Theoretical studies on stable geometries of C_{78}O_6 based on C_{2v}-C_{78}

W Zhang, S Wu & X Wen

Department of Chemistry, Zhejiang University, Hangzhou 310027, China
Email: wushi@zju.edu.cn

Received 20 June 2007; revised 29 September 2007

The semi-empirical AM1 and INDO/CIS methods as well as density function theory have been used to study equilibrium geometries and spectroscopic properties of the possible isomers of C_{78}O_6 based on C_{2v}-C_{78}. The most stable geometry at the ground state of C_{78}O_6 is found to be 28, 29, 30, 31, 52, 53, 70, 71, 73, 78, 75, 76-C_{78}O_6 (A). The C(70)-C(71) and C(75)-C(76) bonds are opened up to form annulene-like structures, whereas the other four bonds are not broken and show epoxy features in C_{78}O_6 (A). The oxygen atoms added tend to approach the sites vacated by the previous oxygen atoms since the conjugation system in C_{2v}-C_{78} is destroyed at these sites. Based on the B3LYP/6-31G optimized geometries, the main absorptions in the electronic spectra and the stretching vibrations of the C=C bonds in the IR spectra of C_{78}O_6 isomers are blue shifted as compared with those of C_{2v}-C_{78} calculated using the INDO/CIS and AM1 method, respectively. The chemical shifts of the carbon atoms in the epoxy and annulene-type structures of C_{78}O_6 isomers, calculated at B3LYP/6-31G level, move upfield.

Since the methylene adducts and oxides of fullerenes are widely used, e. g., in conversion between two functionalization groups and organic photocells, these have been extensively investigated in the past few years. Li et al. have theoretically investigated the monoadduct of C_{60} on the 5/6 bond (the bond between a pentagon and a hexagon), and calculated the electronic spectrum of the adduct. According to Li et al., the planar properties of the pentagon and hexagons near the additive sites disappear. Isomerically pure fullerenols can be prepared from the fullerene peroxides C_{60}(OOr-Bu)_{6} and C_{60}(O)(OOr-Bu)_{6}, promoted by the Lewis acid and the epoxy structures are formed in the intermediate. At the same time, the presence of the Lewis acid stimulates the opening of the O-O and C-O bonds. One carbon atom is deleted from the carbon cage as carbon monoxide, and an open-cage oxafulleroid is produced. The bifunctionalized derivatives, C_{60}(CRCHO)_{2}, with cyclopropane-like structures and construction of disymmetric fullerenes-centered triads have been studied. Among difluoromethylene adducts, C_{60}(CF_{2})_{n} (n = 1–3), mass spectrum shows the monoadduct to contain an open structure whether the added bond is located at the 6/5 or 6/6 bond. Besides the above, mono-, bi- and tri-adducts of C_{60}, higher oxides and adducts of C_{60}(C(COOEt))_{2}, with C_{2v} symmetry have been synthesized by oxidation with KMnO_{4}. In newly synthesized 1, 2, 3, 4, 5, 6-hexaadducts, the formation of the oxa bridges prevents the opening of the rings. Further studies on the monoadduct of C_{70} have been carried out by Yin et al., and the synthesis of C_{70}CHPO_{3}Et_{2} is considered to be a free radical mechanism. A similar study on bi- and tri-adducts of C_{2v}-C_{78} has been reported. C_{78}(C(COOEt))_{2} and C_{78}(C(COOEt))_{3} have also been prepared and characterized, where the added bonds are not open.

The structures of the higher oxides of fullerenes are not well known, and it is very difficult to isolate the pure isomer under the restriction of the experimental conditions. Theoretical studies have the advantage in predicting their possible structures and relative stabilities. Herein we report the theoretical investigation on C_{78}O_{6} isomers, to predict which isomer of C_{78}O_{6} is the most stable one and which bonds are broken. The UV, IR as well as C NMR spectra of C_{78}O_{6} isomers have also been investigated theoretically.

Theory

Since the number of the oxygen atoms in C_{78}O_{6} is large, the possible isomers of C_{78}O_{6} are too numerous to be examined individually even with the semi-empirical method. In view of this, only 14 possible structures of C_{78}O_{6} have been designed. Some of these, such as C_{78}O_{6} (A), C_{78}O_{6} (D), C_{78}O_{6} (E) and C_{78}O_{6} (F), are formed based on the most stable isomer.
of 28, 29, 30, 31, 52, 53, 70, 71, 73, 78, 75, 76-C\textsubscript{78}O\textsubscript{6} (A). This numbering system of C\textsubscript{11}-C\textsubscript{78} \cite{12} (Fig. 1) is established according to the IUPAC rule for the carbon clusters. 28, 29- is used to indicate the bond located by the two carbon atoms C(28) and C(29), which is formed by the first oxygen atom. Then 30, 31- is the additive bond for the second oxygen atom. Similarly, 52, 53-, 70, 71-, and 73, 78- represent the bonds formed by the other three oxygen atoms. Since the five oxygen atoms in C\textsubscript{78}O\textsubscript{5} (A) are added to the above five sites, the isomer 28, 29, 30, 31, 52, 53, 70, 71, 73, 78-C\textsubscript{78}O\textsubscript{5} (A) is labeled in order to show the concrete additive sites of the oxygen atoms. For the isomers of C\textsubscript{78}O\textsubscript{6}, the same numbering method is employed. Other geometries of C\textsubscript{78}O\textsubscript{6} are produced considering the three oxygen atoms located at the same hexagon or two oxygen atoms added to the neighboring 6/6 bonds. We have also considered the geometry with the six added oxygen atoms far away from each other. The full geometry optimization for the above C\textsubscript{78}O\textsubscript{6} isomers without any symmetry restriction has been performed using the AM1 method \cite{13} in Gaussian 03 Program \cite{14}. Then all of the isomers are further optimized using DFT at B3LYP/STO-3G, B3LYP/3-21G and B3LYP/6-31G levels, step by step, in order to utilize the least computation time. These methods are often used to study the energies and structures of the supramolecular complexes \cite{15,16}, fluorescent materials \cite{17} and other organic compounds \cite{18,19}. Then the equilibrium geometries with minima of energy on the potential curve of C\textsubscript{78}O\textsubscript{6} isomers are obtained.

According to Koopmans’ theory, vertical ionization potential (IP) is approximately defined as the negative value of HOMO (the highest occupied molecular orbits) energy, whereas vertical electron affinity (EA) is basically equal to the negative value of LUMO (the lowest unoccupied molecular orbits) energy. Absolute hardness (\eta) is considered to be equal to the half of the difference between IP and EA. The absolute electron negativity (\chi) is defined as the half of the sum for IP and EA. All these values have been calculated at B3LYP/6-31G level. The INDO/CIS model \cite{20} without any adjustment of parameters \cite{21-26} has been utilized to investigate the configuration interaction on the basis of the B3LYP/6-31G optimized geometries of C\textsubscript{78}O\textsubscript{6}. One hundred and ninety-seven configurations including the ground state have been generated by exciting electrons from the 14 HOMO into the 14 LUMO. The IR and \textsuperscript{13}C NMR spectra of some stable isomers of C\textsubscript{78}O\textsubscript{6} have been calculated using the AM1 method and the GIAO method at B3LYP/6-31G level, respectively.

### Results and Discussion

#### Stabilities of geometries

The relative energies of C\textsubscript{78}O\textsubscript{6} isomers are presented in Table 1. The most stable geometry is found to be C\textsubscript{78}O\textsubscript{6} (A) of C\textsubscript{1} symmetry (Fig. 1). The sixth oxygen atom O (84) is added to the C(75)-(C(76) bond based on the most stable geometry of C\textsubscript{78}O\textsubscript{5} (A) \cite{11}. The C(75)-(C(76) bond is near the C(73)-(C(78) bond already activated by the oxygen atom. Then the C(75)-(C(76) bond is also activated and weak, thus leading to the formation of the most stable geometry of C\textsubscript{78}O\textsubscript{6} (A). The newly added oxygen atom is ready to be inserted in the sites nearer to the other oxygen atoms, according to the work reported earlier \cite{27}, which supports the above results. This is the reason why C\textsubscript{78}O\textsubscript{6}(E) is less stable than C\textsubscript{78}O\textsubscript{6} (A). The C(62)-C(63) bond is separated from the C(73)-(C(78) bond by several bonds. Similarly, the stability of C\textsubscript{78}O\textsubscript{5} (F) is lower than that of C\textsubscript{78}O\textsubscript{5} (D), because the C(4)-(C(19) bond in C\textsubscript{78}O\textsubscript{5} (F) is far away from the hexagon added by the three oxygen atoms. There is a pentagon between the C(1)-(C(10) bond in C\textsubscript{78}O\textsubscript{5} (D) and the hexagon added by the three oxygen atoms. C\textsubscript{78}O\textsubscript{6} (D), therefore, possesses higher energy than C\textsubscript{78}O\textsubscript{6} (A).

<table>
<thead>
<tr>
<th>Geometries</th>
<th>Energies (eV)</th>
<th>Geometries</th>
<th>Energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28,29,30,31,52,53,70,71,73,78,75,76-C\textsubscript{78}O\textsubscript{6} (A)</td>
<td>0</td>
<td>1,6,4,5,25,48,34,35,36,37,46-C\textsubscript{78}O\textsubscript{6} (H)</td>
<td>1.12</td>
</tr>
<tr>
<td>1,2,3,4,5,6,69,70,71,72,73,78-C\textsubscript{78}O\textsubscript{6} (B)</td>
<td>0.11</td>
<td>2,3,5,6,14,15,23,24,35,36,47,48-C\textsubscript{78}O\textsubscript{6} (I)</td>
<td>1.38</td>
</tr>
<tr>
<td>41,42,52,63,62,63,70,71,73,78,75,76-C\textsubscript{78}O\textsubscript{6} (C)</td>
<td>0.60</td>
<td>1,10,4,19,41,42,52,63,73,78-C\textsubscript{78}O\textsubscript{6} (J)</td>
<td>1.84</td>
</tr>
<tr>
<td>1,10,28,29,30,31,52,53,70,71,73,78-C\textsubscript{78}O\textsubscript{6} (D)</td>
<td>0.65</td>
<td>28,29,30,31,40,41,42,43,73,78,76-C\textsubscript{78}O\textsubscript{6} (K)</td>
<td>2.01</td>
</tr>
<tr>
<td>28,29,30,31,52,53,62,63,70,71,73,78-C\textsubscript{78}O\textsubscript{6} (E)</td>
<td>0.71</td>
<td>4,19,28,29,35,36,42,43,47,48,73,78-C\textsubscript{78}O\textsubscript{6} (L)</td>
<td>2.03</td>
</tr>
<tr>
<td>4,19,28,29,30,31,52,53,70,71,73,78-C\textsubscript{78}O\textsubscript{6} (F)</td>
<td>0.86</td>
<td>5,6,28,29,35,36,42,43,47,48,73,78-C\textsubscript{78}O\textsubscript{6} (M)</td>
<td>2.40</td>
</tr>
<tr>
<td>28,29,30,31,40,41,42,43,52,53,62,63-C\textsubscript{78}O\textsubscript{6} (G)</td>
<td>0.91</td>
<td>14,15,24,25,34,35,36,37,23,46,47,48-C\textsubscript{78}O\textsubscript{6} (N)</td>
<td>3.12</td>
</tr>
</tbody>
</table>
The bond lengths of C(75)-C(76) in C$_{78}$O$_6$ (A) and C(1)-C(10) in C$_{78}$O$_5$ (D) are changed from 0.1478 and 0.1432 nm to 0.2270 and 0.2287 nm, respectively. These two bonds are considered to be broken to form annulene-like structures. Although the bond lengths of C(62)-C(63) in C$_{78}$O$_5$ (E) and C(4)-C(19) in C$_{78}$O$_5$ (F) are changed from 0.1381 and 0.1424 nm to 0.1524 and 0.1618 nm, respectively, these two bonds are not broken since the original bonds are too short. Thus, the epoxy structures are formed on these two added bonds. The lengths of the bonds C(62)-C(63), C(41)-C(42), C(4)-C(19) and C(1)-C(10) in C$_{78}$O$_6$ (A) are 0.1381, 0.1445, 0.1424 and 0.1432 nm, respectively. Since C(41)-C(42) is the longest bond, the most probable geometry of C$_{78}$O$_7$ is assumed to be C$_{78}$O$_7$ (A) with an extra oxygen atom adding to C(41)-C(42) bond based on C$_{78}$O$_6$ (A).

Besides the isomer with the six oxygen atoms like C$_{78}$O$_6$ (A), there are less stable isomers such as C$_{78}$O$_6$ (B), C$_{78}$O$_6$ (G) and C$_{78}$O$_6$ (N) with two hexagons, each binding three oxygen atoms. When both the two hexagons added by oxygen atoms are located on the opposite positions near the shortest axis in C$_{78}$O$_6$, the isomer is stable. Thus, C$_{78}$O$_6$ (B) is more stable than C$_{78}$O$_6$ (G) and C$_{78}$O$_6$ (N). One reason is that the C(73)-C(78) bond in C$_{78}$O$_6$ (B) is the most possible addition site intersected by the shortest axis in C$_{78}$O (ref. 22). The study also shows that one of the three added bonds in the triaduct of C$_{2v}$-C$_{78}$ must be located at the C(73)-(78) bond$. The other reason is that the activation effect of the epoxy functional groups is easily passed along the shortest axis in C$_{78}$O$_5$. Since C(41)-C(42) is the longest bond, the isomer like C$_{78}$O$_7$ (A) becomes less stable. The three additive sites 23, 35, 36-, and 47, 48- are all less possible sites in C$_{78}$O (ref. 22). When the distance between every two oxygen atoms is increased, the stabilities of the isomers are decreased, for example, C$_{78}$O$_6$ (J), C$_{78}$O$_6$ (L) and C$_{78}$O$_6$ (M).

**Electronic structures at the ground state**

The LUMO-HOMO energy gap of C$_{2v}$-C$_{78}$ is 2.05 eV (ref. 11), which is consistent with 2.02 eV calculated at B3LYP/6-31G* level$. The energies of HOMO and LUMO of C$_{78}$O$_6$ (A) are --6.2304 and --3.7981 eV, respectively (Table 2). The energy gap of C$_{78}$O$_6$ (A) is 2.4322 eV, which is wider than that of C$_{2v}$-C$_{78}$. The energy gaps for the other stable isomers, C$_{78}$O$_6$ (C), C$_{78}$O$_6$ (D), C$_{78}$O$_6$ (E) and C$_{78}$O$_6$ (F) are 2.6123, 2.4754, 2.6088 and 2.5135 eV, respectively. These energy gaps are larger than that of C$_{2v}$-C$_{78}$, which is identical to that reported by Boudon et al.$^{10}$, that the cyclopropane-like derivative has the greater electrochemical band gap (1.78 eV) than that of C$_{2v}$-C$_{78}$. The energy gaps of the less stable isomers, C$_{78}$O$_6$ (I), C$_{78}$O$_6$ (J) and C$_{78}$O$_6$ (N), are around 2.0 eV. It is noted that C$_{78}$O$_6$ (B) and C$_{78}$O$_6$ (K) have narrow energy gaps (1.9010 and 1.9339 eV) because of their elevated HOMO energies and lowered LUMO energies.

The IP and $\chi$ data of C$_{78}$O$_6$ (A)-(N) are higher than those of C$_{2v}$-C$_{78}$ (5.8412 and 4.8243 eV), leading to difficulty in losing electrons. C$_{78}$O$_6$ (B) and C$_{78}$O$_6$ (K) possess lower IP and large EA values in contrast to the other isomers, and are thus reactive. Some of the C$_{78}$O$_6$ isomers, except C$_{78}$O$_6$ (C)-(F), display higher EA values than C$_{78}$ (3.7873 eV), and thus C$_{78}$O$_6$ competes more favorably for electrons than C$_{78}$. This is due to the presence of the oxygen atoms in C$_{78}$O$_6$. The $\eta$ values of C$_{78}$O$_6$ (A)-(H), except C$_{78}$O$_6$ (B), are
larger than that of C_{78} (1.0270 eV), resulting in higher thermal stabilities. The less stable isomers C_{78}O_{6} (K) and C_{78}O_{6} (N) have lower \( \eta \) values. This is according to the principle of maximum hardness\(^{29} \).

The Mulliken charges of O(79)-O(84) in C_{78}O_{6} (A) are -0.356, -0.356, -0.356, -0.357, -0.479 and -0.487. The electrons are attracted from C_{2v}-C_{78} to oxygen atoms. Thus the carbon atoms adjacent to these oxygen atoms carry positive charges. This leads to the formation of polar covalent C-O bonds. The oxygen atoms with negative charges become reactive centers, which can form hydrogen bonds or react with electrophilic reagents.

### Electronic absorption spectra

The strongest absorption peak in the electronic spectrum of C_{2v}-C_{78} is observed at 225.7 nm (ref. 22). Some absorptions beyond 440 nm appear at 449.7, 483.9, 568.9 and 624.9 nm, which are compatible with the experimental results at 440, 490, 545 and 640 nm. The main absorptions at 422.2, 447.3, 461.6 and 518.8 nm of C_{78}O_{6} (A), produced by the \( \pi \rightarrow \pi^* \) electronic transition, are blue-shifted to 454.4, 481.2, 527.5 and 568.9 nm in C_{2v}-C_{78}. The peaks between 200–300 nm of C_{78}O_{6} (A) are denser than those of C_{2v}-C_{78}. When more oxygen atoms are added, the molecular symmetry is reduced, and the absorptions are split. The main peaks in the electronic spectrum of C_{78}O_{6} (C) are situated at 404.5, 439.6, 454.5 and 533.6 nm, blue-shifted relative to the corresponding bands of C_{2v}-C_{78}. The main peaks at 432.4, 453.0 and 529.6 nm of C_{78}O_{6} (D) are blue-shifted relative to 454.4, 481.2 and 568.9 nm of C_{78}, and the two peaks at 466.8 and 501.1 nm of C_{78}O_{6} (D) are formed by the splitting of the peak at 527.5 nm of C_{2v}-C_{78}. There are several other bands with maxima at 430.1, 450.9 and 514.5 nm in C_{78}O_{6} (E) as well as at 418.7, 477.7 and 510.9 nm in C_{78}O_{6} (F). In fact, the main absorptions for C_{78}O_{6} (A), and (C)-(F) are blue-shifted in comparison with those of C_{2v}-C_{78}. From the analysis of the bond lengths near the added sites in C_{78}O_{6} (A), many bonds are intensified, and thus the conjugation effect in the system is strengthened.

The main peaks beyond 420 nm in the electronic spectra appear at 431.1, 487.7, 556.0, 621.0 nm for C_{78}O_{6} (B) and at 439.5, 461.7, 527.5, 576.1 nm for C_{78}O_{6} (G); red-shifted as compared to 422.2, 447.3, 461.6 and 518.8 nm of C_{78}O_{6} (A). This is due to the lower LUMO-HOMO energy gap of C_{78}O_{6} (B) and (G). In view of the valence electrons of the INDO method, HOMO (174) of C_{78}O_{6} (B) is mainly composed of \( P_x \) orbitals of C(51) and C(54), and the contribution coefficients are 0.2078 and 0.2077, respectively. LUMO (175) of C_{78}O_{6} (B) basically comprises \( P_x \) orbitals of C(53) and C(54), and the coefficients are -0.2007 and -0.2130. These carbon atoms are close to the C(69)-C(70) and C(71)-C(72) bonds (see Fig. 1). The addition of oxygen atoms on these two bonds has a large influence on the HOMO and LUMO energies of C_{78}O_{6} (B). The absorptions between 424 and 432 nm are attributed to the closed epoxide structures\(^{5} \), which appear at 422.2 nm in C_{78}O_{6} (A) and 431.1 nm in C_{78}O_{6} (B).

### 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

**Table 2 — Some parameters (eV) of C_{78}O_{6} isomers optimized at B3LYP/6-31G level**

<table>
<thead>
<tr>
<th>Isomers</th>
<th>( E_{\text{HOMO}} )</th>
<th>( E_{\text{LUMO}} )</th>
<th>Energy gap (eV)</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>( \eta )</th>
<th>( \chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{78}O_{6} (A)</td>
<td>-6.2304</td>
<td>-3.7981</td>
<td>2.4322</td>
<td>6.2304</td>
<td>3.7981</td>
<td>1.2161</td>
<td>5.0143</td>
</tr>
<tr>
<td>C_{78}O_{6} (B)</td>
<td>-5.9289</td>
<td>-4.0279</td>
<td>1.9010</td>
<td>5.9289</td>
<td>4.0279</td>
<td>0.9505</td>
<td>4.9784</td>
</tr>
<tr>
<td>C_{78}O_{6} (C)</td>
<td>-6.2491</td>
<td>-3.6368</td>
<td>2.6123</td>
<td>6.2491</td>
<td>3.6368</td>
<td>1.3602</td>
<td>4.9430</td>
</tr>
<tr>
<td>C_{78}O_{6} (D)</td>
<td>-6.2426</td>
<td>-3.7672</td>
<td>2.4754</td>
<td>6.2426</td>
<td>3.7672</td>
<td>1.2377</td>
<td>5.0049</td>
</tr>
<tr>
<td>C_{78}O_{6} (E)</td>
<td>-6.2192</td>
<td>-3.6104</td>
<td>2.6088</td>
<td>6.2192</td>
<td>3.6104</td>
<td>1.3044</td>
<td>4.9148</td>
</tr>
<tr>
<td>C_{78}O_{6} (F)</td>
<td>-6.2764</td>
<td>-3.7628</td>
<td>2.5135</td>
<td>6.2764</td>
<td>3.7628</td>
<td>1.2568</td>
<td>5.0196</td>
</tr>
<tr>
<td>C_{78}O_{6} (G)</td>
<td>-6.1558</td>
<td>-3.9699</td>
<td>2.1859</td>
<td>6.1558</td>
<td>3.9699</td>
<td>0.9390</td>
<td>5.0629</td>
</tr>
<tr>
<td>C_{78}O_{6} (H)</td>
<td>-6.2940</td>
<td>-4.1264</td>
<td>2.1677</td>
<td>6.2940</td>
<td>4.1264</td>
<td>1.0838</td>
<td>5.2102</td>
</tr>
<tr>
<td>C_{78}O_{6} (I)</td>
<td>-6.2168</td>
<td>-4.1835</td>
<td>2.0333</td>
<td>6.2168</td>
<td>4.1835</td>
<td>1.0166</td>
<td>5.2001</td>
</tr>
<tr>
<td>C_{78}O_{6} (J)</td>
<td>-6.0810</td>
<td>-4.0771</td>
<td>2.0039</td>
<td>6.0810</td>
<td>4.0771</td>
<td>1.0019</td>
<td>5.0790</td>
</tr>
<tr>
<td>C_{78}O_{6} (K)</td>
<td>-5.9596</td>
<td>-4.0257</td>
<td>1.9339</td>
<td>5.9596</td>
<td>4.0257</td>
<td>0.9670</td>
<td>4.9926</td>
</tr>
<tr>
<td>C_{78}O_{6} (L)</td>
<td>-6.1754</td>
<td>-3.8872</td>
<td>2.2882</td>
<td>6.1754</td>
<td>3.8872</td>
<td>1.1441</td>
<td>5.0313</td>
</tr>
<tr>
<td>C_{78}O_{6} (M)</td>
<td>-6.1376</td>
<td>-3.8649</td>
<td>2.2727</td>
<td>6.1376</td>
<td>3.8649</td>
<td>1.1364</td>
<td>5.0012</td>
</tr>
<tr>
<td>C_{78}O_{6} (N)</td>
<td>-6.2998</td>
<td>-4.2526</td>
<td>2.0471</td>
<td>6.2998</td>
<td>4.2526</td>
<td>1.0236</td>
<td>5.2762</td>
</tr>
</tbody>
</table>
The main absorptions at 1579.2 and 1856.5 cm\(^{-1}\) of \(\text{C}_7\text{O}_6\) (A) are red-shifted due to decrease in symmetry and the change in interior features. The three oxygen atoms in \(\text{C}_7\text{O}_6\) (B) attract electrons towards the direction opposite to that of the other three oxygen atoms (see Fig. 1), leading to the weakening of some of the C=C bonds. Differences of the IR spectra between \(\text{C}_7\text{O}_6\) (A) and \(\text{C}_7\text{O}_6\) (B) are concentrated at 900–1100 cm\(^{-1}\) (where no obvious absorptions emerge in \(\text{C}_{2\gamma}\text{C}_{78}\)) and 1800 cm\(^{-1}\) (C=C stretching vibration on benzene rings), 1400–1600 cm\(^{-1}\) (C=C stretching vibration on alkenes), and 1800 cm\(^{-1}\) (possibly arisen from the coupling of the C=C double bonds with similar frequencies). The main IR absorptions of \(\text{C}_7\text{O}_6\) (A) and (B) are generally blue-shifted as compared with those of \(\text{C}_{2\gamma}\text{C}_{78}\).

The IR spectra of \(\text{C}_7\text{O}_6\) (D) and (E) are similar to that of \(\text{C}_7\text{O}_6\) (A) because they all contain the basic geometry of \(\text{C}_7\text{O}_6\) (A)\(^{11}\). The absorptions of the other isomers are blue-shifted relative to those of \(\text{C}_7\text{O}_6\) (A). Comparing the main absorptions of \(\text{C}_7\text{O}_6\) (A), (D) and (E) with two broken bonds with those of \(\text{C}_7\text{O}_6\) (B) and (C) with three broken bonds, we can deduce that larger number of broken C=C bonds leads to the red-shift of the IR absorptions, and the IR spectra of the isomers with the same number of broken C=C bonds look alike. The formation of annulene-like structures stimulates the flow of the electrons from \(\text{C}_{78}\) to the oxygen atoms and the relaxation of the nearby C=C bonds.

According to a previous study\(^{11}\), the IR absorptions within 900–1100 cm\(^{-1}\) (where no obvious absorptions emerge in \(\text{C}_{2\gamma}\text{C}_{78}\)) are assigned to the stretching vibrations of the C-O bonds such as the main bands at 932.8 cm\(^{-1}\) in \(\text{C}_7\text{O}_6\) (A), 1003.4 cm\(^{-1}\) in \(\text{C}_7\text{O}_6\) (B), 926.7 cm\(^{-1}\) in \(\text{C}_7\text{O}_6\) (C), 961.4 cm\(^{-1}\) in \(\text{C}_7\text{O}_6\) (D), and 955.3 cm\(^{-1}\) in \(\text{C}_7\text{O}_6\) (E).

**NMR spectra**

The \(^{13}\text{C}\) chemical shifts in the range 150.3–173.9 ppm of \(\text{C}_{2\gamma}\text{C}_{78}\) should be multiplied by a factor of 0.88 in view of the systematic deviation of the B3LYP/6-31G method caused by the small theoretical shielding effect\(^{11}\), in contrast to the experimental results 132–148 ppm (ref. 30). The carbon atoms with the chemical shifts near 180 ppm in \(\text{C}_7\text{O}_6\) (A) are ascribed to the \(sp^2\)-C atoms connected with the oxygen atoms. The shield effects on these carbon atoms are decreased and the chemical shifts shift downfield due to the electron-withdrawing influence of the oxygen atoms. The eight peaks produced by \(sp^3\)-C atoms in the epoxy structures are located at 60.5–71.4 ppm, which is compatible with the experimental result, 58.2 ppm (ref. 9). The four peaks due to the carbon atoms in the annulene-type structures are situated at 97.1, 97.1, 111.7 and 111.8 ppm, which is in agreement with the

---

**Fig. 1** — The B3LYP/6-31G optimized geometries of: (a) \(\text{C}_7\text{O}_6\) (A) and (b) \(\text{C}_7\text{O}_6\) (B).
experimental result 118.7 ppm (ref. 31).

From C$_{2v}$-C$_{78}$ to C$_{78}$O$_6$ (A) and (B), the absorptions in the NMR spectra are split progressively due to the decrease in symmetry. The $^{13}$C chemical shifts in C$_{78}$O$_6$ (B) vary within the ranges 59.2–70.6 ppm ($sp^3$-C atoms in epoxy structures), 98.9–116.9 ppm (annulene-type carbon atoms), and 127.1–181.5 ppm ($sp^2$-C atoms). Due to the oxygen atoms, the neighboring carbon atoms are activated and tend to move downfield. This can also be seen in the NMR spectra of C$_{78}$O$_6$ (C)–(E). There are four carbon atoms of the annulene-like structures of C$_{78}$O$_6$ (C), (D), and (E), respectively, which is the same to that of C$_{78}$O$_6$ (A). On the other hand, C$_{78}$O$_6$ (B) includes six carbon atoms of the annulene-like structures. From the number of the peaks within 97–117 ppm, we can know the number of bonds that are being broken.

In the above study, the most stable isomer of C$_{78}$O$_6$ at the ground state is predicted to be 28, 29, 30, 31, 52, 53, 70, 71, 73, 78, 75, 76-C$_{78}$O$_6$ (A) of two annulene-like and four epoxy structures. The addition of the oxygen atoms activates the bonds nearby, and these bonds become the possible sites for addition of the next oxygen atom. The 6/6 bonds near the C(73)-C(78) bond are more active than the other bonds, according to the predicted stable isomers, since C(73)-C(78), intersected by the shortest axis in C$_{2v}$-C$_{78}$, is the most stable addition site when only one oxygen atom is added. Relative to those of C$_{2v}$-C$_{78}$, the main absorptions in the electronic and IR spectra for most of the stable isomers of C$_{78}$O$_6$ are blue-shifted due to the wide energy gaps and the intensification of the C=C bonds upon the addition of the oxygen atoms, while the $^{13}$C chemical shifts of the carbon atoms on the epoxy and annulene-type structures in C$_{78}$O$_6$ move upfield.

References