

行政院國家科學委員會專題研究計畫 成果報告

奈米電子材料的模擬與計算

計畫類別：個別型計畫

計畫編號：NSC93-2113-M-032-008-

執行期間：93年08月01日至94年10月31日

執行單位：淡江大學化學系

計畫主持人：王伯昌

報告類型：精簡報告

報告附件：出席國際會議研究心得報告及發表論文

處理方式：本計畫可公開查詢

中 華 民 國 95 年 6 月 6 日

Theoretical Investigation of Carbazole Derivatives as Hole-Transporting Materials in OLEDs

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Abstract

Carbazole and its derivatives were widely used as the hole-transporting material. In this study, ab initio DFT B3LYP/6-31G^{*} was performed for the carbazole and 1-, 2-, 3-, 4- and 9- mono-substituted as well as 3,6-disubstituted carbazoles with electron-donating and -withdrawing substituents. The total energies, HOMO and LUMO orbital energies of these compounds at neutral, cation and anion states were obtained based on the optimized geometrical structures. The ionization potential (I_p) and electron affinity (E_a) were generated by means of the DFT calculated total energy of neutral, cation and anion states. These theoretical I_p and E_a were consistent with experimental data. Further investigation on 1-, 2-, 3- and 4-mono-substituted carbazole, we conclude that these carbazole derivatives with electron-donating substituents should decrease their I_p and E_a values while increasing the HOMO and LUMO energies. On the contrary, the mono-substituted carbazole with electron-withdrawing substituent have the opposite results to those carbazole derivatives with electron-donating substituents. Comparing to carbazole, ΔE decreased in the mono-substituted carbazole derivatives with electron-donating and -withdrawing substituents. The substituent effect in 3,6-di-substituted carbazoles is more obvious than that of 3-substituted carbazole. According to the calculated results, the calculated I_p has an excellent agreement with the experimental one-electron oxidation potential (E_{P2}). Presumably, this calculation can be employed to predict EL character for other OLED materials.

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1. Introduction

The research in organic light-emitting diode (OLED) devices is of considerable interest for chemist

and physicist because such materials were used for the flat-panel and full color displays.¹⁻⁶ Since the initial work was found by Tang et al. in 1987, the thin multi-layer OLED was recognized as one of the potential technologies for the next generation of flat-panel display device.⁷ One of the simplest OLED is consisted of ITO (indium tin oxide) anode, hole-transporting layer (HTL), electron-transporting layer (ETL), and Mg-Ag cathode, in which HTL or/and ETL could act as the light-emitting layer⁷. The ITO anode is a transparent semiconductor, which was used for the hole injection due to its work function of 4-5 eV.⁸⁻⁹

During last decade, the intensive research has been carried out to generate the material with high light emitting efficiencies, high thermal stability, and good amorphous film formation property.¹⁰⁻¹² The electro-luminescence (EL) characteristic of OLED materials depend on the appropriate HOMO and LUMO energy levels and the electron and hole motilities. Recently, lots of organic compounds with the different substituent for chromophore were proposed to have a good EL property.¹³⁻¹⁸ Several carbazole derivatives was synthesized and have a sufficient triplet energy being able to host red, green and blue.¹⁴⁻¹⁸ We propose a comparative study to investigate the electronic and structural properties of the carbazole and its derivatives; the carbazole derivatives may have different substituents.

Recently, a series of carbazole derivatives were presented which are widely used for the HTL material.¹⁵ For OLED/HTL materials, the carbazole derivative, 4,4'-bis(9-Carbazolyl)-biphenyl (CBP), was used as host for triplet emitters.^{15-16, 19-20} The CBP have the maximum internal quantum efficiencies up to 80%.^{18,19} Very recently, Hang et al. proposed a novel HTL molecule, which contain 1,4-bis-(carbazolyl)-benzene as a central unit with different numbers of diphenylamine moieties as the peripheral group.²¹ Two kinds of carbazole-based molecules, in which 4-methylphenyl-substituted carbazole as the central core is connected with diphenylamine and carbazole at 3,6-position, are very promising hole-transporting material for EL devices.²² Carbazole-based polymers such as poly-(vinylcarbazole) (PVK) have been used as hole-transporting and photo conducting materials.²²⁻²⁷ Organic light-emitting diodes (OLEDs) made with PVK, which could serve as HTL, and 8-hydroxyquinoline (Alq₃) were studied.²⁴ The brightness of that reached the maximum value

2300cd/m².²⁴ Device in which the emitting layer of OLEDs being formed by PVK blend with other polymeric systems have shown remarkable increase in luminescence efficiency, as compared with those in which PVK was not incorporated.²⁸ Poly-(3,6-di-tert-butyl-N-(p-ethynylphenyl) carbazole) [poly(t-Bu₂CzPA)] in conjunction with iridium complex exhibited electro-luminescence (13-18cd/m²) characteristic.²⁹

Recently, a number of works have been published which included both the theoretical and experimental investigation of carbazole and its derivatives concerning its electronic structure, UV-Vis absorption, and the adiabatic ionization potential (I_p).³⁰⁻³⁸ Nitzsche et al. show that the HOMO of carbazole is a π orbital with b₁ symmetry.³² The π orbital has a large electron density localized on the amine nitrogen atom of carbazole ring. The UV absorption spectra structures of carbazole were studied using the atom monopole-dipole interaction (AMDI).³¹ Brière et al. presented a study of structural, electronic, and optical properties of poly-(2,7-carbazole).³⁹ It is important that a through knowledge of the electronic properties of monomeric molecular to understand the polymeric electro-physical processes. In this work, we select carbazole and its derivatives to study their electronic and geometrical structures. The ab initio DFT B3LYP calculation with 6-31G* basis set was used to generate the geometrical and electronic structures for carbazole and its derivatives with the neutral, the anion and the radical-cation states. The related ionization potential (I_p), energy gap ($\Delta E = \text{LUMO} - \text{HOMO}$) and electron affinity (E_a) were generated by used the calculated electronic structures and total energies of these carbazole derivatives. To investigate the substitution effect of carbazole, twenty-eight carbazole derivatives were used for DFT calculation with a symmetry consideration.

2. Computations

According to the symmetry analysis, the parent carbazole ring has the C_{2v} point group. Thus, we consider 1-, 2-, 3- and 4- C-substituted (compounds 1 – 15) and 9- N-substituted (compounds 23 – 28) for mono-substituted and 3,6- C-substituted for di-substituted (compounds 16 – 22) carbazole derivatives in this calculation. The molecular structures of these carbazole derivatives are shown in Fig. 1. The

optimized geometrical structures of carbazole and its derivatives were generated by using ab initio DFT B3LYP/6-31G*, HF/6-31G* and the semi-empirical AM1, PM3 calculation methods. The calculated geometrical parameters carbazole and the experimental data are shown in Table 1. Comparing the experimental and calculated geometrical parameters, the calculated bond lengths by DFT B3LYP/6-31G* and HF/6-31G* fall within $\pm 0.029\text{\AA}$ and $\pm 0.034\text{\AA}$ error margin, respectively.⁴⁰⁻⁴¹ In the semi-empirical AM1 and PM3 methods, the derivation of the bond lengths from the experimental results is $\pm 0.046\text{\AA}$ (AM1) and $\pm 0.036\text{\AA}$ (PM3). According to these calculations, we conclude that DFT B3LYP/6-31G* optimized geometries are in excellent agreement with the experimental results. Thus, the DFT B3LYP/6-31G* method will be used for the following calculations. The DFT, HF, AM1 and PM3 methods are implemented in the GAUSSIAN 03 program package.⁴²

3. Result and Discussion

3.1 Ionization potential and electron affinity

The total energy, orbital energies of HOMO and LUMO for the ground-state carbazole and its derivatives were calculated by means of the ab initio DFT B3LYP/6-31G* method based on the fully optimized geometry. These calculated total energies included for the neutral, the anion and the radical-cation states. The ionization potential (I_p) and electron affinity (E_a) for these derivatives was determined by the following equations:

$$I_p = E_t(\text{RC}) - E_t \quad (1)$$

$$E_a = E_t - E(\text{A}) \quad (2)$$

Where E_t , $E_t(\text{RC})$ and $E(\text{A})$ are the calculated total energies for the neutral, the radical-cation and the anion states, respectively. The energy gap is the orbital energies difference between HOMO and LUMO ($\Delta E = \text{LUMO} - \text{HOMO}$). These energy gaps for carbazole and its derivatives are presented in Table 2. The I_p value was obtained by the calculated total energy difference between the radical-cation and the neutral states. We attempted to determine the correlation energy among the electron oxidation potential ($E_{p/2}$), the I_p and the orbital energy of HOMO. The corresponding regression equations are given as follows:

$$I_p = -0.9449 \text{ HOMO} + 1.9769 \quad r^2 = 0.9675 \quad (3)$$

$$I_p = 1.5656 E_{P/2} + 5.3204 \quad r^2 = 0.9670 \quad (4)$$

$$\text{HOMO} = -1.4717 E_{P/2} - 3.7564 \quad r^2 = 0.9321 \quad (5)$$

r^2 is the regression constant. The correlations were obtained in these cases linearly (Figs. 3a-3c). Although, the I_p values for several carbazole derivatives are still unknown, these regression equations may provide a simple formula to predict the I_p of carbazole derivatives from the orbital energy of HOMO.

In the present paper, the electron affinity (E_a) is the total energy difference between the neutral (E_t) and the anionic states ($E_t(\text{RA})$) in these derivatives.⁴⁶ The total energy for the neutral and the anionic states of carbazole and its derivatives are calculated by using ab initio DFT B3LYP method. The calculated E_a are collected in Table 2. Except for compounds 13 and 22 (0.10 eV for compound 13 and 0.97 eV for compound 22), other carbazole derivatives have negative calculated E_a value. The negative E_a was raised by the incomplete cancellation of electronic self-interaction energy due to the using of inexact density functional and a finite basis set.⁴⁶⁻⁴⁸ Compounds 13 and 22 have positive E_a since they contain the NO_2 substituent, which is the electron-withdrawing group and it may reduce π electron density in the carbazole ring.

3.2. Substitution effect in mono-substituted carbazole

In order to investigate the substituent effect of I_p and E_a with different substitution position in carbazole derivatives, the electron-withdrawing $-\text{CN}$ and electron-donating $-\text{NH}_2$ groups were added in the carbazole ring with region selective reaction. Compounds 1- 15 are the 1-, 2-, 3- and 4-C-substituted carbazole derivatives (Fig. 2). The calculated molecular energies of HOMO, LUMO, I_p and E_a for these mono-substituted carbazole derivatives are shown in Table 2.

Since the electron-withdrawing substituent deduced the π electron overlap in the carbazole ring; the I_p and E_a values increased while decreasing the orbital energies of HOMO and LUMO in this investigation. The orbital energy of LUMO decreased much more than that of HOMO decreasing in CN-substituted carbazole derivatives (compounds 1, 4, 12, 15). Thus, the ΔE decrease in these carbazole derivatives; and

the substitution position effect increased as the following order: 4- > 1- > 2- > 3- for carbazole derivatives with an electron withdrawing –CN substituent. According to the Table 2, 2-substituted carbazole with electron-withdrawing substituent have higher calculated I_p and E_a values than those in 1-, 3- and 4-substituted carbazole derivatives (7.66 vs. 7.62, 7.54, 7.58 eV). The 3-substituted carbazole with electron-withdrawing group has the lowest calculated I_p (7.54 eV) and E_a (-0.44 eV) values in these carbazole derivatives. Comparing the calculated I_p value of electron-withdrawing substituted carbazole (Table 2), we conclude that the substitution position effect increase as the following order: 2- > 1- > 4- > 3-; and the calculated E_a values increasing of these derivatives are as the following order: 2- > 1- = 4- > 3-.

Contrarily, the electron-donating substituent increases the π electron overlap in the carbazole ring. The calculated I_p and E_a values decreased while increasing the orbital energies HOMO and LUMO for the carbazole derivatives with the electron-donating substituent. According to the electronic structure analysis, the orbital energy of HOMO increases more than that of LUMO increasing in NH₂-carbazole derivatives (compounds 1, 3, 5 and 14). Thus, the ΔE decreased in these carbazole derivatives as the following order: 2- > 4- > 1- > 3-. According to the Table 2, the calculated I_p and E_a values in the 3- NH₂ carbazole is higher than those of 1-, 2- and 4- NH₂- carbazole, and the ΔE in 2-NH₂-substituted carbazole is higher than those of 1-, 3- and 4- NH₂- carbazole (4.46 vs. 4.33, 4.03, 4.38 eV). Table 2 indicates that the substitution effect decrease in the following order: 2- > 1- > 4- > 3-, and the substitution effect of the E_a are in the following order: 2- > 4- > 1- > 3- for NH₂-substituted carbazole. Due to this calculation, we conclude that 2-substituted carbazole has higher calculated I_p and E_a than those of 1-, 3- and 4-substituted carbazole.

3.3. Substituents effect in carbazole derivatives

In order to investigate the substituent effect in carbazole derivatives, electron-withdrawing and electron-donating substituents were used for 3-, 9- and 3,6- substituted carbazole. These carbazole derivatives have been generated by the organic synthesis. According to the experimental data, the carbazole ring can be easily substituted at 3-, 9- and 3,6- positions or linked to other moieties.⁴⁹ To

investigate the substituents effect, we used the ab initio DFT B3LYP method to determine the orbital energies of HOMO and LUMO, I_p and E_a for these carbazole derivatives.

In the present paper, we added the electron-donating NH_2 , $\text{N}(\text{CH}_3)_2$, CH_3 and OCH_3 groups, and the electron-withdrawing F, Cl, Br, CN and NO_2 groups for the 3-substituted carbazole as substituents (compounds 5 -13, Fig. 1). The DFT calculated results of these derivatives are shown in Table 2. As calculations, the calculated I_p , E_a and ΔE values decreased while increasing the orbital energies of HOMO and LUMO for these carbazole derivatives with electron-donating substituents (compounds 5 - 8). The substituent effect in 3-substituted carbazole with electron-donating groups has the following order: $-\text{N}(\text{CH}_3)_2 > -\text{NH}_2 > -\text{OCH}_3 > -\text{CH}_3$. On the contrary, the I_p and E_a increased while decreasing the orbital energy LUMO and ΔE for these 3-substituted carbazoles with electron-donating substituents. Comparing the HOMO energy of carbazole derivatives, 3-substituted carbazole with $-\text{CN}$ and $-\text{NO}_2$ electron-withdrawing groups increased, but these values for $-\text{F}$, $-\text{Cl}$ and $-\text{Br}$ electron-withdrawing substituted carbazole derivatives decreased. We proposed that this difference might be caused by the lone pair electron in the electron-withdrawing substituent, which may increase the π electron overlap in the carbazole ring increasing the orbital energy of HOMO. Comparing the calculated I_p and E_a values of 3-substituted carbazole with electron-withdrawing groups (compounds 9 -13), the substituent effect has the following order: $-\text{NO}_2 > -\text{CN} > -\text{Cl} > -\text{Br} > -\text{F}$. This order presented an excellent agreement with the experimental $E_{p/2}$ value.

In order to investigate the substitution effect in di-substituted carbazole derivatives, we selected 3,6-substituted carbazole derivatives with electron withdrawing and electron-donating substituents (compounds 16 - 22). This calculation reveals that 3,6-di-substituted carbazole have more substituent effect than that of 3-mono-substituted carbazole. Comparing the ΔE , I_p and E_a of these derivatives, they have the same trend for the substituents effect in mono-substituted and di-substituted carbazole. Theoretically, the organic compound with small ΔE may provide a appropriate EL characteristic, 3,6-disubstituted carbazole derivatives generate the smallest ΔE of carbazole derivatives which could be applied to develop the new hole-transporting materials.⁵⁰

For 9-N-substituted carbazole derivatives with the electron-withdrawing substituents, 9-CH₃, 9-C₂H₅, 9-isoC₃H₇, 9-C₂H₃ and 9-C₆H₅-carbazoles (compounds 23 - 27) and the electron-donating substituent -CH₃CO have been used for the present study. The ΔE , I_p and E_a values were generated that were based on the DFT B3LYP calculated HOMO and LUMO energies for these derivatives (Table 2). Since there are lone pair electrons in the amine nitrogen atom of carbazole, the electron-donating substituent at 9-N- position may increase the electron overlap in the carbazole ring. Thus, the calculated HOMO and LUMO energies of these carbazole derivatives increase except 9-C₂H₃- and 9-C₆H₅-carbazoles. According to the electronic structure analysis, the orbital energy HOMO increases much more than that of the orbital energy increasing of LUMO in 9-C₂H₃- and 9-C₆H₅-carbazole. Thus, the ΔE decreases in these carbazole derivatives comparing with the carbazole. The vinyl and phenyl group at 9-N-position in carbazole delocalize the lone pair electron on the amine nitrogen atom and reduce the electron overlap in the carbazole ring. This may decrease the HOMO while increasing the LUMO energies, respectively. For the 9-substituted carbazole derivatives, the I_p values decreased with electron-donating substituent. The substituent effect of these derivatives has the following order: -C₆H₅ > iso-C₃H₇ > -C₂H₅ > -CH₃ > -C₂H₃. The order of calculated E_a of these 9-N-carbazole derivatives is similar to those of calculated I_p . The 9-substituted carbazoles with electron-withdrawing substituent (as compound 19) may reduce the π electron density of carbazole ring and their orbital energies of HOMO and LUMO are decreased. Comparing with carbazole, the orbital energy LUMO decreases much more than those of HOMO decreasing in 9-substituted carbazole with electron-withdrawing substituent. The ΔE of the compound 19 are increase. The HOMO increases much more than that LUMO in 9-substituted carbazole with electron donating substituent. As above calculated results, we conclude that the ΔE of the 3-, 6- and 9-substituted and 3,6-di-substituent carbazole decreased except 9-C₆H₅, 9-C₂H₃ and 9-CH₃CO-carbazoles. The I_p and E_a of these carbazole derivatives with electron donating substituent decreased while those of carbazole derivatives with electron withdrawing substituent increasing.

4. Conclusion

The, ΔE , I_p , E_a and the HOMO and LUMO energies of carbazole and its derivatives were calculated by means of ab initio DFT B3LYP/6-31G* method. We found that the calculated ionization potentials (I_p) of the carbazole and its derivatives were related to the one-electron oxidation potential ($E_{P/2}$) values with a linear correlation. This equation may be easily used for predicting the $E_{P/2}$ and I_p for other carbazole derivatives. For the substituted position effect of mono-substituted carbazole, we proposed that 1-, 2-, 3- and 4-substituted carbazoles with electron-donating group increased the HOMO and LUMO energies while decreasing the I_p and E_a . In contrast, the substitution at 1-, 2-, 3- and 4-substituted carbazole with electron-withdrawing group should decrease the molecular orbital energies HOMO and LUMO but the I_p and E_a should increase. Both electron-withdrawing and -donating substituents decrease the energy gap (ΔE) between the HOMO and LUMO. The substitution at 9-position in carbazole derivatives with electron-donating substituent should decrease ΔE , I_p and E_a but those with acceptor substituent increases ΔE , I_p and E_a . Comparing the substituents effect in carbazole derivatives, the substituents effect in di-substituted with different substituents are more obvious than that of mono-substituted carbazole. The 3,6-disubstituted carbazole with different substituents have been applied to improve the hole-transporting material.⁴² Furthermore, this calculation may predict the trend of ΔE , I_p and E_a values in the carbazole derivatives with different substituent. Furthermore, this calculation may be extended to the molecular design for developing a new hole-transporting material.

Acknowledgements

We would like to thank the National Science Council of Taiwan for financial support of this work.

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Figure captions:

Figure 1 Structure of carbazole

Figure 2 Structures of carbazole derivatives

Figure 3(a) Plot of calculated -HOMO molecular energies *vs.* I_p value

Figure 3(b) Plot of the experimental $E_{P/2}$ value *vs.* calculated I_p value

Figure 3(c) Plot of the experimental $E_{P/2}$ value *vs.* calculated -HOMO molecular energies

Figure 1

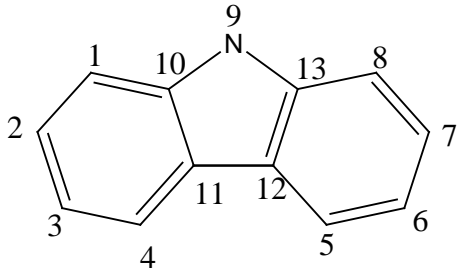
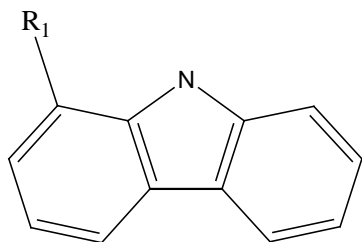
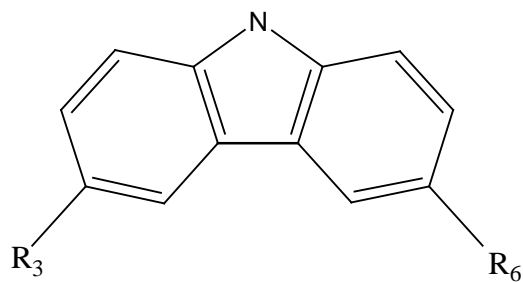


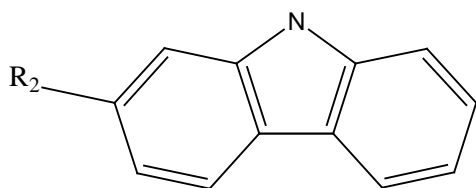
Figure 2



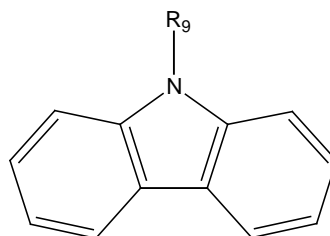
1: $R_1 = \text{NH}_2$ 2: $R_1 = \text{CN}$



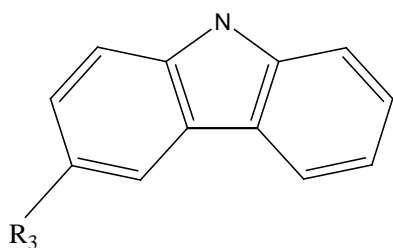
16: $R_3 = R_6 = \text{NH}_2$ 17: $R_3 = R_6 = \text{CH}_3$
 18: $R_3 = R_6 = \text{OCH}_3$ 19: $R_3 = R_6 = \text{Cl}$
 20: $R_3 = R_6 = \text{Br}$ 21: $R_3 = R_6 = \text{CN}$
 22: $R_3 = R_6 = \text{NO}_2$



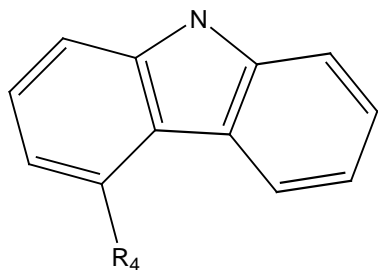
3: $R_2 = \text{NH}_2$ 4: $R_2 = \text{CN}$



23: $R_9 = \text{CH}_3$ 24: $R_9 = \text{C}_2\text{H}_5$
 25: $R_9 = \text{iso-C}_3\text{H}_7$ 26: $R_9 = \text{CHCH}_2$
 27: $R_9 = \text{C}_6\text{H}_5$ 28: $R_9 = \text{CH}_3\text{CO}$



5: $R_3 = \text{NH}_2$ 6: $R_3 = \text{N}(\text{CH}_3)_2$
 7: $R_3 = \text{CH}_3$ 8: $R_3 = \text{OCH}_3$
 9: $R_3 = \text{F}$ 10: $R_3 = \text{Cl}$
 11: $R_3 = \text{Br}$ 12: $R_3 = \text{CN}$
 13: $R_3 = \text{NO}_2$



14: $R_4 = \text{NH}_2$ 15: $R_4 = \text{CN}$

Figure 3(a)

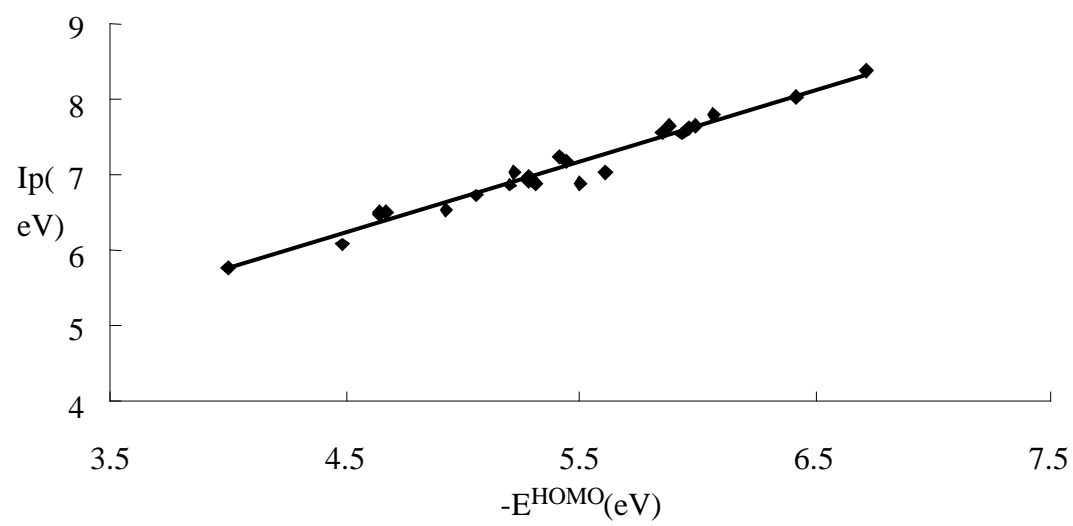


Figure 3(b)

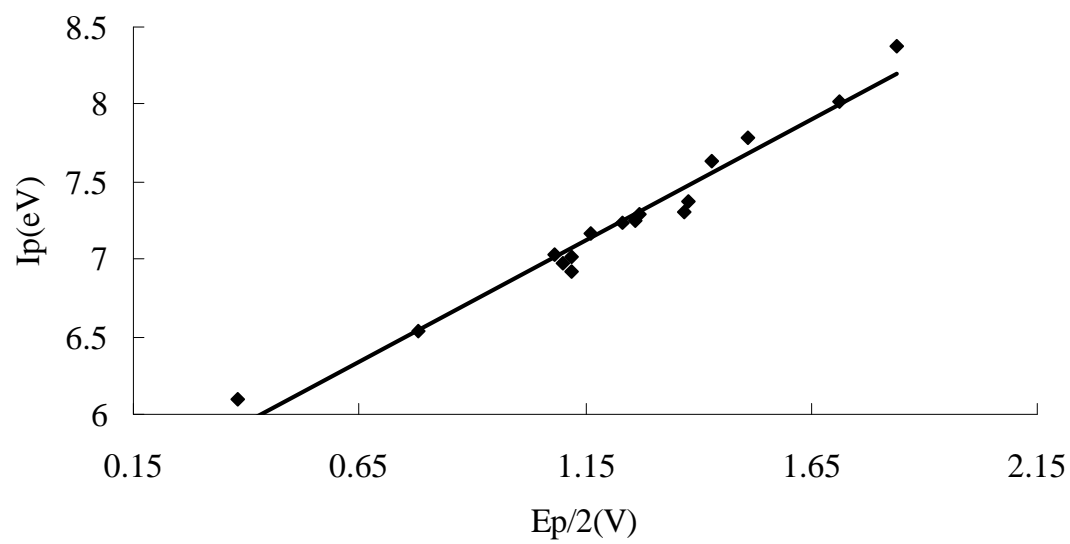


Figure 3(c)

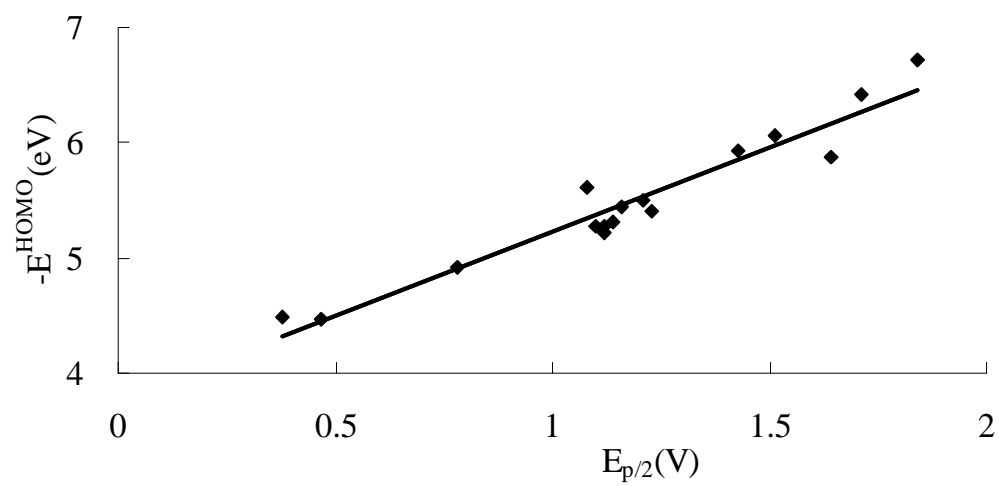


Table 1 Comparison of calculated geometries for carbazole with experimental data.

Bond and angle	Semi-empirical		Ab initio (6-31G* basis set)		Exp ^a
	AM1	PM3	HF	B3LYP	
C1-C2	1.392	1.386	1.380	1.393	1.390
C2-C3	1.392	1.400	1.390	1.400	1.398
C3-C4	1.392	1.380	1.380	1.390	1.395
C4-C11	1.380	1.390	1.390	1.400	1.400
C1-C10	1.390	1.390	1.380	1.390	1.395
N9-C10	1.400	1.410	1.380	1.385	1.414
C10-C11	1.450	1.440	1.400	1.420	1.404
C11-C12	1.450	1.440	1.450	1.450	1.467
C1-C2-C3	121.5	121.5	121.4	121.3	121.3
C2-C3-C4	121.0	121.4	120.5	120.9	120.4
C3-C4-C11	119.0	118.4	119.2	119.1	119.5
N9-C10-C11	109.4	108.9	108.5	108.5	108.8
C10-C11-C12	106.3	107.2	106.8	106.7	107.1
C10-N9-C13	108.5	108.2	109.5	109.9	108.3
C10-C1-C2	118.0	117.4	117.7	117.7	117.7
C1-C10-C11	120.7	121.2	122.0	121.7	122.3
C10-C11-C4	120.0	120.2	119.2	119.3	118.8

For the bond designation as shown in Fig. 1. The bond lengths are in Å and bond angles in ° (degree).

^a Ref. [40, 41].

Table 2 Calculated the molecular energies LUMO (eV), HOMO (eV), ΔE (= LUMO - HOMO), I_p (ionization potential), E_a (electron affinity) and experimental oxidation potential ($E_{p/2}$) of carbazole and its derivatives.

Compound	HOMO ^a (eV)	LUMO ^a (eV)	ΔE^a (eV)	I_p^a (eV)	E_a^a (eV)	Experimental $E_{p/2}^b$ (V)	I_p^c (eV)
Carbazole	-5.44	-0.63	4.82	7.17	-1.04	1.16	7.87
1	-4.65	-0.33	4.33	6.50	-1.31	-	-
2	-5.96	-1.61	4.35	7.62	-0.11	-	-
3	-4.65	-0.19	4.46	6.47	-1.42	-	-
4	-5.99	-1.61	4.38	7.66	-0.05	-	-
5	-4.46	-0.44	4.03	6.53	-1.09	0.47	7.24
6	-4.49	-0.52	3.97	6.09	-1.13	0.38	7.10
7	-5.22	-0.57	4.65	7.02	-1.05	1.12	7.77
8	-5.06	-0.63	4.44	6.73	-1.06	-	-
9	-5.41	-0.79	4.63	7.24	-0.86	1.23	-
10	-4.98	-0.71	4.27	7.29	-0.74	1.27	7.88
11	-4.79	-0.76	4.03	7.25	-0.72	1.26	8.01
12	-5.93	-1.20	4.73	7.54	-0.44	1.43	-
13	-6.07	-1.93	4.14	7.79	0.10	1.51	8.44
14	-4.68	-0.30	4.38	6.51	-1.34	-	-
15	-5.85	-1.63	4.22	7.58	-0.11	-	-
16	-4.00	-0.33	3.67	5.77	-1.31	-	-
17	-5.20	-0.57	4.63	6.87	-1.05	-	-
18	-4.93	-0.60	4.33	6.54	-1.16	0.78	-
19	-4.93	-0.87	4.05	7.38	-0.37	1.38	8.44
20	-4.68	-0.95	3.73	7.31	-0.35	1.37	8.14
21	-6.42	-1.77	4.65	8.02	-0.02	1.71	-
22	-6.72	-2.42	4.03	8.37	0.97	1.84	-
23	-5.28	-0.49	4.79	6.97	-1.04	1.10	7.75
24	-5.28	-0.60	4.68	6.92	-1.04	1.12	-
25	-5.31	-0.57	4.73	6.88	-1.03	1.14	-
26	-5.61	-0.68	4.93	7.03	-1.01	1.08	7.70
27	-5.50	-0.65	4.84	6.90	-0.97	1.21	7.60
28	-5.88	-0.98	4.90	7.65	-0.59	1.64	8.06

a: Calculated by using the ab initio DFT B3LYP/6-31G* method.

b: Data from refs. [43, 44].

c: Calculated by using the semiempirical PM3 method, data from ref. [45].

