.51	0.18	1.91	0.0 (136.7)	4.24
MP2/cc-pVDZ	3.64	0.14	2.06	0.0 (137.1)	3.39
Bifluorene					
HF/6-31G	3.34	0.05	1.81	0.0 (136.1)	3.33
HF/6-31G(d)	3.44	0.06	1.67	0.0 (135.2)	3.43
HF/6-311G(d,p)	3.30	0.05	1.40	0.0 (134.1)	3.29
HF/6-311++G(2d,2p)	3.12	0.05	1.28	0.0 (134.0)	3.10
B3LYP/6-31G	1.99	0.03	2.94	0.0 (143.3)	1.97
B3LYP/6-31G(d)	2.12	0.02	2.79	0.0 (142.7)	2.10
B3LYP/6-311G(d,p)	2.13	0.01	2.29	0.0 (141.0)	2.12
B3LYP/6-311++G(2d,2p)	1.87	0.01	2.24	0.0 (141.5)	1.85
B3LYP/cc-pVDZ	1.75	0.02	2.45	0.0 (142.2)	1.73
B3LYP/cc-pVTZ	1.89	0.03	2.47	0.0 (142.0)	1.88
BH&HLYP/6-31G	2.32	0.02	2.76	0.0 (141.9)	2.31
BH&HLYP/6-31G(d)	2.44	0.01	2.59	0.0 (141.1)	2.43
BH&HLYP/6-311G(d,p)	2.38	0.01	2.19	0.0 (139.8)	2.37
BH&HLYP/6-311++G(2d,2p)	2.14	0.01	2.13	0.0 (140.2)	2.12
BH&HLYP/cc-pVDZ	2.04	0.02	2.28	0.0 (140.7)	2.03
BH&HLYP/cc-pVTZ	2.12	0.02	2.38	0.0 (141.0)	2.11
MP2/6-31G	4.26	0.06	1.88	0.0 (134.8)	4.26
MP2/6-31G(d)	4.13	0.04	2.15	0.0 (136.1)	4.12
MP2/6-311G(d,p)	3.95	0.04	1.98	0.0 (136.2)	3.92
MP2/cc-pVDZ	3.16	0.02	2.14	0.0 (137.7)	3.14

Table 4 Fitted potential parameters for single-bond torsional potential of bicarbazole and bifluorene.

Methods	Basis set	V_1	V_2	V_3	V_4	V_5	V_6
	Bicarbazole						
B3LYP	6-31G	0.163	0.993	-0.0001	-2.540	0.025	-0.418
	6-31G(d)	0.174	0.705	0.0043	-2.572	0.026	-0.428
	6-311G(d,p)	0.180	0.120	-0.0053	-2.352	0.034	-0.400
	6-311++G(2d,2p)	0.187	0.316	0.0015	-2.135	0.031	-0.349
	cc-pVDZ	0.193	0.638	-0.0028	-2.151	0.032	-0.302
	cc-pVTZ	0.185	0.539	-0.0059	-2.255	0.035	-0.372
BH&HLYP	6-31G	0.146	0.505	0.005	-2.692	0.022	-0.460
	6-31G(d)	0.160	0.204	0.011	-2.710	0.024	-0.468
	6-311G(d,p)	0.169	-0.208	0.006	-2.465	0.026	-0.436
	6-311++G(2d,2p)	0.178	-0.044	0.013	-2.272	0.025	-0.395
	cc-pVDZ	0.179	0.193	0.008	-2.278	0.025	-0.352
	cc-pVTZ	0.177	0.249	0.006	-2.374	0.025	-0.408
MP2	6-31G	-0.050	-2.344	0.288	-3.967	-0.040	-0.765
	6-31G(d)	-0.026	-1.840	0.357	-3.860	-0.081	-0.640
	6-311G(d,p)	0.157	-1.683	-0.012	-3.452	0.130	-0.777
	cc-pVDZ	0.180	-0.873	0.031	-2.971	0.044	-0.585
	Bifluorene						
B3LYP	6-31G	0.013	1.339	-0.020	-2.432	0.022	-0.3736
	6-31G(d)	0.008	1.060	-0.017	-2.465	0.021	-0.3840
	6-311G(d,p)	0.005	0.528	-0.021	-2.273	0.027	-0.3635
	6-311++G(2d,2p)	0.006	0.707	-0.012	-2.081	0.024	-0.3194
	cc-pVDZ	0.010	0.987	-0.018	-2.088	0.025	-0.2752
	cc-pVTZ	0.006	0.920	-0.022	-2.202	0.028	-0.3334
BH&HLYP	6-31G	0.013	0.862	-0.017	-2.568	0.017	-0.416
	6-31G(d)	0.009	0.579	-0.015	-2.583	0.017	-0.423
	6-311G(d,p)	0.008	0.211	-0.015	-2.370	0.019	-0.400
	6-311++G(2d,2p)	0.012	0.360	-0.008	-2.189	0.015	-0.364
	cc-pVDZ	0.002	0.574	-0.012	-2.220	0.018	-0.301
	cc-pVTZ	0.010	0.638	-0.016	-2.300	0.019	-0.371
MP2	6-31G	-0.030	-1.656	-0.015	-3.387	0.044	-0.730
	6-31G(d)	-0.008	-1.258	-0.020	-3.459	0.044	-0.719
	6-311G(d,p)	-0.004	-1.252	-0.026	-3.250	0.058	-0.707
	cc-pVDZ	0.050	-0.513	-0.018	-2.825	-0.016	-0.501



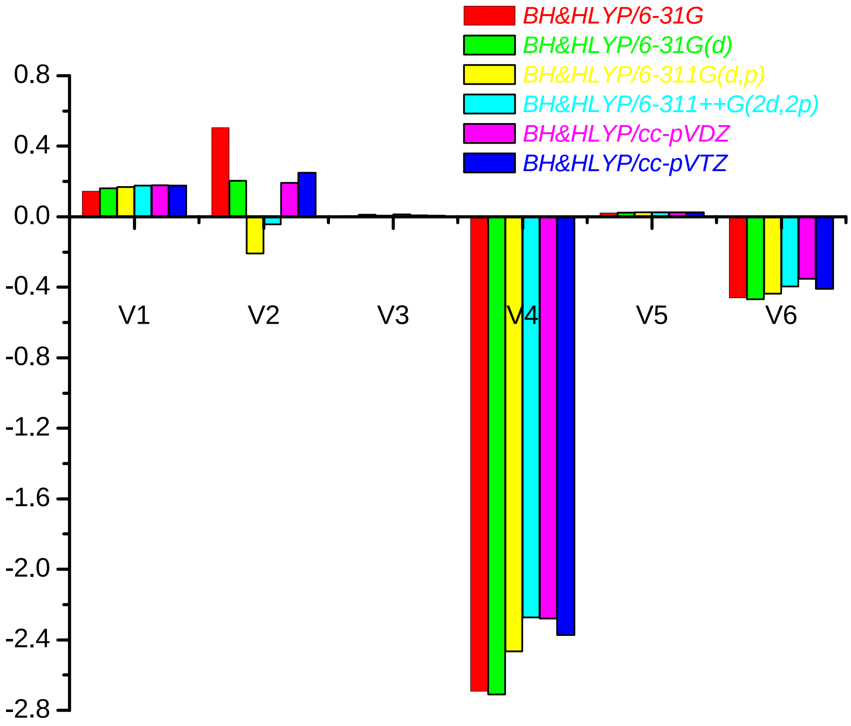


Figure 24 Fourier potential parameters for bicarbazole calculated by B3LYP, BH&HLYP level of theory at several basis sets.

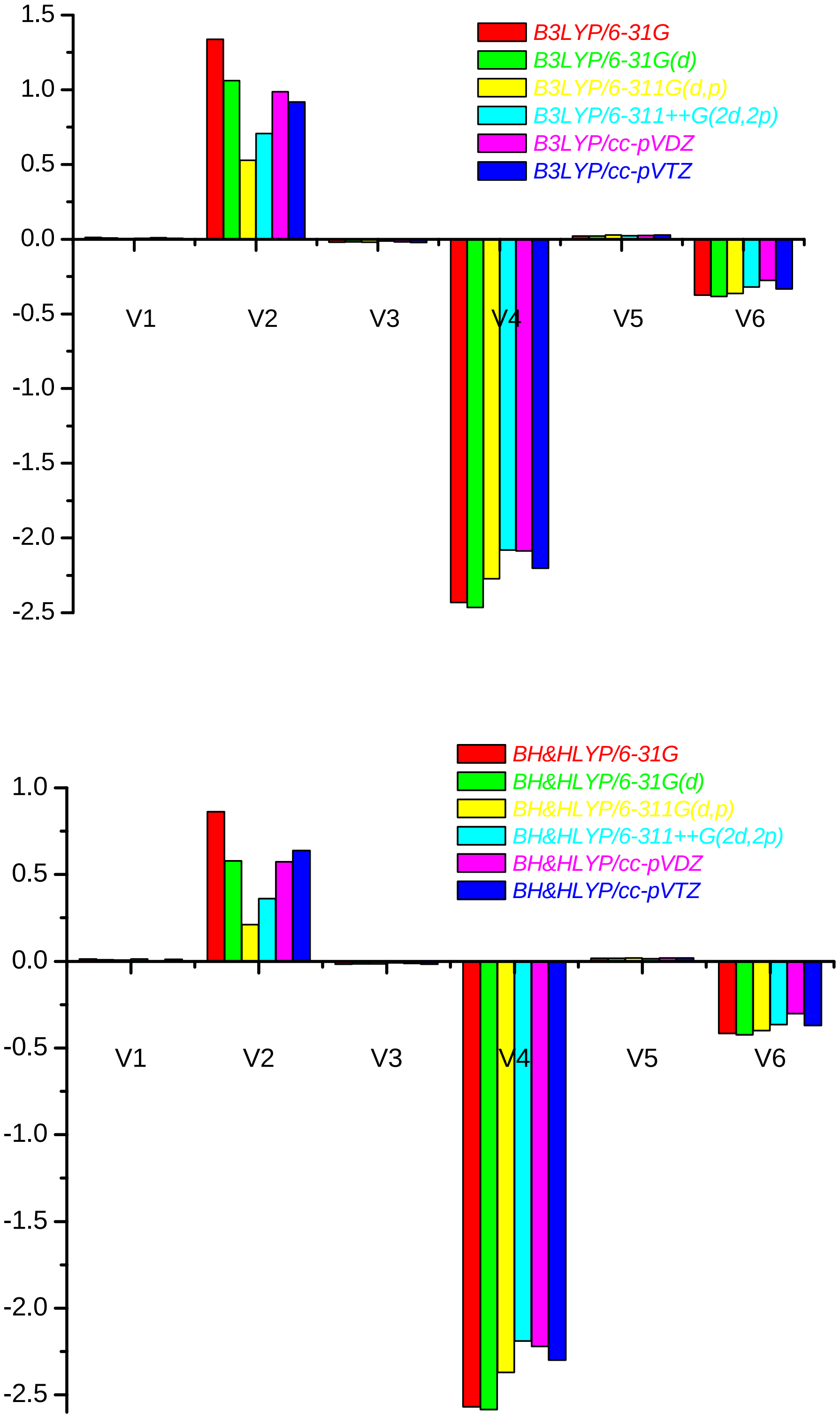
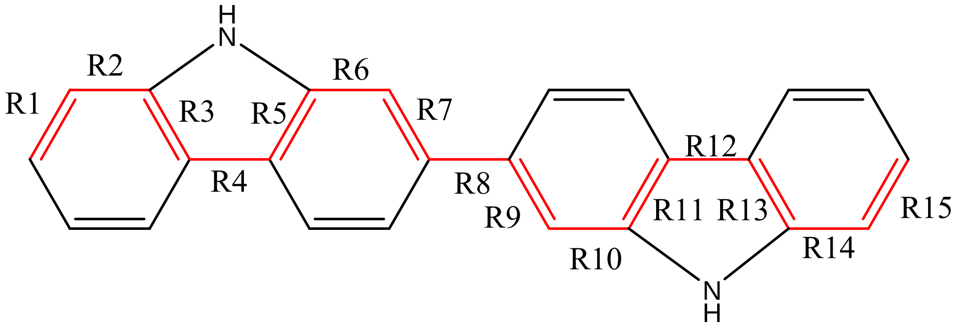


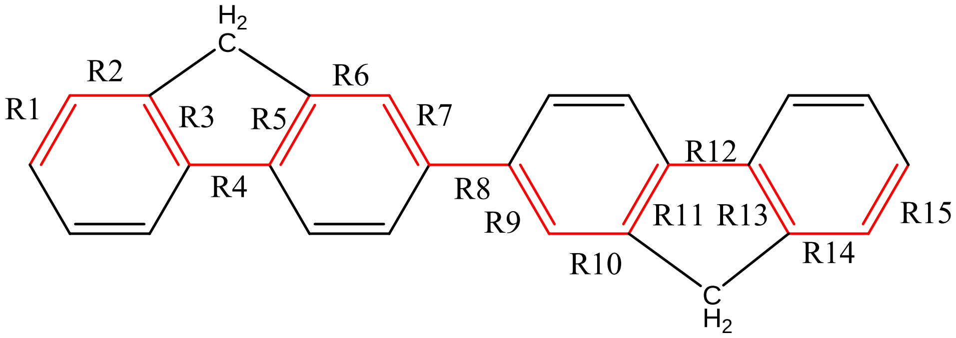
Figure 25 Fourier potential parameters for bifluorene calculated by B3LYP, BH&HLYP level of theory at several basis sets.

2. Structure and Excitation Energy of Bicarbazole and Bifluorene

The relative energies for the bifluorene and bicarbazole molecules show global minimum at anti-gauche conformation (Figure 26). At all levels of description, and in agreement with previous *ab initio* investigations (Almenningen, 1985), the lowest energy conformation of bifluorene and bicarbazole are very similar preferred structure. Structure and numbering scheme of bicarbazole and bifluorene are depicted in Figure 26.



(a) Bicarbazole



(b) Bifluorene

Figure 26 Structure and numbering scheme of (a) bicarbazole and (b) bifluorene models.

The optimized bond lengths and dihedral angles between the subunits of bicarbazole and bifluorene by using B3LYP and BH&HLYP at several basis sets are summarized in Table 5 and 6, respectively. It is interesting to point out that by increasing of the conjugation length observed for bifluorene compared to bicarbazole and substituting a carbon atom by nitrogen in the hetero-aromatic dimeric species quite remarkable changes are observed regarding the steric effects. The two systems under study with B3LYP and BH&HLYP methods were compared to gain the best structure for studying the electronic and optical properties. Combining Table 5 with Table 6 shows that the results of the optimized structures for bicarbazole and bifluorene molecules have the similar conformations, and bond angles do not suffer appreciable variation with the B3LYP and BH&HLYP methods in the bicarbazole molecule, as well as bifluorene molecule. But the bond lengths from B3LYP calculations are longer than the distance from BH&HLYP calculations, as it can be seen from Figure 27. This clearly indicates that the increase of substituting a nitrogen atom by carbon in the hetero-aromatic for bifluorene molecule compared to bicarbazole does not significantly affect the conformation of the molecule. The electronic nature of the substituent is seen to play a key role on the preferred structure and properties of the dimers. Therefore, this method can test the best geometries optimized of the ground state for studying lowest vertical excitation energy by using TD-(B3LYP/6-311++G(2d,2p)) calculations at the optimized geometries of the ground state.

Table 5 Equilibrium geometrical parameters of bicarbazole in the ground state obtain from B3LYP and BH&HLYP methods at several basis sets.

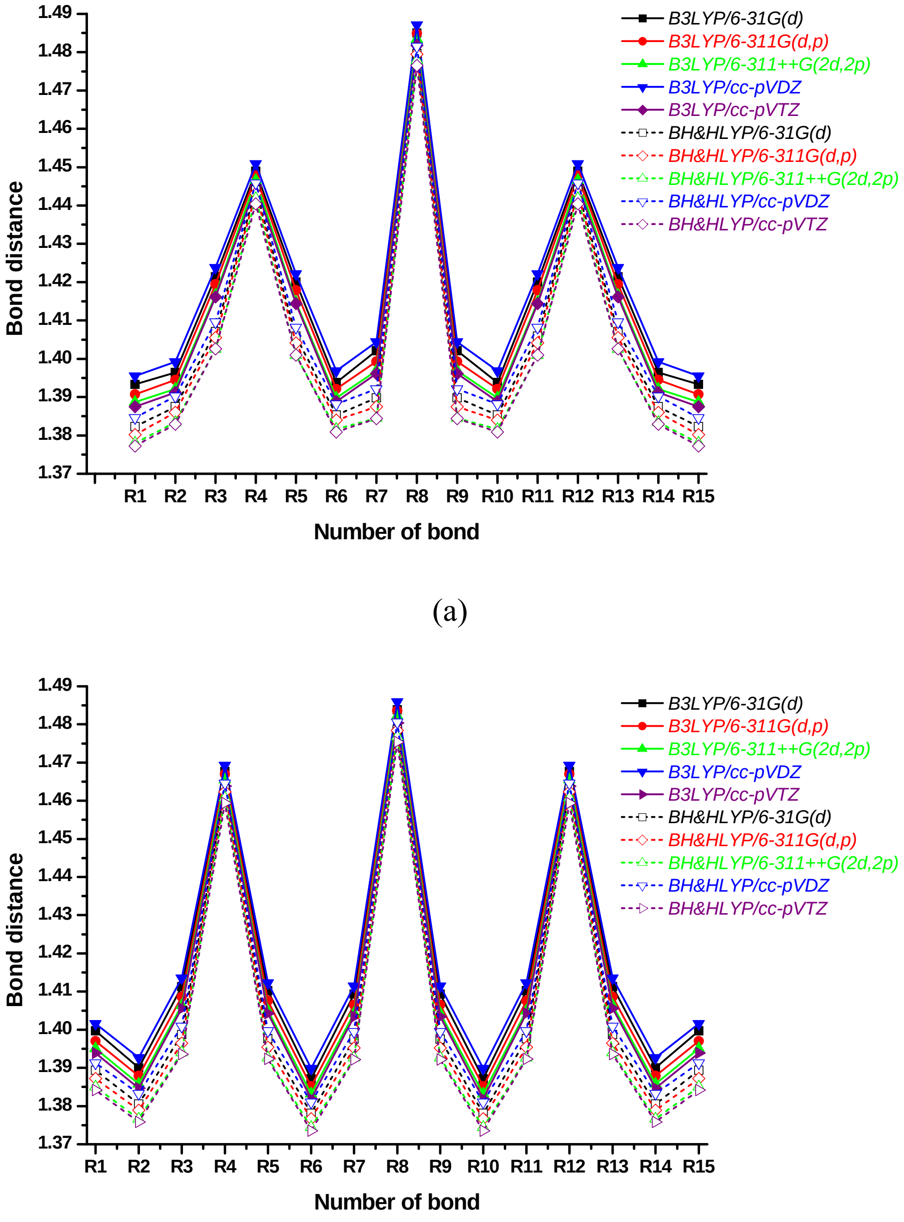
Distance (Å)	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(d,p)	B3LYP/ 6-311++G(2d,2p)	B3LYP/ cc-pVDZ	B3LYP/ cc-pVTZ
R1	1.393	1.391	1.389	1.396	1.388
R2	1.396	1.394	1.392	1.399	1.391
R3	1.421	1.419	1.417	1.424	1.416
R4	1.449	1.448	1.447	1.451	1.445
R5	1.420	1.418	1.415	1.422	1.414
R6	1.394	1.392	1.390	1.397	1.389
R7	1.402	1.399	1.397	1.404	1.396
R8	1.485	1.485	1.483	1.487	1.482
R9	1.402	1.399	1.397	1.404	1.396
R10	1.394	1.392	1.390	1.397	1.389
R11	1.420	1.418	1.415	1.422	1.414
R12	1.449	1.448	1.447	1.451	1.445
R13	1.421	1.419	1.417	1.424	1.416
R14	1.396	1.394	1.392	1.399	1.391
R15	1.393	1.391	1.389	1.396	1.388

Distance (Å)	BH&HLYP/ 6-31G(d)	BH&HLYP/ 6-311G(d,p)	BH&HLYP/ 6-311++G(2d,2p)	BH&HLYP/ cc-pVDZ	BH&HLYP/ cc-pVTZ
R1	1.382	1.380	1.378	1.385	1.377
R2	1.388	1.386	1.383	1.390	1.383
R3	1.407	1.406	1.402	1.410	1.403
R4	1.444	1.443	1.442	1.446	1.440
R5	1.406	1.404	1.401	1.408	1.401
R6	1.385	1.384	1.382	1.388	1.381
R7	1.390	1.388	1.384	1.392	1.384
R8	1.480	1.480	1.478	1.482	1.476
R9	1.390	1.388	1.384	1.392	1.384
R10	1.385	1.384	1.382	1.388	1.381
R11	1.406	1.404	1.401	1.408	1.401
R12	1.444	1.443	1.442	1.446	1.440
R13	1.407	1.406	1.402	1.410	1.403
R14	1.388	1.386	1.383	1.390	1.383
R15	1.382	1.380	1.378	1.385	1.377

Table 6 Equilibrium geometrical parameters of bifluorene in the ground state obtain from B3LYP and BH&HLYP methods at several basis sets.

Distance (Å)	B3LYP/ 6-31G(d)	B3LYP/ 6-311G(d,p)	B3LYP/ 6-311++G(2d,2p)	B3LYP/ cc-pVDZ	B3LYP/ cc-pVTZ
R1	1.400	1.397	1.395	1.402	1.394
R2	1.390	1.388	1.386	1.393	1.385
R3	1.411	1.409	1.406	1.414	1.406
R4	1.468	1.467	1.466	1.469	1.464
R5	1.410	1.408	1.405	1.412	1.404
R6	1.387	1.385	1.383	1.390	1.382
R7	1.409	1.407	1.404	1.411	1.403
R8	1.484	1.484	1.482	1.486	1.480
R9	1.409	1.407	1.404	1.411	1.403
R10	1.387	1.385	1.383	1.390	1.382
R11	1.410	1.408	1.405	1.412	1.404
R12	1.468	1.467	1.466	1.469	1.464
R13	1.411	1.409	1.406	1.414	1.406
R14	1.390	1.388	1.386	1.393	1.385
R15	1.400	1.397	1.395	1.402	1.394

Distance (Å)	BH&HLYP/ 6-31G(d)	BH&HLYP/ 6-311G(d,p)	BH&HLYP/ 6-311++G(2d,2p)	BH&HLYP/ cc-pVDZ	BH&HLYP/ cc-pVTZ
R1	1.389	1.387	1.385	1.391	1.384
R2	1.381	1.379	1.377	1.383	1.376
R3	1.399	1.397	1.394	1.401	1.394
R4	1.463	1.462	1.461	1.465	1.459
R5	1.398	1.395	1.393	1.400	1.392
R6	1.378	1.377	1.374	1.381	1.374
R7	1.398	1.395	1.393	1.400	1.392
R8	1.479	1.478	1.477	1.481	1.475
R9	1.398	1.395	1.393	1.400	1.392
R10	1.378	1.377	1.374	1.381	1.374
R11	1.398	1.395	1.393	1.400	1.392
R12	1.463	1.462	1.461	1.465	1.459
R13	1.399	1.397	1.394	1.401	1.394
R14	1.381	1.379	1.377	1.383	1.376
R15	1.389	1.387	1.385	1.391	1.384



(a)

(b)

Figure 27 Bond lengths of (a) bicarbazole and (b) bifluorene from B3LYP and BH&HLYP calculations at several basis sets.

The calculated vertical excitation energies and oscillator strengths for the most relevant three singlet excited states in bicarbazole and bifluorene molecules are listed in Table 7 and 8. Despite the good agreement between the calculated excitation energies and the experimental data, it is also necessary to check the validity of the methods for optimized of ground state geometry by B3LYP and BH&HLYP methods. Table 7 shows that the first excitation $S_0 \rightarrow S_1$ electronic transition appears to have the highest intensity as determined by its large oscillator strength (*f*). The lowest lying singlet excited state is strongly optically allowed and dominated by a configuration in which an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied orbital (LUMO). Comparing to experimental excitation energies available in all cases, it can be seen that the TD-B3LYP/6-311++G(2d,2p) excitation energy calculations give excellent prediction of the excitation energies for the $S_0 \rightarrow S_1$ transition in the range of 0.1-0.2 eV. However, the TD-B3LYP/6-311++G(2d,2p) at BH&HLYP calculations can provide relatively accurate predictions of vertical excitation energies for both molecules. Compared with the available experimental excitation energies, TD-B3LYP/6-311++G(2d,2p) at BH&HLYP calculations have on average deviation of the calculated excitation energies for about 0.01 eV. Therefore, we can conclude that the BH&HLYP optimize geometry method is considered to be the most suitable approach to calculate the ground state geometry, and it was employed to investigate the details of the different states of electronic transitions.

Table 7 Excitation energy (E_{ex}) and oscillator strength (*f*) of bicarbazole as obtained by TD-B3LYP/6-311G(2d,2p), based on B3LYP and BH&HLYP geometries using several basis sets.

Methods	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$		$S_0 \rightarrow S_3$	
	E_{ex} (eV)	*f*	E_{ex} (eV)	*f*	E_{ex} (eV)	*f*
B3LYP						
6-31G(d)	3.75	1.0830	3.77	0.0043	3.79	0.0791
6-311G(d,p)	3.79	1.0281	3.80	0.0048	3.81	0.1168
6-311++G(2d,2p)	3.80	1.0465	3.81	0.0046	3.82	0.1070
cc-pVDZ	3.75	1.0667	3.77	0.0044	3.78	0.0891
cc-pVTZ	3.79	1.0676	3.81	0.0045	3.83	0.0923
BH&dHLYP						
6-31G(d)	3.85	0.9302	3.86	0.0047	3.87	0.2026
6-311G(d,p)	3.88	0.6922	3.88	0.0051	3.89	0.4275
6-311++G(2d,2p)	3.89	0.7639	3.89	0.0049	3.90	0.3624
cc-pVDZ	3.84	0.8928	3.85	0.0048	3.86	0.2356
cc-pVTZ	3.88	0.9245	3.88	0.0047	3.90	0.2113
Experimental[a]	3.85					

[a](Belletete *et al.*, 2004)

Table 8 Excitation energy (E_{ex}) and oscillator strength (*f*) of bifluorene as obtained by TD-B3LYP/6-311G(2d,2p), based on B3LYP and BH&HLYP geometries using several basis sets.

Methods	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$		$S_0 \rightarrow S_3$	
	E_{ex} (eV)	*f*	E_{ex} (eV)	*f*	E_{ex} (eV)	*f*
B3LYP						
6-31G(d)	3.74	1.3522	4.23	0.0003	4.34	0.0002
6-311G(d,p)	3.77	1.3431	4.26	0.0003	4.36	0.0004
6-311++G(2d,2p)	3.78	1.3484	4.27	0.0003	4.37	0.0004
cc-PVDZ	3.73	1.3490	4.22	0.0003	4.32	0.0001
cc-pVTZ	3.77	1.3547	4.27	0.0003	4.38	0.0003
BH&HLYP						
6-31G(d)	3.84	1.3377	4.31	0.0004	4.41	0.0009
6-311G(d,p)	3.86	1.3307	4.34	0.0004	4.43	0.0013
6-311++G(2d,2p)	3.87	1.3355	4.35	0.0004	4.45	0.0014
cc-pVDZ	3.83	1.3354	4.30	0.0004	4.40	0.0008
cc-pVTZ	3.87	1.3429	4.34	0.0004	4.45	0.0011
Experimental[a]	3.87					

[a](Bouchard *et al.*, 2003)