Theoretical Investigation on Electronic Transition of Carbazole-Based Molecules by TD-DFT Methods

1. Conformational Analysis of Carbazole-Based Molecules

The structures of carbazole-based molecules, as illustrated in Figure 21, can be separated into 2 types: Cz-copolymerized with five-membered (Cz-co-Th and Cz-co-F) and six-membered (Cz-dimer, Cz-co-P and Cz-co-Fl) aromatic ring systems. The torsional energy curves, as shown in Figure 35, indicate that Cz-copolymerized with furan-membered aromatic rings is more stable in a planar configuration, and has higher energy barriers to rotation, than Cz-copolymerized with thiophene and with six-membered aromatic ring monomers. The structures of carbazole-based molecules have been previously investigated using the HF/6-31G(d) method (Belletete *et al.*, 2004). The results indicated that the Cz-dimer and Cz-co-Th are nonplanar in their ground electronic states, whereas Cz-co-F is completely planar. The same behavior has been found for the bithiophene molecule (Duarte *et al.*, 2003). It seems that the DFT methods tend to predict geometries closer to planarity than the conventionally correlated *ab initio* methods like MP2. Therefore, this work concentrates on the effect of the basis set on the torsional energy curves by using the B3LYP density function, and MP2 for comparison.

One point that should be considered is which level of calculations is the most appropriate method for a carbazole-based system. The relative energies of the stationary points, including data from B3LYP and MP2 calculations with larger basis sets, are reported in Table 17. The sensitivity of the relative energy to the size of the basis set is evident. It can also be seen that the B3LYP energy barrier at 6-311G(d,p) and 6-311++G(2d,2p) are in agreement with MP2 results. For example, in the case of Cz-dimer with the orthogonal configuration, the energies are 2.151, 2.092 and 2.054 kcal/mol by the B3LYP/6-311G(d,p), B3LYP/6-311++G(2d,2p) and MP2/cc-pVDZ levels of theory respectively, while at lower levels of theory, the B3LYP/6-31G and

B3LYP/6-31G(d) methods, relative energies were overestimated by about 0.8-1.2 kcal/mol. Similar results were observed for other carbazole-based molecules.

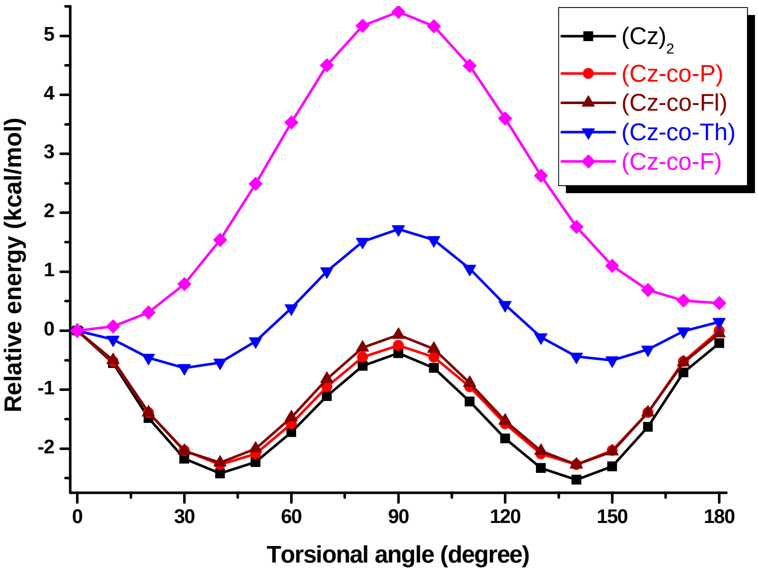


Figure 35 Torsional energy curves of carbazole-based molecules as obtained by B3LYP/6-311G(d,p) calculations.

The relative energies for the Cz-dimer, Cz-co-P, Cz-co-Fl and Cz-co-Th molecules show two local minima with the syn-gauche and anti-gauche forms, whereas Cz-co-F has local minima with the syn and anti forms (Figure 35). At all levels of description, and in agreement with previous *ab initio* investigations, the anti-gauche conformation is the energetically preferred structure of carbazole-based molecules. From Figure 35, the lowest energy conformation of Cz-dimer, Cz-co-P and Cz-co-Fl are very similar. The torsional energy curves are close to that obtained for biphenyl by using the same level of calculations (Karpfen *et al.*, 1997). This clearly indicates that the increase of the conjugation length observed for Cz-dimer, Cz-co-P and Cz-co-Fl compared to biphenyl does not significantly affect the conformation of the molecule. In contrast to the cases of carbazole-co-five membered aromatic rings (Cz-co-Th and Cz-co-F), a rather different characteristic is observed near the 0^{o} planar stationary point. The structure of Cz-co-Th is slightly less twisted than the Cz-co-six-membered ring monomers. Accordingly, the inter-ring distances between carbazole monomer and the five-membered ring monomers are slightly shorter. As expected, a five-membered aromatic ring creates less steric hindrance than a six-membered ring, however, the thiophene monomer induces higher steric effects than the furan monomer, due to the larger atomic size of sulfur compared to the oxygen atom.

The relative energies of the rotamers were then fitted to a six-term truncated Fourier expansion and the results are shown in Table 18. In all cases, the simple Fourier representation (see equation 1) of the torsional curve is sufficiently accurate when using a six-term expansion. The parameters obtained from B3LYP using 6-31G, 6-31G(d), 6-311G(d,p) and 6-311++G(2d,2p) basis sets and MP2 using the cc-pVDZ basis set were analyzed. The quality of the basis sets is interesting in regards to the Pople basis set for the calculation of carbazole-based molecules. 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, and MP2 coefficients are compiled in Table 18.

The fitted parameters for carbazole dimer and carbazole-co-five-membered aromatic rings show a similar pattern as biphenyl. It was found that V_2, followed by V_4, shows the largest variations with the different calculation methods and basis sets. For instance, in the case of Cz-dimer (Table 18), the coefficients V_2 and V_4 vary by 0.4 and 0.3, respectively, when comparing all the basis sets. The other coefficients, V_1, V_3, V_5 and V_6, vary less (about 0.1) and are generally negligible. The fitted torsional parameters show the expected trends with comparable V_2 and V_4 parameters from MP2 and B3LYP. From the fitted parameters of carbazole-co-six-membered aromatic rings, it is noted that a three parameter representation, V_2, V_4 and V_6, is sufficient in most cases. It can be seen that the MP2/cc-pVDZ energy values are always in agreement with the B3LYP/6-311G(d,p) and B3LYP/6-311++G(2d,2p) values for the Fourier fit coefficients, whereas the B3LYP/6-31G and B3LYP/6-31G(d) basis sets deviate slightly.

Table 17 Energy (in kcal/mol) of stationary points of the torsional energy curves for carbazole-based molecules relative to the lowest energy conformation. (Values in parentheses are torsional angles in degrees at the local minimum).

Methods	syn	syn-gauche	perpendicular	anti-gauche	anti
Cz-dimer					
B3LYP/6-31G	2.373	0.120	2.854	0.0 (142.7)	2.185
B3LYP/6-31G(d)	2.518	0.115	2.835	0.0 (142.0)	2.166
B3LYP/6-311G(d,p)	2.535	0.111	2.151	0.0 (140.1)	2.327
B3LYP/6-311++G(2d,2p)	2.236	0.110	2.092	0.0 (141.0)	2.016
MP2/cc-pVDZ	3.644	0.138	2.054	0.0 (137.1)	3.388
Cz-co-FL					
B3LYP/6-31G	2.124	0.129	2.880	0.0 (143.0)	2.093
B3LYP/6-31G(d)	2.255	0.164	2.721	0.0 (142.2)	2.224
B3LYP/6-311G(d,p)	2.270	0.228	2.200	0.0 (140.6)	2.218
B3LYP/6-311++G(2d,2p)	2.000	0.196	2.149	0.0 (141.3)	1.935
MP2/cc-pVDZ	3.340	0.124	2.071	0.0 (137.2)	3.288
Cz-co-P					
B3LYP/6-31G	2.109	0.0 (37.5)	2.721	0.0 (142.5)	2.109
B3LYP/6-31G(d)	2.245	0.0 (38.3)	2.574	0.0 (141.7)	2.245
B3LYP/6-311G(d,p)	2.274	0.0 (40.5)	2.028	0.0 (139.5)	2.274
B3LYP/6-311++G(2d,p)	2.015	0.0 (39.9)	1.968	0.0 (140.1)	2.015
MP2/cc-pVDZ	3.202	0.0 (43.0)	1.906	0.0 (137.0)	3.202
Cz-co-Th					
B3LYP/6-31G	0.249	0.0 (24.8)	3.226	0.249	0.546
B3LYP/6-31G(d)	0.484	0.0 (28.8)	2.994	0.141	0.652
B3LYP/6-311G(d,p)	0.633	0.0 (31.8)	2.348	0.128	0.782
B3LYP/6-311++G(2d,2p)	0.404	0.0 (29.0)	2.390	0.126	0.531
MP2/cc-pVDZ	1.134	0.0 (36.0)	2.167	0.195	1.335
Cz-co-F					
B3LYP/6-31G	0.0 (0.0)	-	6.128	-	0.526
B3LYP/6-31G(d)	0.0 (0.0)	-	5.675	-	0.429
B3LYP/6-311G(d,p)	0.0 (0.0)	-	5.409	-	0.473
B3LYP/6-311++G(2d,2p)	0.0 (0.0)	-	4.982	-	0.507
MP2/cc-pVDZ	0.0 (0.0)	-	4.416	-	0.476

Table 18 Fitted torsional parameters, obtained by various methods for carbazole-based molecules.

Parameters	B3LYP/ 6-31G	B3LYP/ 6-31G*	B3LYP/ 6-311G(d,p)	B3LYP/ 6-311++G(2d,2p)	MP2/ cc-pVDZ
Cz-dimer					
V_1	0.807	0.846	0.864	0.787	0.751
V_2	1.667	1.422	0.838	0.918	1.210
V_3	0.649	0.686	0.689	0.611	0.568
V_4	-1.729	-1.710	-1.498	-1.396	-1.470
V_5	0.672	0.709	0.722	0.634	0.596
V_6	0.184	0.205	0.244	0.216	0.225
Cz-co-FL					
V_1	-0.041	-0.0381	-0.046	-0.054	-0.035
V_2	1.171	0.8911	0.338	0.518	-0.689
V_3	0.027	0.0227	0.024	0.019	0.012
V_4	-2.480	-2.5135	-2.300	-2.100	-2.902
V_5	-0.016	-0.0163	-0.030	-0.030	-0.028
V_6	-0.400	-0.4096	-0.382	-0.337	-0.554
Cz-co-P					
V_1	0.000	0.000	0.000	0.000	0.000
V_2	1.014	0.742	0.134	0.289	-0.761
V_3	0.000	0.000	0.000	0.000	0.000
V_4	-2.429	-2.465	-2.247	-2.051	-2.768
V_5	0.000	0.000	0.000	0.000	0.000
V_6	-0.402	-0.413	-0.381	-0.336	-0.535
Cz-co-Th					
V_1	0.258	0.160	0.141	0.141	0.159
V_2	2.884	2.501	1.743	1.988	1.102
V_3	0.030	0.008	0.009	-0.011	0.042
V_4	-1.228	-1.396	-1.300	-1.115	-1.619
V_5	0.009	-0.001	-0.001	-0.004	0.000
V_6	-0.055	-0.074	-0.102	-0.065	-0.170
Cz-co-F					
V_1	0.448	0.339	0.351	0.391	0.276
V_2	5.847	5.455	5.195	4.740	4.233
V_3	0.076	0.098	0.117	0.109	0.207
V_4	-0.798	-0.886	-0.756	-0.698	-0.862
V_5	0.002	-0.008	0.005	0.008	-0.007
V_6	0.019	0.005	-0.023	-0.012	-0.055

Thus the basis set size affects the calculation of the torsional energy, with the larger sets giving more realistic results. It is noted that the B3LYP/6-311G(d,p) and B3LYP/6-311++G(2d,2p) calculations predict relative energies of the carbazole-based conformations in good agreement with MP2/cc-pVDZ methods. Taking this into account, it can be concluded that the B3LYP/6-311G(d,p) method is appropriate, in terms of both accuracy and computing time, for the ground state geometry optimization and therefore, it can be used for further analysis.

2. Excitation Energy of Carbazole-Based Molecules

For a better understanding of the electronic properties of carbazole-based molecules, the excitation energy, based on the first and second singlet-singlet electronic transitions were studied. The vertical first and second excitation energies were calculated by TD-DFT with different *xc*-potentials; BLYP, BP86, BH&HLYP, PBE1PBE and B3LYP functions with the 6-311++G(2d,2p) basis set, using B3LYP/6-311G(d,p) optimized geometries. The electronic properties in terms of excitation energy (E_{ex}) and oscillator strength (*f*) were then calculated.

The performance of different TD-DFT methods, for accurate prediction of the lowest vertical excitations of the carbazole-based compounds, compared to the results obtained by ZINDO and SAC-CI methods and available experimental data are shown in Table 19. Comparing to experimental excitation energies available for Cz-dimer and Cz-co-Fl (3.85 and 3.83 eV, respectively), it can be seen that TD-PBE1PBE/6-311++G(2d,2p) calculations give excellent prediction of the excitation energies for the S_1 transition (3.84 and 3.83 eV, respectively). TD-B3LYP calculations with the same basis set and the ZINDO method provide similar results with a difference of about 0.12 eV compared to experimental data. However, TD-BLYP and TD-BP86 calculations at the same level underestimate excitation energies by about 0.5 eV. On the other hand, TD-BH&HLYP/6-311++G(2d,2p) and SAC-CI/95 methods overestimate excitation energies by about 0.5 eV.

The energetics of Cz-co-Th, as obtained from all methods, show similar trends to those found with Cz-dimer and Cz-co-Fl molecules. For Cz-dimer and Cz-co-Fl molecules, the first excitation S_1 electronic transition appears to have the highest intensity as determined by its large oscillator strength (*f*). In contrast to Cz-co-P, the oscillator strength obtained from all methods of calculations indicated clearly that S_2 is the main contribution to the electronic transition. As there is no experimental data available for comparison, the TD-PBE1PBE excitation energy was used as a reference. As expected, only the results obtained by TD-B3LYP calculations were comparable with that of the TD-PBE1PBE excitation energy, with a difference of about 0.10 eV. The other methods gave differences in the range of 0.3-0.5 eV.

With the carbazole-copolymerized with five-membered aromatic ring, TD-PBE1PBE and TD-B3LYP calculations with the same basis set predicted excitation energies for Cz-co-Th (3.89 and 3.84 eV, respectively) in good agreement with experimental data (3.84 eV), while other methods gave differences in the range of 0.3-0.5 eV. Furthermore, the second excitation S_2 plays a major role in the electronic transitions of Cz-co-Th. In the case of Cz-co-F, for which experimental data is not available, it was found that the second excitation S_1 has the highest intensity according to the oscillator strength values and the predicted excitation energies obtained from TD-PBE1PBE and TD-B3LYP methods are nearly equal.

Table 19 Excitation energy (E_{ex}) and oscillator strength (*f*) of carbazole-based molecules as obtained by different TD-DFT calculations using the 6-311++G(2d, 2p) basis set, based on B3LYP/6-311G(d,p) geometry. (Values in parentheses represent the difference to experimental data (Belletete *et al.*, 2004).

	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$	
Methods	E_{ex} (eV)	*f*	E_{ex} (eV)	*f*
Cz-dimer				
TD-BLYP	3.21 (0.64)	0.002	3.36	0.812
TD-BP86	3.18 (0.67)	0.002	3.32	0.806
TD-B3LYP	3.72 (0.13)	1.072	3.76	0.005
TD-PBE1PBE	3.84 (0.01)	1.141	3.88	0.006
TD-BH&HLYP	4.21 (0.36)	1.300	4.40	0.008
ZINDO	3.71 (0.14)	1.255	3.85	0.028
SAC-CI/D95	4.33 (0.48)	0.092	4.43	1.660
Experimental	3.85		-	
Cz-co-FL				
TD-BLYP	3.14 (0.69)	0.010	3.29	0.923
TD-BP86	3.16 (0.67)	0.011	3.32	0.918
TD-B3LYP	3.72 (0.11)	1.187	3.75	0.029
TD-PBE1PBE	3.83 (0.00)	1.259	3.87	0.031
TD-BH&HLYP	4.11 (0.28)	1.366	4.31	0.031
ZINDO	3.72 (0.11)	1.321	3.86	0.016
SAC-CI/D95	4.24 (0.41)	0.057	4.56	1.736
Experimental	3.83		-	
Cz-co-P				
TD-BLYP	3.37	0.018	3.69	0.493
TD-BP86	3.39	0.018	3.72	0.496
TD-B3LYP	3.83	0.025	4.05	0.596
TD-PBE1PBE	3.93	0.026	4.15	0.628
TD-BH&HLYP	4.33	0.035	4.38	0.675
ZINDO	3.87	0.086	3.91	0.612
SAC-CI/D95	4.02	0.052	4.56	0.785
Cz-co-Th				
TD-BLYP	3.25	0.015	3.43 (0.41)	0.537
TD-BP86	3.28	0.015	3.47 (0.37)	0.544
TD-B3LYP	3.73	0.022	3.78 (0.06)	0.670
TD-PBE1PBE	3.85	0.024	3.89 (0.05)	0.704
TD-BH&HLYP	4.26	0.030	4.12 (0.28)	0.758
ZINDO	3.82	0.011	3.60 (0.24)	0.919
SAC-CI/D95	3.99	0.054	4.38 (0.54)	0.886
Experimental[a]	-		3.84	
Cz-co-F				
TD-BLYP	3.30	0.017	3.41	0.597
TD-BP86	3.32	0.017	3.44	0.601
TD-B3LYP	3.74	0.239	3.76	0.563
TD-PBE1PBE	3.84	0.545	3.86	0.297
TD-BH&HLYP	4.05	0.877	4.25	0.036
ZINDO	3.52	0.915	3.79	0.010
SAC-CI/D95	4.16	0.044	4.39	0.936

Table 20 Excitation energies (E_{ex}), oscillator strengths (*f*), and wave function composition (wf) for the low singlet electronic states of carbazole-based compounds, obtained from TD-(PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p)) calculations.

State	Symmetry	wf	E_{ex} (eV)	*f*	Experiment[a]
	Cz-dimer				
S_1	Singlet-A	H→L (87%)	3.84	1.141	3.85
S_2	Singlet-A	H-1→L (84%)	3.88	0.006	-
S_3	Singlet-A	H-2→L (84%)	3.89	0.053	-
S_4	Singlet-A	H→L +1 (73%)	4.40	0.004	-
	Cz-co-FL				
S_1	Singlet-A	H→L (87%)	3.83	1.259	3.83
S_2	Singlet-A	H-1→L (84%)	3.87	0.031	-
S_3	Singlet-A	H→L+1 (60%), H→L+2 (20%)	4.32	0.005	-
S_4	Singlet-A	H-1→L+1 (13%), H→L+1 (-17%), H→L+2 (48%)	4.55	0.096	-
	Cz-co-P				
S_1	Singlet-A	H→L (83%)	3.93	0.026	-
S_2	Singlet-A	H-1→L (79%)	4.15	0.628	-
S_3	Singlet-A	H-3→L (20%), H-1→L+1 (61%)	4.84	0.001	-
S_4	Singlet-A	H-4→L (17%), H-1→L+2 (29%), H→L+2 (25%)	4.98	0.283	-
	Cz-co-Th				
S_1	Singlet-A	H-1→L (87%)	3.85	0.024	-
S_2	Singlet-A	H→L (84%)	3.89	0.704	3.84
S_3	Singlet-A	H-4→L (-8%), H→L+1 (75%)	4.72	0.098	-
S_4	Singlet-A	H-2→L (53%), H-1→L+1 (-25%)	4.86	0.065	-
	Cz-co-F				
S_1	Singlet-A	H-1→L (26%), H→L (57%)	3.84	0.545	-
S_2	Singlet-A	H-1→L (59%), H→L (-25%)	3.86	0.297	-
S_3	Singlet-A	H-3→L (-12%), H→L+1 (66%)	4.76	0.151	-
S_4	Singlet-A	H→L+2 (90%), H→L+4 (6%)	4.90	0.001	-

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

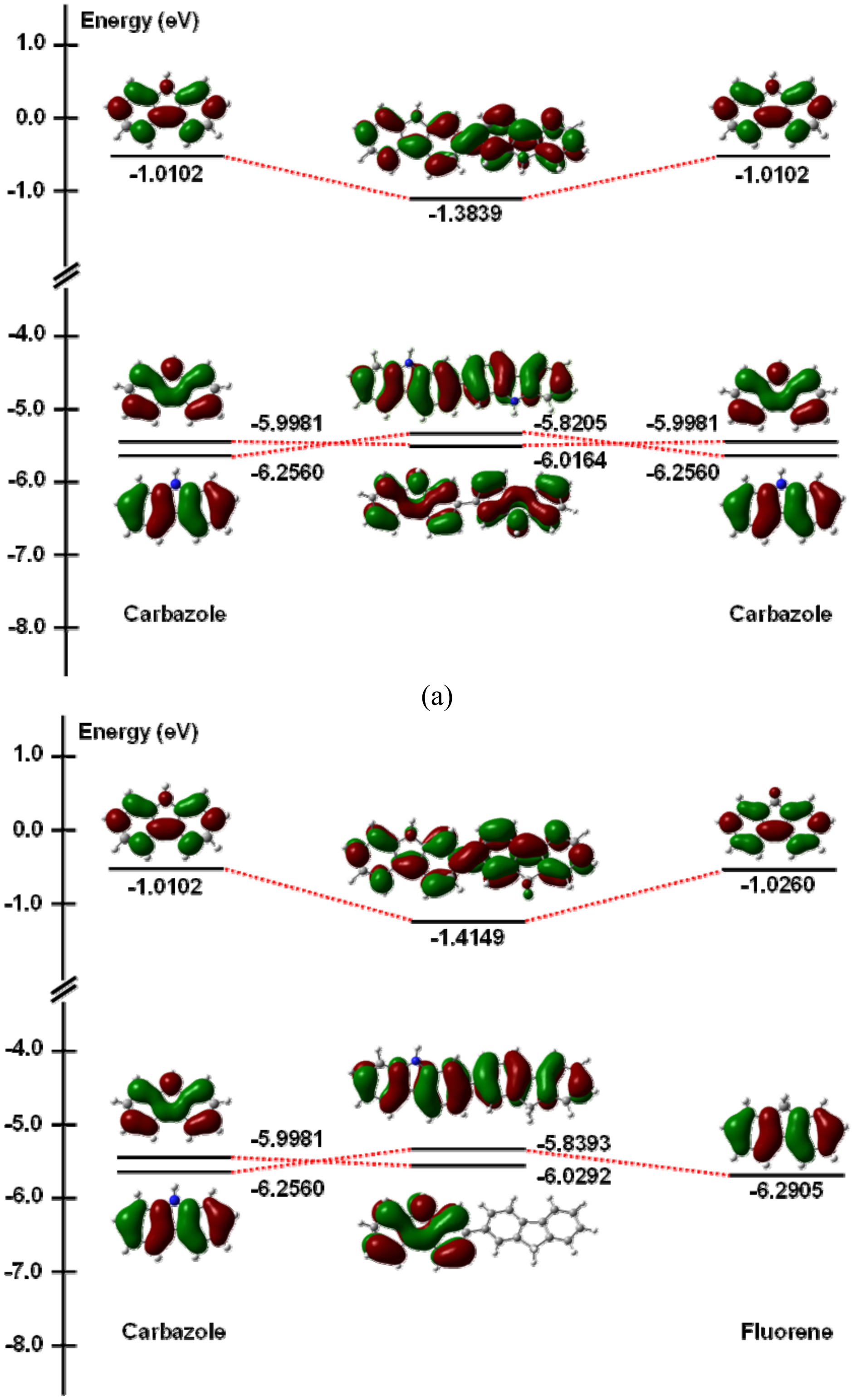
According to these results, the excitation energies vary somewhat with the hybrid functional employed in the TD-DFT calculations. However, the TD-PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p) calculations can provide relatively accurate predictions of vertical excitation energies for carbazole-based molecules. Compared with the available experimental excitation energies for Cz-dimer, Cz-co-Fl and Cz-co-Th, the average deviation of the calculated excitation energies is only 0.05

eV. Therefore, the TD-PBE1PBE method is considered to be the most suitable approach to estimate the absorption energy, and it was employed to investigate the details of the different states of electronic transitions.

To look at the details of the electronic transitions, the four lowest dipole-allowed excitation energies and oscillator strengths of each carbazole-based molecule were calculated at TD-PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p) level. The results are summarized in Table 20 and include experimental data. These results can be used to describe the possible excitations of all carbazole-based molecules. From the data in Table 20, it was found that for Cz-dimer and Cz-co-Fl, the S_1 excitation corresponds mainly to the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (H→L) as indicated by large oscillator strengths, $f = 1.141$ and 1.259, respectively. On the other hand, the S_2, S_3 and S_4 electronic transitions of each compound possess very small oscillator strengths and therefore, these can be considered as forbidden transitions. In contrast, for Cz-co-P, the first S_1 electronic transition is almost forbidden (f = 0.0262), while the S_2 electronic transition has a larger oscillator strength (f = 0.628). These characteristics are demonstrated in Figures 36 and 37 which describe the TD-PBE1PBE calculated HOMO and LUMO energies as a function of monomer units in carbazole-based molecules. From these figures, it can be observed how the frontier electronic levels of the carbazole monomer are affected by the incorporation of different monomer units. The energies of the frontier electronic levels of Cz-dimer (Figure 36(a)) and Cz-co-Fl (Figure 36(b)) indicate that there is anti-bonding between the bridged carbon atoms in the HOMO, and bonding between the bridged carbon atoms and the conjoint carbon atoms in the same benzene ring in the LUMO. The HOMO orbital of Cz-dimer and Cz-co-Fl are fully delocalized over the conjugated backbone. On the contrary, this characteristic could not be found in the Cz-co-P molecule (Figure 37) as the shape of the delocalized HOMO is drastically different, being localized on the phenyl unit and delocalized in the carbazole unit. This can be rationalized by the fact that the energy separation between the HOMO of carbazole and the HOMO of phenyl units is large (1.289 eV) and there is a weak interaction between the two building blocks. In contrast, the energy separation between the HOMO-1 of carbazole and the HOMO of phenyl is smaller (1.031 eV), which promotes a stronger interaction resulting in a delocalized HOMO-1 orbital for Cz-co-P. Therefore, the S_2 electronic transition with the wave function composed of H-1→L can occur in Cz-co-P. However, this transition is not stable due to the lower oscillator strength ($f = 0.628$).

The excitation of the S_2 state is mainly described by the promotion of one electron from the HOMO to the LUMO for Cz-co-Th and Figure 37 and 38(a) confirms the allowed H→L transition. For Cz-co-P and Cz-co-Th, the excitation energies of S_2 electronic transitions are more affected by the rotation of the subunits. This is reasonable since the delocalized orbitals over the whole molecule promote the allowed transition (HOMO-1 of Cz-co-P in Figure 37 and HOMO of Cz-co-Th as shown in Figure 38(a)).

The electronic transition, S_1 state of Cz-co-F, corresponding to the allowed H→L transition (Figure 38(b)), is somewhat different from the Cz-co-Th transition due to the main configuration. However, the low oscillator strength ($f = 0.545$) indicates that this excitation is rather unstable. These results are in agreement with Belletete *et al.* (2004) as they found that it was not possible to measure the optical properties of Cz-co-P and Cz-co-F molecules. It is worth noting that using TD-PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p) calculations is helpful in understanding the excitation of such carbazole-based molecules as Cz-co-P and Cz-co-F. The electronic transition properties derived by using the TD-DFT method can contain useful structural and electronic information for designing novel conducting polymer materials.



(a)

(b)

Figure 36 HOMO-LUMO energy diagram of (a) Cz-dimer and (b) Cz-co-Fl, calculated by TD-(PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p)).

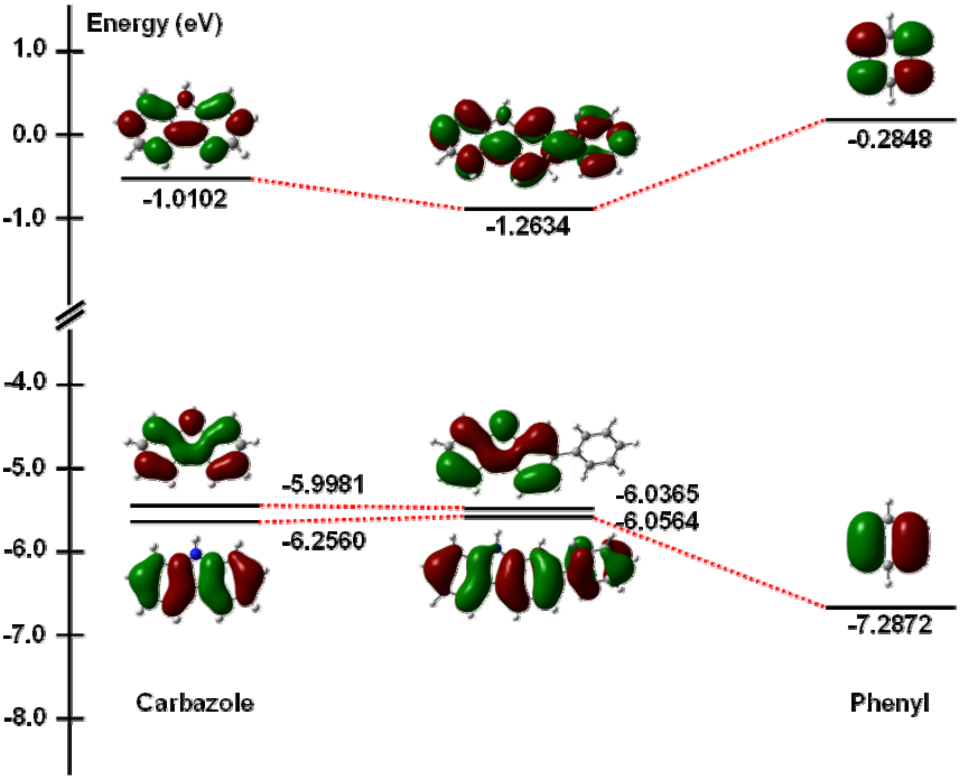
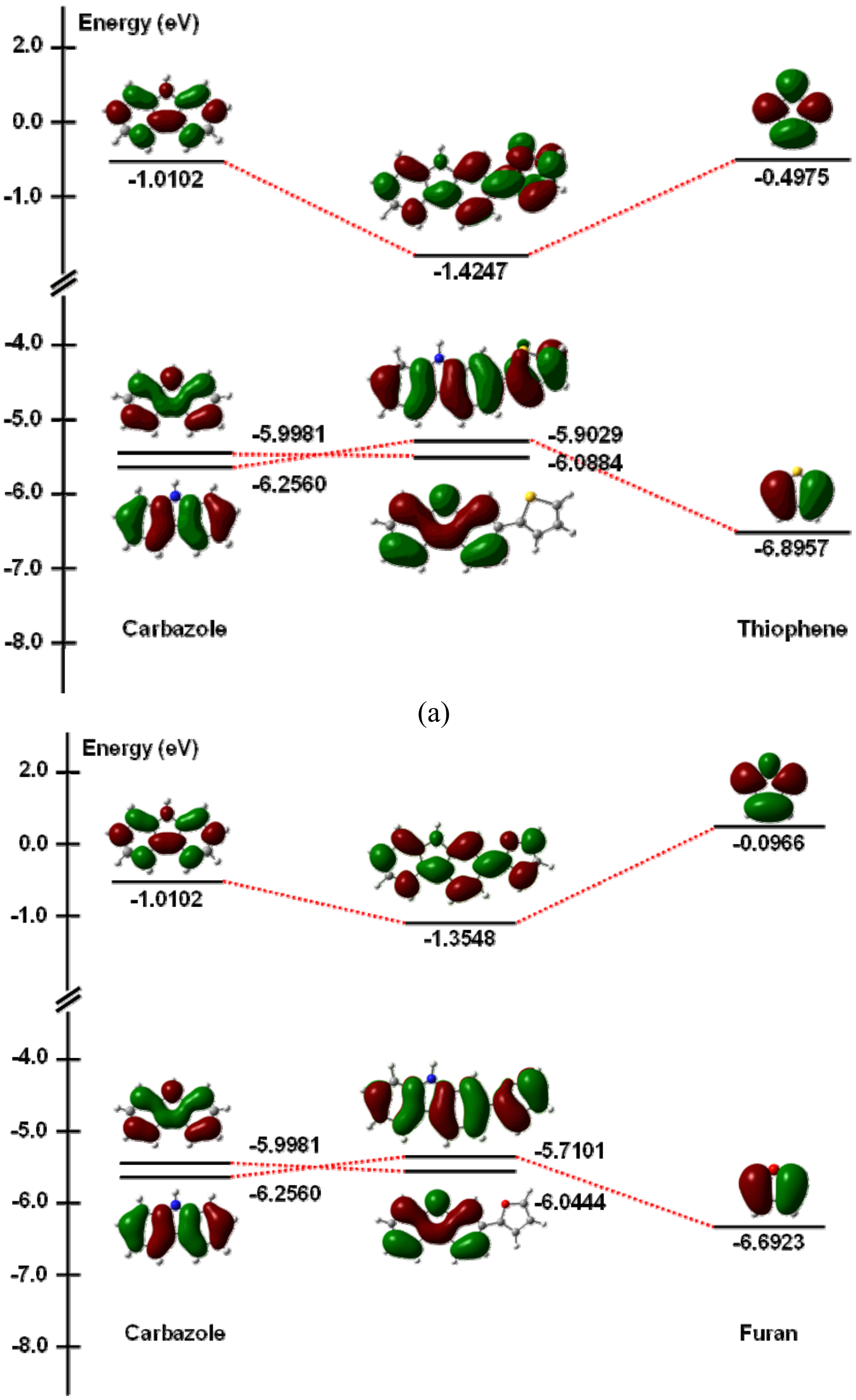


Figure 37 HOMO-LUMO energy of Cz-co-P, calculated by TD-(PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p)).



(a)

(b)

Figure 38 HOMO-LUMO energy diagram of (a) Cz-co-Th and (b) Cz-co-F calculated, by TD-(PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p)).