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Theoretical Studies on Stabilities and Spectroscopy of C₇₈O₅

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The semi-empirical AM1 and INDO/CIS methods as well as density function theory were used to study equilibrium geometries and spectroscopic properties of the possible isomers of C₇₈O₅ based on C_{2v}-C₇₈. The most stable geometry of C₇₈O₅ is 28,29,30,31,52,53,70,71,73,78-C₇₈O₅(A) with one annulene-like structure and four epoxide structures. Compared with that of C_{2v}-C₇₈, the blue-shift in the electronic absorption spectra of C₇₈O₅ isomers is predicted. The reason for the blue-shift effect is discussed and the electronic transitions are assigned. The IR and NMR spectra of C₇₈O₅ are explored with the AM1 and B3LYP/6-31G methods based on the B3LYP/6-31G optimized geometries.

Key words: C₇₈O₅, B3LYP/6-31G, Electronic spectrum, IR, ¹³C NMR**I. INTRODUCTION**

The availability of gram quantities of pure fullerenes by simple chromatographic methods leads to numerous investigations of the chemical properties of fullerenes. The synthesis and characterization of oxygenated fullerenes open a wide way for studying chemical reactions of fullerenes. Some experimental as well as theoretical efforts are concentrated on exploring the regioselectivity of addition reactions of fullerene oxides. Creegan *et al.* has synthesized and characterized C₆₀O using mass spectrum, UV, IR and ¹³C NMR spectra [1]. Balch *et al.* have investigated the C_s isomer of C₆₀O₂. They believe that its first UV band is blue-shifted relative to that of C₆₀O and no IR bands exist above 1450 cm⁻¹ [2]. Hamano *et al.* have prepared C₆₀O₂ and C₆₀O₃, and discussed the effect of epoxide structures on the ¹³C NMR spectrum [3]. Deng *et al.* have isolated the two isomers of C₆₀O₂ and obtained C₆₀O_n (n=1-5) utilizing the HPLC experiment [4]. Malhotra *et al.* have observed C₆₀O₅ using mass spectrum, and measured IR and NMR spectra of oxygenated fullerenes [5]. Wood *et al.* have also proven the existence of C₆₀O_n (n=2-5) [6]. Balch *et al.* and Eisler *et al.* have achieved C₁₂₀O, C₁₂₀O₂ and C₁₃₀O from C₆₀O and C₆₀ or C₇₀ [7,8]. Tian *et al.* calculate the structures of six possible isomers and the electronic spectrum of C₆₀O₂ using the INDO/CIS method [9]. Wang *et al.* perform similar optimization for C₆₀O₃ based on the most stable isomer of C₆₀O₂. They conclude that the first UV peak of C₆₀O₃ is blue-shifted in contrast to that of C₆₀O₂ [10]. The relative stabilities of C₇₈O, C₇₈O₂, C₇₈O₃ and C₇₈O₄ isomers have been studied using INDO series of methods [11-14]. Though C₇₈O_n has not been synthe-

sized yet, synthesis of C₆₀O_n and the higher oxides of other fullerenes has been achieved. It will not be long before C₇₈O_n is obtained experimentally in the same way. The structures of the higher oxides of fullerenes are not well known and it is very difficult to isolate the pure isomer under the restrictions of experimental conditions. Theoretical study exhibits the advantages of predicting their possible structures and relative stabilities. Here the electronic structures and UV, IR as well as ¹³C NMR spectra of C₇₈O₅ are reported to predict the possible additive sites and spectroscopic properties of the isomers.

II. RESEARCH APPROACH

When the number of the added oxygen atoms is increased, the possible isomers are too numerous to be examined individually even with the semi-empirical method. The isomers of C₇₈O₅ studied here were chosen from the stable isomers of C₇₈O_n (n=1-4). Based on C_{2v}-C₇₈, the most stable isomer 73,78-C₇₈O (according to the IUPAC numbering system shown in Fig.1) was selected from all of the 34 possible isomers [11]. In view of the several stable isomers of C₇₈O, an oxygen atom was added to different bonds to get 22 possible isomers and the most stable isomer 28,29,73,78-C₇₈O₂ was obtained [12]. In the same way, the most stable geometries for C₇₈O₃ and C₇₈O₄ were found to be 28,29,30,31,52,53-C₇₈O₃ and 28,29,30,31,52,53,73,78-C₇₈O₄ from 21 and 24 possible isomers, respectively [13,14]. On the basis of the previous C₇₈O₄ results, another oxygen atom was inserted into the 21 possible sites to get C₇₈O₅ isomers. Full geometry optimization without any symmetry restrictions for these isomers was performed using the AM1 method in GAUSSIAN 03 program and the equilibrium geometries were determined [15]. The most stable six isomers were further optimized using density function theory (DFT) at B3LYP/STO-3G, 3-21G and

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6-31G levels, step by step. Based on the B3LYP/6-31G optimized geometries, the electronic spectra of the $C_{78}O_5$ isomers were computed using the INDO/CIS method without any adjustment of the parameters [16]. There were 197 electronic excited states based on the ground state through the excitation of electrons from the 14 HOMO (the highest occupied molecular orbitals) to the 14 LUMO (the lowest unoccupied molecular orbitals). The IR and ^{13}C NMR spectra of $C_{78}O_5$ isomers were calculated using the AM1 method and the GIAO method at B3LYP/6-31G level.

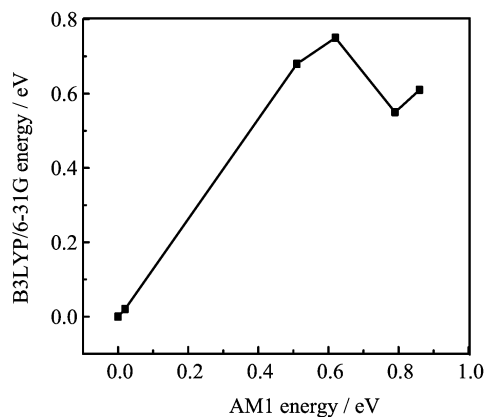


FIG. 1 Energy comparison of $C_{78}O_5$ isomers at B3LYP/6-31G level and with AM1 method.

III. RESULTS AND DISCUSSION

A. Relative energies with the AM1 method

The relative energies of $C_{78}O_5$ isomers by taking that of $C_{78}O_5(A)$ as the reference are presented in Table I. The most stable geometry was found to be $C_{78}O_5(A)$ of C_s symmetry. The atoms O(79), O(80) and O(81) are added to the same hexagon which is passed by the longest axis of $C_{2v}-C_{78}$ (Fig.2). The atom O(82) is inserted into the C(73)–C(78) bond which is intersected by the shortest axis of $C_{2v}-C_{78}$, and O(83) is added to the C(70)–C(71) bond. The former four oxygen atoms form epoxides, whereas the latter one leads to an annulene-like structure. The former four bridged bonds are the same as in the most stable isomer of $C_{78}O_4$ [14]. The fifth bond C(70)–C(71) is situated between two fused hexagons (6–6 bond) added by O(79) and O(82), and is weakened owing to the addition of the previous four oxygen atoms. The inductive effect of the oxygen atoms in $C_{78}O_4$ enhances the chemical reactivity of the double bonds nearby but this effect decreases with increasing distance. Thus the fifth oxygen atom is located near the previous four ones. The former four stable isomers possess very close energies, thus it is possible to get the mixture experimentally.

$C_{78}O_5(E)$ and $C_{78}O_5(F)$ are based on the most stable

TABLE I AM1 optimized relative energy of $C_{78}O_5$ isomers

Geometries	Energy/eV
28,29,30,31,52,53,70,71,73,78- $C_{78}O_5(A)$	0
28,29,30,31,52,53,73,78,75,76- $C_{78}O_5(B)$	0.02
28,29,30,31,35,36,52,53,73,78- $C_{78}O_5(C)$	0.51
28,29,30,31,52,53,35,56,73,78- $C_{78}O_5(D)$	0.62
28,29,30,31,40,41,42,43,52,53- $C_{78}O_5(E)$	0.79
28,29,30,31,52,53,42,43,62,63- $C_{78}O_5(F)$	0.86
28,29,30,31,40,41,42,43,73,78- $C_{78}O_5(G)$	0.88
2,3,28,29,30,31,52,53,73,78- $C_{78}O_5(H)$	0.91
28,29,30,31,52,53,42,43,73,78- $C_{78}O_5(I)$	0.93
1,2,28,29,30,31,52,53,73,78- $C_{78}O_5(J)$	0.95
28,29,30,31,32,33,52,53,73,78- $C_{78}O_5(K)$	1.03
28,29,30,31,52,53,62,63,73,78- $C_{78}O_5(L)$	1.05
28,29,30,31,34,35,52,53,73,78- $C_{78}O_5(M)$	1.18
11,12,28,29,30,31,32,33,52,53- $C_{78}O_5(N)$	1.19
11,12,28,29,30,31,52,53,73,78- $C_{78}O_5(O)$	1.20
1,10,28,29,30,31,52,53,73,78- $C_{78}O_5(P)$	1.45
28,29,30,31,51,70,52,53,73,78- $C_{78}O_5(Q)$	1.46
28,29,30,31,52,53,69,70,73,78- $C_{78}O_5(R)$	1.60
2,3,28,29,30,31,52,53,73,78- $C_{78}O_5(S)$	1.74
28,29,30,31,52,53,51,70,54,71- $C_{78}O_5(T)$	1.93
26,27,28,29,49,50,51,70,52,53- $C_{78}O_5(U)$	2.02

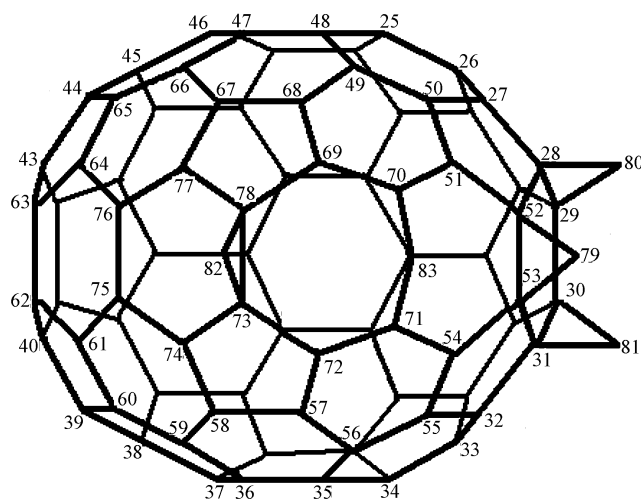


FIG. 2 The B3LYP/6-31G optimized geometry of $C_{78}O_5(A)$.

isomer of $C_{78}O_3(A)$ [13]. In $C_{78}O_5(G)$ and $C_{78}O_5(U)$, two added hexagons are separated, and each binds two oxygen atoms. These structures are the most stable isomers of $C_{78}O_2$ [12]. The epoxide functional groups have an activation effect on the adjacent π bonds, thus the oxygen atoms tend to add the same hexagon. According to the previous calculations, the isomers with the oxygen atoms on 6–5 bonds and those with the separated bridged oxygen atoms possess higher energies [12,14]. These similar isomers of $C_{78}O_5$ are not consid-

ered here. The reactivity enhancement produced by the inductive effect of the oxygen atoms becomes negligible for the bonds separated by more than two bonds. In these structures, the oxygen atoms are so far apart that the five epoxide groups exert chemical influence on the carbon cage independently, therefore they behave like a $C_{78}O$ molecule [11]. These conclusions are in good agreement with the experimental [3,4] and theoretical [9,10] results that the oxygen atoms are easily added to the 6–6 bonds near already existing epoxy structures. It is predicted that the next oxygen atom should be located near the previous six ones based on the above conclusion.

B. Optimized structures at B3LYP/6-31G level

The relative energies of the six lowest-energy isomers of $C_{78}O_5$ at B3LYP/6-31G level are 0, 0.02, 0.68, 0.75, 0.55 and 0.61 eV. The stable sequence of the six isomers is as follows: $C_{78}O_5(A) > C_{78}O_5(B) > C_{78}O_5(E) > C_{78}O_5(F) > C_{78}O_5(C) > C_{78}O_5(D)$. There is a stability disagreement of $C_{78}O_5$ (C), (D), (E) and (F) between the AM1 optimized results and B3LYP/6-31G results as shown in Fig.1. In view of the calculation accuracy, the optimized energies at B3LYP/6-31G level are more reliable. The original MNDO method is poor in the description of some chemical problems. An amended parametrization MNDO-AM1 method was developed to correct it, but it has been proven to overestimate. Additionally, the AM1 model has an inadequate Hamiltonian for some atoms at a certain distance [17]. $C_{78}O_5$ (A) and (B) at B3LYP/6-31G level are compatible with those using AM1 method. They are the most stable two isomers of the six. Although there is a little energy difference between these two stable isomers, an intermediate still exists when the oxygen atom is transferred from the added bond to another, and the barrier energy is estimated to be large. Thus the two isomers can be synthesized and isolated experimentally. The optimized geometry for $C_{78}O_5(A)$ is shown in Fig.2. The lengths of the C(28)–C(29), C(30)–C(31), C(52)–C(53) and C(73)–C(78) bonds added by oxygen are 0.15, 0.15, 0.15 and 0.16 nm, respectively. These bonds are not broken to form the four epoxy structures, which is similar to that of $C_{78}[C(COOEt)_2]_3$ [18]. But the length of the added C(70)–C(71) bond becomes 0.23 nm, which is open to form an 1,6-oxido [10] annulene structure. With the addition of the oxygen atoms, the bonds of C(54)–C(71), C(71)–C(72), C(32)–C(33), C(11)–C(12), C(57)–C(72) and C(58)–C(74) near the additive sites are shortened from 0.142, 0.143, 0.138, 0.138, 0.143 and 0.143 to 0.139, 0.140, 0.137, 0.137, 0.141 and 0.141 nm, respectively. Thus these bonds are intensified. On the contrary, the bonds of C(53)–C(54), C(72)–C(73) and C(73)–C(74) are lengthened from 0.146, 0.145 and 0.145 to 0.152,

0.151 and 0.150 nm, respectively. The lengths of the open bonds C(75)–C(76) in $C_{78}O_5(B)$, C(35)–C(36) in $C_{78}O_5(C)$ and C(35)–C(56) in $C_{78}O_5(D)$ are 0.23, 0.23 and 0.23 nm, respectively.

C. Electronic structures at the ground state

Based on the B3LYP/6-31G optimized geometry, the LUMO-HOMO energy gap of $C_{2v}-C_{78}$ is 2.05 eV, which is consistent with 2.02 eV calculated by Sun *et al.* using the B3LYP/6-31G* level [19]. The energies of HOMO $A''(171)$ and LUMO $A'(172)$ of $C_{78}O_5(A)$ are -6.17 and -3.69 eV, respectively. Its energy gap is 2.48 eV. The energy gaps for the other five stable isomers are 2.48, 2.57, 2.53, 2.10 and 2.22 eV. These energy gaps are larger than that of C_{78} . This is consistent with Boudon's experiment [20] that the derivative of $C_{2v}-C_{78}$ with the cyclopropane structure has a wider electrochemical energy gap of 1.78 V than the 1.62 V of $C_{2v}-C_{78}$. Then the stability of $C_{78}O_5$ to the excitation of electrons will become greater. The electron affinities of $C_{78}O_5$ isomers are expected to increase with the number of oxygen atoms incorporated, and thus the higher oxides of C_{78} compete more favorably for electrons than C_{78} .

The Mülliken charges of O(79)–O(83) of $C_{78}O_5$ (A) at B3LYP/6-31G level are -0.36 , -0.36 , -0.36 , -0.36 and -0.49 . The carbon atoms adjacent to these oxygen atoms carry the positive charges 0.13, 0.13, 0.10, 0.12, 0.12, 0.10, 0.04, 0.04, 0.06 and 0.06. This leads to the formation of the polar covalent C–O bonds, and the flow of the electrons from C_{78} to oxygen atoms. The oxygen atoms with the negative charges will become a center of reactions, which can form a hydrogen bond or react with electrophilic reagents. The carbon atoms next to the added bonds are also ready for the reaction with electrophilic reagents since they have relatively large negative charges. This is why the next added oxygen atom should be situated here. It is inferred that $C_{78}O_5(A)$ is more polar than the other isomers since these five oxygen atoms reside close to each other on the same side of the carbon cage. Therefore, the polar isomer of $C_{78}O_5$ is more abundant than the less polar one in the HPLC experiment.

D. Electronic absorption spectra

The INDO/CIS method has been proved successful in elucidating electronic spectra for C_{60} [9,10], C_{78} , C_{80} derivatives [21,22] and other organic compounds [23,24]. The main absorption peaks in the electronic spectrum of $C_{2v}-C_{78}$ are consistent with the experimental results [14]. The first peak of $C_{78}O_5(A)$ appears at 527.9 nm (Table II), which is produced by the $\pi \rightarrow \pi^*$ electronic transition of $A''(171) \rightarrow A'(173)$. The molecular orbital (MO) $A''(171)$ is mainly composed of the p_z atomic

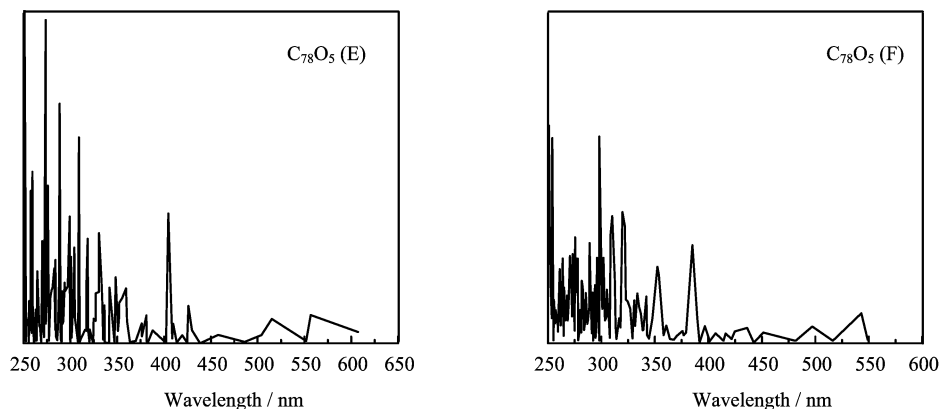


FIG. 3 The electronic spectra of $C_{78}O_5$ (E) and $C_{78}O_5$ (F).

orbital of C(37) with a combination coefficient 0.17. Likewise, $A'(173)$ is comprised of p_y of C(19) with a coefficient 0.23. The contribution coefficients of lone pairs of electrons on s orbitals of O(79), O(80), O(81), O(82) and O(83) to molecular orbitals $A'(12)$, $A''(10)$, $A''(10)$, $A'(3)$ and $A'(13)$ are -0.35 , 0.30 , -0.30 , -0.31 and 0.36 , respectively. The first peak of $C_{78}O_5$ (B) is located at 507.6 nm, which is generated by the electronic transition of $A'(170) \rightarrow A'(172)$.

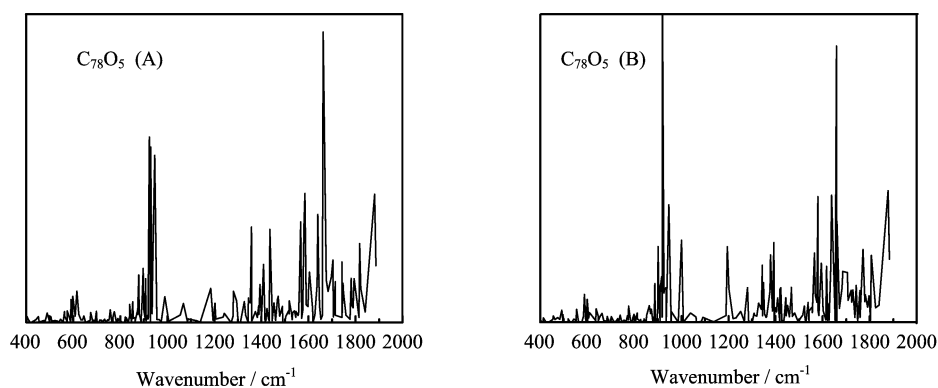
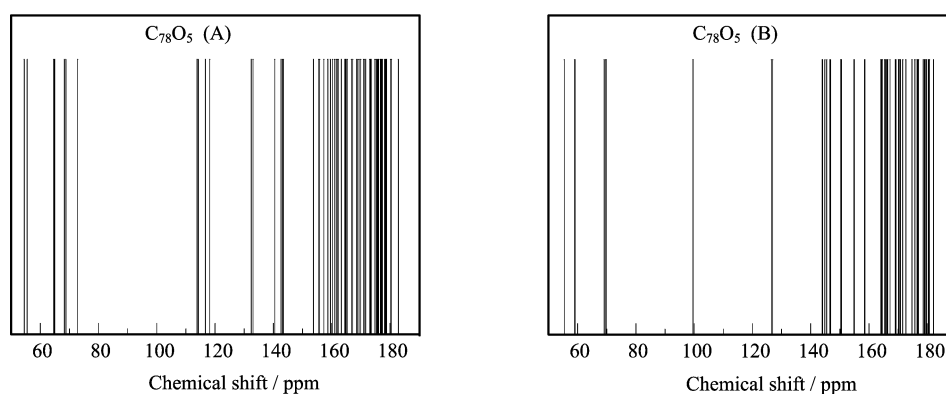
TABLE II Calculated electronic spectra for the stable isomers of $C_{78}O_5$

Isomers	λ/nm	f	Configuration	Coefficients
$C_{78}O_5$ (A)	527.9	0.002	$A''(171) \rightarrow A'(173)$	0.867
	503.3	0.038	$A'(170) \rightarrow A'(172)$	0.593
	499.7	0.009	$A''(171) \rightarrow A'(172)$	0.856
	467.0	0.038	$A'(170) \rightarrow A''(174)$	-0.530
	459.0	0.006	$A'(169) \rightarrow A'(173)$	0.661
	445.2	0.036	$A'(169) \rightarrow A'(172)$	0.580
$C_{78}O_5$ (B)	507.6	0.038	$A'(170) \rightarrow A'(172)$	-0.636
	491.6	0.035	$A''(171) \rightarrow A'(172)$	-0.799
	467.3	0.009	$A'(170) \rightarrow A'(173)$	-0.534
	461.2	0.012	$A'(169) \rightarrow A'(173)$	0.544
	448.1	0.022	$A'(169) \rightarrow A'(173)$	-0.494
	445.3	0.017	$A'(169) \rightarrow A'(172)$	-0.582
$C_{78}O_5$ (C)	529.9	0.002	$(171) \rightarrow (173)$	0.838
	509.2	0.027	$(171) \rightarrow (172)$	-0.570
	498.0	0.006	$(171) \rightarrow (172)$	-0.626
	474.6	0.010	$(171) \rightarrow (174)$	-0.542
	471.9	0.018	$(171) \rightarrow (174)$	0.480
	452.7	0.009	$(168) \rightarrow (173)$	0.545
$C_{78}O_5$ (D)	528.0	0.0013	$(171) \rightarrow (173)$	0.833
	509.3	0.0269	$(170) \rightarrow (172)$	0.503
	500.5	0.0092	$(171) \rightarrow (172)$	-0.719
	465.1	0.0407	$(170) \rightarrow (174)$	0.613
	457.5	0.0098	$(169) \rightarrow (173)$	0.608
	445.5	0.0217	$(169) \rightarrow (172)$	-0.558

The first peaks in the electronic spectra of $C_{78}O_5$ (E) and $C_{78}O_5$ (F) appear at 556.8 and 543.0 nm (Fig.3), which are aroused by the $\pi \rightarrow \pi^*$ electronic transitions of $A'(171) \rightarrow A'(172)$ and $(171) \rightarrow (172)$, respectively. In fact, the first absorptions for $C_{78}O_5$ (A)-(F) are blue-shifted relative to that of C_{2v} - C_{78} . Analysis of the bond lengths near the added sites in $C_{78}O_5$ (A) shows that many bonds are intensified, thus the conjugation effect in the system is strengthened. Opposing this, the ten π -electrons are reduced owing to the addition of the five oxygen atoms, and the system becomes less conjugated. Then the energy gap is widened and the blue-shift of the first UV absorption of $C_{78}O_5$ (A) in contrast to that of C_{2v} - C_{78} takes place.

E. IR spectra

The IR spectrum of C_{2v} - C_{78} matches the experimental results within the 500-1000 cm^{-1} narrow bands, the 1000-1300 cm^{-1} flat region and the 1300-1600 cm^{-1} strong sharp peaks [25]. The first peaks of C_{2v} - C_{78} and $C_{78}O_5$ (A) are 1885.5 and 1886.7 cm^{-1} (Fig.4). $C_{78}O_5$ (A) has no bands beyond 1900 cm^{-1} , demonstrating that no C-H or C=O units exist. Meanwhile, the absorptions are split and intensity of absorptions around 900-1000 cm^{-1} is enhanced, which results from the formation of the C-O bond. Differences of IR spectra between $C_{78}O_5$ (A) and $C_{78}O_5$ (B) are concentrated on intensity of absorptions within 900-1000 cm^{-1} (the C-O stretching vibrations), 1400-1600 cm^{-1} (C=C stretching vibration on benzene rings), 1600-1700 cm^{-1} (C=C stretching vibration on alkenes), and 1800 cm^{-1} (possibly arising from the coupling of the C=C double bonds with approximate frequencies). The main IR absorptions of $C_{78}O_5$ (A) and (B) are generally blue-shifted compared with those of C_{78} . This indicates that the C=C bonds are strengthened with the shrinkage of the conjugated carbon cage after the addition of five oxygen atoms.

FIG. 4 IR spectra of $C_{78}O_5$ (A) and (B).FIG. 5 ^{13}C NMR spectra of $C_{78}O_5$ (A) and $C_{78}O_5$ (F).

F. NMR spectra

^{13}C chemical shifts of the 21 unique carbon atoms in C_{2v} - C_{78} at the B3LYP/6-31G level are within 150.3-173.9 ppm, which is bigger than experimental results of 132-148 ppm [26]. Thus the multiplier for B3LYP/6-31G method should be 0.88 because of the systematic errors in the theoretical shielding values for fullerenes [19]. $C_{78}O_5$ (A) of C_s symmetry has 41 unique carbon atoms, where four types contain one carbon atom and the others include two carbon atoms. Their chemical shifts range from 54.5 to 182.9 ppm (Fig.5). The main peaks are mainly distributed within 120-180 ppm, which is the sp^2 -C atom region. This is basically consistent with 128-164 ppm in the cyclopropane-type derivative of C_{2v} - C_{78} [18]. The carbon atom peaks near 180 ppm are ascribed to the sp^2 -C atoms close to the oxygen atoms. The shield effects on these carbon atoms are lessened and the chemical shifts are changed downfield owing to the electron-withdrawing influence of the oxygen atoms. The eight peaks produced by sp^3 -C atoms in the epoxide structures are located at 50-80 ppm, which is compatible with the experimental results 57.7 and 57.8 ppm [18]. The two peaks arising from the carbon atoms in the annulene-type structure are situated at 113.8 and 114.2 ppm, which matches the experi-

mental value 118.7 ppm for the same type of carbon atoms in $C_{70}CH_2$ [27]. $C_{78}O_5$ (B) also has C_s symmetry. ^{13}C chemical shifts vary within the range of 55.4-69.8 ppm (sp^3 -C atoms in epoxy structures), 99.6 ppm (annulene-type carbon atoms), and 126.5-182.1 ppm (sp^2 -C atoms).

IV. CONCLUSION

The most stable isomer of $C_{78}O_5$ at the ground state was calculated to be 28,29,30,31,52,53,70,71,73,78- $C_{78}O_5$ (A) with an annulene-like structure and four epoxide structures. The added oxygen atoms tend to approach each other. The addition of the oxygen atoms activates the bonds nearby, and these bonds become the possible sites to receive the next oxygen atom. Relative to those of C_{2v} - C_{78} , the first peaks in the electronic spectra and the main IR absorptions of $C_{78}O_5$ isomers are blue-shifted due to their wider energy gaps and the intensification of the C=C bonds after the addition of oxygen atoms. In addition, the ^{13}C chemical shifts of the bridged carbon atoms in $C_{78}O_5$ are moved upfield with the formation of sp^3 carbon atoms.

V. ACKNOWLEDGMENT

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