Theoretical Studies on Stabilities and Spectroscopy of C$_{80}$CH$_2$

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Abstract

The electronic structures and stabilities of the nine possible isomers of C$_{80}$CH$_2$ based on C$_{80}$(D$_{5d}$) were studied using density function theory (DFT) at B3LYP/6-31G level. Based on the optimized geometries, the electronic spectra, IR and $^{13}$C NMR spectra of the isomers of C$_{80}$CH$_2$ were calculated using INDO/CIS, PM3 and B3LYP/6-31G methods, respectively. The most stable geometry of C$_{80}$CH$_2$ is predicted to be 27,28–C$_{80}$CH$_2$(A) with an annulene structure, where the additive bond is 6/6 bond near the equatorial belt of C$_{80}$(D$_{5d}$). Compared with those of C$_{80}$(D$_{5d}$), the first absorptions in the electronic spectra and main absorptions in the IR spectra of the stable C$_{80}$CH$_2$ isomers are red-shifted. The $^{13}$C chemical shifts of the bridged carbon atoms in the cyclopropane structures in comparison with those in the annulene structures are changed upfield. The aromaticities are better maintained in the annulene structures than cyclopropane structures according to the NICS values of C$_{80}$CH$_2$ at B3LYP/6-31G level.

Keywords: C$_{80}$CH$_2$, B3LYP/6-31G, electronic spectra, $^{13}$C NMR, NICS.

1. Introduction

The functionalization of fullerenes has been an interesting research topic for scientists. One of the C$_{80}$ isoomers with D$_{5d}$ symmetry has been successfully isolated and characterized with $^{13}$C NMR and UV spectra. The $^{13}$C NMR results suggested that there are five types of carbon atoms in C$_{80}$(D$_{5d}$). The energy gap of C$_{80}$(D$_{5d}$) calculated using AM1 method is 4.72 eV. C$_{80}$(D$_{5d}$) has been found to be the lowest-energy isomer with the wide energy gap at HF/4-31G level. The optical gap of C$_{80}$ is reduced and the UV-vis-NIR absorption is red-shifted owing to the addition of the two CF$_3$ groups. Many exohedral adducts of C$_{80}$ like Sc$_4$N@C$_{80}$(CH$_2$)$_2$NR and n-Bu$_4$N$^+$(Sc$_4$C$_8$@C$_{80}$ (Ad))$^-$ have been synthesized with the help of the high stabilities improved by endohedral complexes containing metal or other groups. On one hand, the reactivity of C$_{80}$ can be improved due to the dense negative charge on the surface caused by the electronic transfer from the inside metals to the fullerene cage. On the other hand, the X-ray determination can be easily performed because of the cycloaddition of the adamantylidene carbene (Ad) to the cage. The methylene adducts of C$_{60}$ and C$_{70}$ can be prepared by direct carbene addition and dipolar cycloadditions of diazo compounds. Similar covalent derivatives of C$_{78}$ have been obtained through the reaction between fullerenes and diethyl 2-bromomalonate. These derivatives like T$_n$–C$_{78}$(COOH)$_2$$_n$ can be used as electrolytes. Hitherto, the methylene adducts of C$_{80}$(D$_{5d}$) have not been synthesized.

Although C$_{80}$O has been studied theoretically, C$_{80}$CH$_2$ based on C$_{80}$(D$_{5d}$) has not been investigated yet. Herein the nine possible geometries of C$_{80}$CH$_2$ are explored to predict the properties of C$_{80}$CH$_2$ and simulate similar derivatives. First, we want to know which geometry of C$_{80}$CH$_2$ is the most stable one and whether the additive bond is opened. Then we want to study the electronic structures and spectroscopy of C$_{80}$CH$_2$. Finally, we want to study the aromaticity of C$_{80}$CH$_2$ through computing the NICS values.

2. Research Approach

An initial geometry of C$_{80}$(D$_{5d}$) was drawn in Chem3D, and the full geometry optimization without any...
symmetric restriction was performed using PM3 method and DFT at B3LYP/STO-3G, B3LYP/3-21G and B3LYP/6-31G levels progressively in Gaussian 03 program package.12 These methods have been used to study the electronic structures and stabilities of the supramolecular complexes,13 conducting polymers,14 and other organic compounds.15 Then the equilibrium geometry of C\textsubscript{80}(D\textsubscript{5d}) was obtained. There are 5 unique carbon atoms and nine kinds of C–C bonds in C\textsubscript{80}(D\textsubscript{5d}). Based on the optimized geometry of C\textsubscript{80}(D\textsubscript{5d}) at B3LYP/6-31G level, CH\textsubscript{2} was added to the nine different bonds above the equatorial belt of C\textsubscript{80}(D\textsubscript{5d}), respectively. In the isomer 27,28–C\textsubscript{80}CH\textsubscript{2}(A) (Figure 1), 27,28- stands for the bond added by CH\textsubscript{2}. This numbering system was according to the IUPAC rule for carbon clusters.16 These isomers of C\textsubscript{80}CH\textsubscript{2} were optimized in the same way as the above, then the equilibrium geometries with the minimum energy of C\textsubscript{80}CH\textsubscript{2} were accomplished. According to Koopmans' theory, vertical ionization potential (IP) is approximately defined as the negative value of HOMO (the highest occupied molecular orbital) energy. Vertical electron affinity (EA) is defined as the negative value of LUMO (the lowest unoccupied molecular orbital) energy. Absolute hardness ($\eta$) is equal to the half of the difference between IP and EA. Absolute electron negativity ($\chi$) is defined as the half of the sum for IP and EA. All these variables were calculated at B3LYP/6-31G level.

Based on the B3LYP/6-31G optimized geometries of C\textsubscript{80}CH\textsubscript{2}, the electronic spectra were computed using INDO/CIS method without any adjustment of the parameters.17 One hundred and ninety-seven configurations including the ground state were generated by exciting electrons from 14 HOMOs to 14 LUMOs. The IR spectra were calculated using PM3 method. The $^{13}$C NMR spectra and NICS (nucleus independent chemical shifts) values of the isomers were calculated on GIAO (gauge-including atomic orbitals) method at B3LYP/6-31G level. The NICS values were used to measure the aromaticity, which was proposed by Schleyer et al.19

3. Results and Discussion

Relative energies at B3LYP/6-31G level: The optimized results of C\textsubscript{80}(D\textsubscript{5d}) were compared with the experimental values and other calculation results to assure the reliability of the method. The bond lengths of C\textsubscript{80}(D\textsubscript{5d}) at B3LYP/6-31G level are within the range of 0.1395–0.1473 nm, which is consistent with the ranges of 0.1391–0.1462 and 0.140–0.146 nm calculated using ZINDO and SCF-MO methods.20,21 The length and width in the polar and equatorial directions of C\textsubscript{80}(D\textsubscript{5d}) are 0.9169 and 0.6773 nm, which are in agreement with the calculated results (0.946 and 0.716 nm).21 The ratio between the long and short axes of C\textsubscript{80}(D\textsubscript{5d}) is 1.35, which is compatible with the experimental value 1.3.1

According to the relative energies of C\textsubscript{80}CH\textsubscript{2} isomers (Table 1), the most stable geometry of C\textsubscript{80}CH\textsubscript{2} is found to be 27,28–C\textsubscript{80}CH\textsubscript{2}(A), where the CH\textsubscript{2} group is added to the C(27)–C(28) bond near the equatorial belt of C\textsubscript{80}(D\textsubscript{5d}) (Figure 1). The length 0.1468 nm of the C(27)–C(28) bond is relatively larger than the others in C\textsubscript{80}(D\textsubscript{5d}) since the C(27)–C(28) bond is surrounded by four neighboring hexagons. Thus the C(27)–C(28) bond is weak and easy to undergo an addition. The second stable isomer is

Figure 1. The optimized geometries of 27,28–C\textsubscript{80}CH\textsubscript{2} and 1,9–C\textsubscript{80}CH\textsubscript{2} at B3LYP/6-31G level.
1.9-C₈₀CH₂(B), where the C(1)–C(9) bond inserted by CH₂ is between the two fused hexagons (6/6 bond) and near the pole of C₂v(D₁d). In C₈₀CH₂(C), (D) and (E), the C–C bonds added by CH₂ are formed by a hexagon and pentagon (6/5 bonds). In general, the 6/6 bonds in C₈₀CH₂(B) are easier to be added than 6/5 bonds.

The isomers with annulene structures of C₈₀CH₂ are more stable than those with cyclopropane structures since the cyclic tension can be reduced in the annulene structures. The lengths of the additive bonds in C₈₀CH₂(A), (C), (D), and (E) are 0.2312, 0.2225, 0.2208, and 0.2208 nm, respectively. These bonds are broken, thus the annulene structures are formed. The lengths of the additive bonds in C₈₀CH₂(B), (F), and (G) are 0.1633, 0.1658, and 0.1592 nm. These bonds are not opened, thus the cyclopropane structures are formed. The weak additive bonds 0.1468, 0.1473, 0.1462, 0.1457, 0.1435, and 0.1459 nm in C₈₀CH₂(A), (C), (D), (E), (H) and (I) lead to the formation of the annulene structures. The strong additive bonds 0.1395, 0.1399, and 0.1404 nm in C₈₀CH₂(B), (F), and (G) result in the generation of the cyclopropane structures. The angle of C(27)–C(81)–C(28) in the annulene structure of C₈₀CH₂(A) is 101.8°, basically consistent with 111.5° in C₈₀O.⁵

### Table 1. Relative energies (Eₖ) and some parameters (eV) of C₈₀CH₂ isomers at B3LYP/6-31G level.

<table>
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<tr>
<th>Compounds</th>
<th>Eₖ</th>
<th>E_HOMO</th>
<th>E_LUMO</th>
<th>Energy gap</th>
<th>IP</th>
<th>EA</th>
<th>η</th>
<th>χ</th>
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<tr>
<td>27,28–C₈₀CH₂(A)</td>
<td>0</td>
<td>-5.1193</td>
<td>-4.0363</td>
<td>1.0830</td>
<td>5.1193</td>
<td>5.0355</td>
<td>0.3484</td>
<td>5.5778</td>
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<td>1,9–C₈₀CH₂(B)</td>
<td>0.5007</td>
<td>-5.0355</td>
<td>-3.9484</td>
<td>1.0871</td>
<td>5.0355</td>
<td>3.9484</td>
<td>0.5436</td>
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<tr>
<td>25,26–C₈₀CH₂(C)</td>
<td>0.5551</td>
<td>-5.1220</td>
<td>-3.9811</td>
<td>1.1410</td>
<td>5.1220</td>
<td>3.9811</td>
<td>0.5705</td>
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<td>1,2–C₈₀CH₂(D)</td>
<td>0.5714</td>
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<td>9,10–C₈₀CH₂(E)</td>
<td>0.7021</td>
<td>-5.0671</td>
<td>-4.0246</td>
<td>1.0425</td>
<td>5.0671</td>
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<td>0.5212</td>
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<td>10,11–C₈₀CH₂(F)</td>
<td>0.8680</td>
<td>-4.9582</td>
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<td>0.9415</td>
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<tr>
<td>26,27–C₈₀CH₂(G)</td>
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<td>-5.1582</td>
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<td>5.1582</td>
<td>3.8842</td>
<td>0.6370</td>
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<tr>
<td>10,26–C₈₀CH₂(H)</td>
<td>1.0803</td>
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### Optimized parameters at B3LYP/6-31G level: The energies of HOMO and LUMO of C₈₀CH₂(A) are -5.1193 and -4.0363 eV. The energy gap of C₈₀CH₂(A) is 1.0830 eV, which is wider than 1.0523 eV of C₈₀(D₁d). This calculation result is similar to the experiment showing that the electrochemical band gap 1.78 eV of bisadduct of C₇₈(CH₂) is larger than 1.0523 eV. The energy gaps of C₈₀CH₂(B), (C), (D) and (E) are 1.1410, 1.0871, 1.1410 and 1.0525, respectively. These bonds are broken, thus the annulene structures are formed. The weak additive bonds 0.1395, 0.1399, and 0.1404 nm in C₈₀CH₂(B), (F), and (G) result in the generation of the cyclopropane structures. The angle of C(27)–C(81)–C(28) in the annulene structure of C₈₀CH₂(A) is 101.8°, basically consistent with 111.5° in C₈₀O.⁵

In C₈₀CH₂(A) with C₈₀ symmetry, the Mulliken atomic charges of the bridged carbon atoms C(27) and C(28) are all 0.0202. The Mulliken charges of C(81), H(82) and H(83) in CH₂ are -0.3816, 0.1703 and 0.1721, respectively, so the bonds C(27)–C(81) and C(28)–C(81) are polar covalent bonds. The Mulliken charge on CH₂ is -0.0392, thus the electrons are attracted from C₈₀(D₁d) to the CH₂ group.

### Electronic absorption spectra: The main absorption peaks in the electronic spectrum of C₈₀(D₁d) are located at 628.6, 490.6, 423.7, 360.3, 333.2, and 324.9 nm. These absorptions can be comparable to the experimental results of 880, 845, 569, 484, and 446 nm after being multiplied with a factor 1.4. The error is mainly caused by the less configurations used in the calculation and systematic deviation of ZINDO method for higher fullerenes. The strongest peak of C₈₀(D₁d) appears at 237.3 nm.

Since the absorption at 657.2 nm of C₈₀(D₁d) arising from HOMO to LUMO is electronically forbidden transition, the first peak at 633.1 nm, the main absorptions at 598.8, 497.6, 371.1, 361.3, 352.0, and the strongest peak at 244.0 nm of C₈₀CH₂(A) are red-shifted relative to those of C₈₀(D₁d) (Figure 2). The first and main absorptions of C₈₀CH₂(B) compared with those of C₈₀CH₂(A) are blue-shifted owing to the wide energy gap. The first and main absorptions of C₈₀CH₂(C) and (D) in contrast to those of C₈₀(D₁d) are red-shifted. When CH₂ is added to C₈₀(D₁d), the symmetry is reduced, and the peaks split with the decrease in oscillator strength. The more obvious red-shift for the first absorption of C₈₀CH₂(I) relative to that of C₈₀(D₁d) takes place because of the narrow energy gap.

### IR spectra: There exist some narrow bands within 500–1000 cm⁻¹, flat region within 1000–1300 cm⁻¹ and some strong sharp peaks within 1300–1700 cm⁻¹ in the IR spectrum of C₈₀(D₁d). The main absorptions at 933.4, 1551.2, and 1685.0 cm⁻¹ of C₈₀(D₁d) are ascribed to the puckering vibration of the aryl rings and stretching vibrations of the C–C and C=C bonds. These absorptions split with the decreased intensity in the isomers of C₈₀CH₂, which is caused by the addition of the CH₂ group and the decrease in the symmetry.
The strongest peak at 1675.3 cm$^{-1}$ of C$_{80}$CH$_2$(A) (Figure 3) compared with 1685.0 cm$^{-1}$ of C$_{80}$($D_5d$) is red-shifted, thus the C=C bonds in C$_{80}$CH$_2$(A) are weakened. A new absorption at 3153.7 cm$^{-1}$ of C$_{80}$CH$_2$(A) is produced, which is attributed to the C–H stretching vibration. The main peaks at 1675.3, 1682.4, and 1675.6 cm$^{-1}$ of C$_{80}$CH$_2$(A), (C), and (I) compared with 1685.0 cm$^{-1}$ of C$_{80}$($D_5d$) are red-shifted, whereas the absorptions at 1686.6 and 1688.7 cm$^{-1}$ of C$_{80}$CH$_2$(B) and (F) are blue-shifted. The Mulliken charges of the CH$_2$ groups in C$_{80}$CH$_2$(A), (C) and (I) are negative –0.0392, –0.0195, and –0.0068, whereas 0.1918 and 0.1938 of C$_{80}$CH$_2$(B) and (F) are positive. Since the electrons are attracted from C$_{80}$($D_5d$) to the CH$_2$ groups in C$_{80}$CH$_2$(A), (C), and (I), the electron density on C$_{80}$($D_5d$) is reduced and the C=C bonds are weakened. On the contrary, the electron density on the cage is increased owing to the positive charges of CH$_2$ in C$_{80}$CH$_2$(B) and (F). A similar calculation has shown that the four characteristic bands of C$_{80}$O compared with those of C$_{80}$ are red-shifted, supporting our conclusion.

Since the electronegativities of the CH$_2$ groups in the order of C$_{80}$CH$_2$(A), (C), (I), (B), and (F) are decreasing, the polarities of the C–H bonds are weakened and the covalence characters increased. Thus the strong C–H stretching vibrations at 3153.7, 3163.8, 3168.8, 3174.3, and 3174.6 cm$^{-1}$ in these isomers are gradually intensified.

NMR spectra: The $^{13}$C signals of the five unique carbon atoms in C$_{80}$($D_5d$) are within 124.4–165.4 ppm, which are in agreement with 128.9–163.9 ppm. The lines with the chemical shifts at 152.7 and 165.4 ppm are ascribed to the first and second unique carbon atoms near the pole of C$_{80}$($D_5d$), which correspond to the experimental values 156.3 and 163.9 ppm. The lines with the chemical shifts at 164.4, 124.4, and 156.5 ppm are assigned as the third, forth, and fifth types of the carbon atoms in C$_{80}$($D_5d$), and twenty carbon atoms are included in each type.

In C$_{80}$CH$_2$(A), the signals are distributed within 116.9–174.6 ppm, which arises from the sp$^3$–C atoms on the cage (Figure 4). This range is wider than that of C$_{80}$($D_5d$), which is caused by the decrease in symmetry upon the addition of CH$_2$. The peak at 19.2 ppm of C$_{80}$CH$_2$(A) arises from the sp$^3$–C atom in the CH$_2$ group. The experiment shows that the chemical shifts of the methylene carbon atoms in the isomers of C$_{70}$CH$_2$ are within 13.8–34.0 ppm. The signals at 179.3 ppm are generated by the bridged carbon atoms C(27) and C(28), which...
are shifted downfield compared with the value of 156.5 ppm for C_{80}(D_{5d}). The electron densities on C(27) and C(28) are lowered owing to the electronegativity of CH_2. In C_{80}CH_2(B), the signal at 16.5 ppm is assigned as the sp^3-C atom and the signals of the bridged carbon atoms appear at 78.2 and 92.2 ppm. It has been indicated that the chemical shifts of the bridged carbon atoms in the cyclopropane structure of C_{80}CH_2 are 71.0 ppm. At the same time, the region of the chemical shifts for the signals of sp^3-C atoms in C_{80}CH_2(B) is changed upfield because of the increased electron density on the cage.

The signals at 19.2, 24.9, and 30.1 ppm of the sp^3-C atoms in the order of C_{80}CH_2(A), (C), and (I) are changed downfield because of the decreased electron density. At the same time, the regions of the chemical shifts produced by the sp^3-C atoms in these isomers are changed upfield to 116.9–174.6, 116.0–174.0, and 107.2–172.2 ppm, respectively, because of the increased electron density on the cage. In C_{80}CH_2(I), the signals at 107.8 and 107.7 ppm result from the bridged carbon atoms in the annulene structure, which are shifted upfield relative to those of C_{80}(D_{5d}) owing to the positive charge on CH_2. These values are similar to 118.0 ppm of the bridged carbon atoms in the annulene isomer of C_{70}CH_2.23

**Aromaticity:** The NICS value of C_{80}(D_{5d}) at B3LYP/6-31G level was calculated to appear at –8.83 ppm. This method has been successfully used to study the NICS value of C_{84}(D_2). The NICS values of C_{80}CH_2(A), (C), (D), (H), and (I) with the annulene structures are located at –7.30, –4.34, –8.73, –7.44, and –6.65 ppm. These values are higher than that of C_{80}(D_{5d}) and are similar to the ^3He experimental chemical shifts at –27.46 and –27.82 ppm for the two annulene isomers of C_{70}CH_2; higher than –28.81 ppm corresponding to C_{70}(D_{5d}). The large magnetic cyclic current is maintained in these C_{80}CH_2 isomers owing to the formation of the annulene structures. The NICS values of C_{80}CH_2(B) and (F) with the cyclopropane structures are situated at –9.85 and –14.63 ppm. These values are lower than that of C_{80}(D_{5d}), which is similar to the C_{80}CH_2 isomers compared with those of C_{80}(D_{5d}) are also red-shifted owing to the negative charges on the CH_2 groups. The ^13C chemical shifts of the bridged carbon atoms in C_{80}CH_2 with cyclopropane structures are moved upfield upon the formation of the sp^3-C atoms. The bonds near the CH_2 group are activated, becoming the most possible addition sites of the next CH_2 atom.

### 5. References

Povzetek

S pomočjo teorije gostotnih funkcionalov (DFT) na nivoju B3LYP/6-31G smo preučili elektronsko strukturo in stabilnost devetih možnih izomerov C₈₀CH₂, ki temeljijo na strukturi C₈₀(D₅d). Glede na optimizirane geometrije smo z metodami INDO/CIS, PM3 in B3LYP/6-31G izračunali elektronske, IR in ¹³C NMR spektre izomerov C₈₀CH₂. Kot najbolj stabilno geometrijsko obliko C₈₀CH₂ smo napovedali 27,28–C₈₀CH₂(A) z anulensko strukturo, kjer je adicija potekla na vez 6/6 blizu ekvatorialnega pasu molekule C₈₀(D₅d). Položaj prve absorpcijske črte v elektronskih spektreih in območje glavnih absorpcij v IR spektreih so za C₈₀CH₂ v primerjavi z C₈₀(D₅d) pomakanji bolj v rdeče območje. Kemijski premiki v ¹³C NMR spektreih so za mostne atome v ciklopropanski strukturi premaknjeni v višje polje. Aromatičnost je večja v anulenski kot v ciklopropanski strukturi, kar je skladno z NICS vrednostmi za C₈₀CH₂ napovedanimi na nivoju B3LYP/6-31G.
Supporting materials:

Figure 1. The electronic spectra of $C_{80}(D_{5d})$, $C_{80}CH_2(D)$ and (I) using INDO/CIS method.
Figure 2. The IR spectra of $\text{C}_{80}(D_{5d})$, $\text{C}_{80}\text{CH}_2(C)$, (F), and (I) using PM3 method.
Figure 3. The $^{13}$C NMR spectra of $C_{80}(D_{5d})$, $C_{80}CH_2(D)$, (C), and (I) at B3LYP/6-31G level.