TABLE I Optimized energies[a] and LUMO-HOMO energy gaps of $C_{78}O$ isomers

Isomers	Energy/eV	L-H gap/eV	Isomers	Energy/eV	L-H gap/eV	Isomers	Energy/eV	L-H gap/eV
73,78-$C_{78}O$	0	5.0276	49,68-$C_{78}O$	0.9379	4.7408	7,24-$C_{78}O$	1.4353	4.5168
6,7-$C_{78}O$	0.2119	4.8137	29,30-$C_{78}O$	1.1913	4.6946	9,10-$C_{78}O$	1.4716	4.4755
26,27-$C_{78}O$	0.2700	4.7490	47,48-$C_{78}O$	1.2084	4.6222	25,26-$C_{78}O$	1.5803	4.1696
52,53-$C_{78}O$	0.3113	4.8725	9,29-$C_{78}O$	1.2115	4.5210	51,52-$C_{78}O$	1.6561	3.9772
1,10-$C_{78}O$	0.3944	4.8032	24,25-$C_{78}O$	1.2251	4.6711	7,8-$C_{78}O$	1.7150	4.4379
28,29-$C_{78}O$	0.5181	4.6739	28,52-$C_{78}O$	1.2377	4.5096	69,78-$C_{78}O$	1.7174	3.8972
25,48-$C_{78}O$	0.7180	4.8159	49,50-$C_{78}O$	1.2475	4.7411	70,71-$C_{78}O$	1.8313	4.6437
23,24-$C_{78}O$	0.7242	4.6834	69.70-$C_{78}O$	1.2962	4.5585	48,49-$C_{78}O$	2.0318	4.4959
8,9-$C_{78}O$	0.8350	4.7232	27,28-$C_{78}O$	1.3034	4.7294	5,6-$C_{78}O$	2.2197	4.5030
68,69-$C_{78}O$	0.9024	4.9367	1,6-$C_{78}O$	1.3191	4.6556	67,68-$C_{78}O$	2.3009	3.5677
51,70-$C_{78}O$	0.9026	4.7768	8,26-$C_{78}O$	1.3226	4.6069			
50,51-$C_{78}O$	0.9308	4.7642	27,50-$C_{78}O$	1.4190	4.1497			

[a] The optimized energy is the relative energy of an isomer to the energy of 73,78-$C_{78}O$.

(Table I) by taking that of 73,78-$C_{78}O$ as the reference. The most stable isomer was found to be 73,78-$C_{78}O$ with group C_{2v}. 73,78-$C_{78}O$ can be synthesized and isolated because of its lower energy and wider HOMO-LUMO energy gap. The added 73,78-bond (6−6 bond) is located between the two hexagons and is intersected by the shortest C_2 axis of C_{78} with group C_{2v}. The second stable isomer is 6,7-$C_{78}O$ with group C_1. It is less stable by 0.2119 eV than 73,78-$C_{78}O$. The oxygen bridge bond is also a 6−6 bond situated near the shortest C_2 axis of C_{78} with group C_{2v}. There are little differences between energies of 52,53-$C_{78}O$, 1,10-$C_{78}O$, 6,7-$C_{78}O$ and 26,27-$C_{78}O$. In the former nine stable isomers, all of the added bonds are 6−6 bonds, whereas in the unstable isomers all of the inserted bonds are 6−5 bonds. Therefore the 6−6 isomers were more stable than the 6−5 isomers for $C_{78}O$, which was in agreement with the previous calculations [5,6]. These 6−6 bonds have at least one apex connected with a pentagon, and they display more characters of double bonds than the others. Thus these types of 6−6 bonds are easy to be inserted by oxygen.

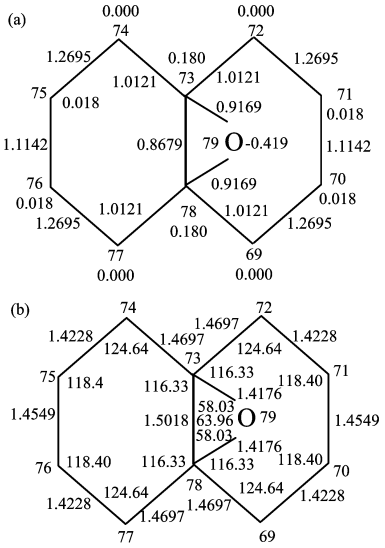

FIG. 2 Some optimized structure of 73,78-$C_{78}O$. (a) Bond orders and Mulliken charges; (b) Bond lengths (Å) and angles (°).

B. Optimized structures of $C_{78}O$ isomers

In 73,78-$C_{78}O$, the bond length and the bond order of the C−C bond added by oxygen are 1.5018 Å and 0.8679 (Fig.2), respectively. This C−C bond with an epoxide structure is formed, which is similar to that of $C_{78}C(COOEt)_2$ [6]. In 6,7-$C_{78}O$, the C(6)−C(7) bond with the bond length of 1.5318 Å is not broken and an epoxide structure is produced. In the other isomers, the lengths of the C−C bonds inserted by oxygen range from 1.4933 to 1.6175 Å . The epoxide structures are also generated in both 6−6 bonds and 6−5 bonds. In 73,78-$C_{78}O$, the Mulliken charge of the oxygen atom was −0.419 (Fig.2), and all of the charges of the two adjacent carbon atoms were 0.180. This leads to the formation of the polar covalent bonds. The oxygen atom with the negative charge will become a center of reactions, which can form a hydrogen bond or react with electrophilic reagents.

C. Electronic structures at the ground state

73,78-$C_{78}O$ is a stable closed-shell molecule. The energies of HOMO $b_2(159)$ and LUMO $a_1(160)$ are

TABLE II Electronic spectra of the stable isomers for $C_{78}O$

λ/nm	f	Transition	λ/nm	f	Transition
		73,78-$C_{78}O$			6,7-$C_{78}O$
562.4	0.0142	b_2 (159)→a_1 (160), −0.7844	590.6	0.0248	(158)→(160), −0.7999
543.4	0.0039	b_2 (159)→b_2 (162), −0.9412	562.2	0.0222	(157)→(160), −0.8522
518.6	0.0255	b_1 (158)→b_1 (161), −0.7810	531.9	0.0015	(159)→(161), −0.6682
505.9	0.0035	b_1 (158)→b_2 (162), 0.5972	520.8	0.0129	(156)→(160), −0.5207
471.1	0.0068	b_1 (156)→b_2 (162), 0.7448	514.2	0.0209	(159)→(161), −0.5749
467.2	0.0037	b_1 (156)→b_1 (161), 0.8193	503.3	0.0037	(158)→(162), 0.7581
		26,27-$C_{78}O$			52,53-$C_{78}O$
657.1	0.0056	(158)→(160), 0.7715	585.5	0.0091	a′(159)→a′(161), 0.5672
613.1	0.0072	(159)→(160), −0.7531	574.1	0.0204	a′(159)→a′(160), −0.9141
540.9	0.0193	(157)→(160), −0.8542	560.1	0.0016	a′(159)→a′(162), −0.7935
517.4	0.0060	(158)→(161), −0.6498	538.0	0.0104	a′(159)→a′(161), −0.5661
510.0	0.0049	(156)→(162), −0.6181	528.9	0.0100	a″(158)→a′(160), 0.6132
502.5	0.0157	(159)→(162), −0.6998	507.7	0.0068	a″(158)→a′(161), −0.5586

More long wave absorption peaks were chosen where oscillation strength was bigger than 0.0010.

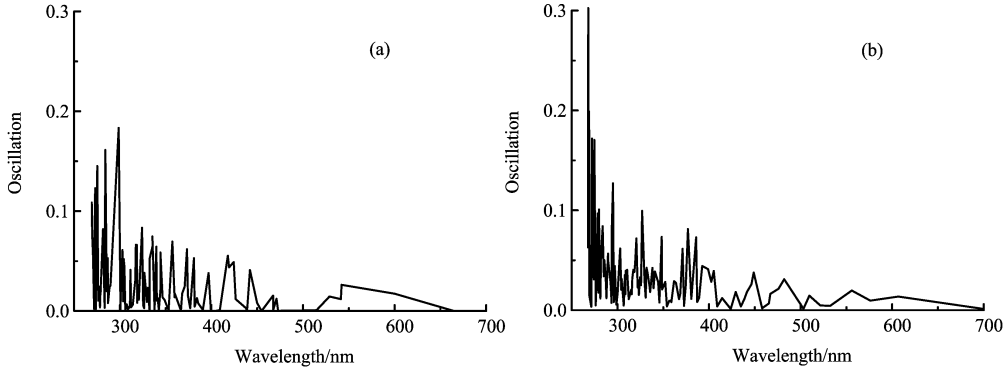

FIG. 3 The electronic spectra of 1,10-$C_{78}O$(a) and 28,29-$C_{78}O$(b).

−6.3626 and −1.3350 eV, respectively. Its HOMO-LUMO energy gap is 5.0276 eV. The HOMO energies of 6,7-$C_{78}O$, 26,27-$C_{78}O$ and 52,53-$C_{78}O$ are −6.4056, −6.3142 and −6.3169 eV, respectively. And their LUMO energies are −1.5919, −1.5652 and −1.4444 eV, respectively. Their HOMO-LUMO energy gaps are 4.8137, 4.7490 and 4.8725 eV, respectively. These energy gaps are larger than that of C_{2v}-C_{78} (4.4434 eV [12]), which leads to the blue-shift of their electronic absorption spectra.

D. Electronic spectroscopy

The main absorption peaks in the electronic spectrum of C_{78} with group C_{2v} are consistent with the experimental results [5]. The first peak of 73,78-$C_{78}O$ appears at 562.4 nm, (Table II) which was arisen from the $\pi\rightarrow\pi^*$ electronic transition of HOMO b_2(159)→LUMO a_1(160). The coefficients of 2s, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals of the oxygen atom in molecular orbitals (2), (126), (63) and (79) are −0.3273, 0.6109, −0.3739 and 0.3119, respectively. These coefficients are the biggest among all the orbital coefficients. It indicates that the atomic orbitals of O play an important role in lowering the HOMO energy of 73,78-$C_{78}O$. The first peak of 6,7-$C_{78}O$ is located at 590.6 nm, which was generated by the electronic transition of (158)→(160). The first absorptions of 73,78-$C_{78}O$ and 6,7-$C_{78}O$ are blue-shifted, relative to that of C_{2v}-C_{78} , because of their bigger energy gaps. The first absorption of 26,27-$C_{78}O$ was computed to be at 657.1 nm, which was attributed to the electronic transition of (158)→(160). The largest coefficients of 2s, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals of the oxygen atom in MO (5), (86), (199) and (124) are −0.3081, 0.2869, 0.3615 and −0.5290, respectively. The

TABLE III Wavelengths and oscillation strength in electronic spectra of $C_{78}O$

λ/nm	f	λ/nm	f	λ/nm	f	λ/nm	f	λ/nm	f
25,48-$C_{78}O$		23,24-$C_{78}O$		8,9-$C_{78}O$		68,69-$C_{78}O$		51,70-$C_{78}O$	
659.0	0.0026	707.1	0.0056	674.2	0.0028	600.3	0.0129	636.0	0.0114
596.8	0.0094	621.0	0.0128	595.6	0.0287	564.8	0.0130	612.1	0.0070
586.2	0.0071	580.2	0.0195	558.0	0.0151	548.8	0.0030	564.5	0.0117
50,51-$C_{78}O$		49,68-$C_{78}O$		29,30-$C_{78}O$		47,48-$C_{78}O$		9,29-$C_{78}O$	
630.5	0.0080	657.2	0.0357	695.0	0.0073	692.4	0.0173	755.4	0.0063
602.3	0.0244	633.9	0.0109	607.4	0.0214	642.9	0.0256	630.2	0.0049
561.0	0.0157	576.5	0.0100	604.1	0.0219	616.5	0.0125	583.3	0.0052
24,25-$C_{78}O$		28,52-$C_{78}O$		49,50-$C_{78}O$		69,70-$C_{78}O$		27,28-$C_{78}O$	
662.5	0.0095	768.1	0.0163	712.2	0.0037	747.5	0.0154	698.9	0.0174
638.8	0.0195	624.3	0.0059	620.3	0.0122	617.2	0.0175	654.1	0.0101
705.0	0.0078	592.3	0.0022	560.0	0.0226	604.3	0.0317	594.8	0.0445
1,6-$C_{78}O$		8,26-$C_{78}O$		27,50-$C_{78}O$		7,24-$C_{78}O$		9,10-$C_{78}O$	
694.9	0.0075	733.9	0.0274	912.5	0.0422	721.7	0.0223	730.6	0.0185
657.6	0.0200	679.9	0.0034	729.0	0.0044	674.6	0.0151	662.4	0.0025
623.6	0.0112	624.9	0.0035	651.4	0.0150	641.3	0.0016	608.3	0.0022
25,26-$C_{78}O$		51,52-$C_{78}O$		7,8-$C_{78}O$		69,78-$C_{78}O$		70,71-$C_{78}O$	
864.8	0.0809	1053.8	0.0428	762.1	0.0109	999.6	0.0728	642.0	0.0236
698.8	0.0190	707.3	0.0170	666.4	0.0025	836.2	0.0016	611.3	0.0281
659.9	0.0015	668.2	0.0123	567.3	0.0378	698.5	0.0121	564.0	0.0059

HOMO energy is lessened and the LUMO energy lifted due to the oxygen atom.

The first UV peaks of 1,10-$C_{78}O$ and 28,29-$C_{78}O$ appear at 542.1 and 606.8 nm (Fig.3), respectively. In 1,10-$C_{78}O$, a$''$(159) and a$'$(160) were mainly constituted by p_y of C(72) and p_x of C(18) with the coefficients of 0.1767 and 0.1602, respectively. While the coefficients of 2s, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals of the oxygen atom in MO (5), (66), (121) and (78) are −0.3079, −0.3069, −0.4827 and 0.2708, respectively. The O atom changed the HOMO energy of 1,10-$C_{78}O$.

The first UV peaks of the other less stable isomers 27,50-$C_{78}O$, 25,26-$C_{78}O$, 51,52-$C_{78}O$ and 69,78-$C_{78}O$ (Table III) were red-shifted relative to that of C_{78} with group C_{2v}. The first band of 67,68-$C_{78}O$ at 1432.8 nm in the NIR region was not observed experimentally owing to the highest total energy and the least energy gap (Table I).

IV. CONCLUSION

The most stable isomer of $C_{78}O$ was calculated to be 73,78-$C_{78}O$ with an epoxide structure. The 6−6 bonds, with at least one apex connected with a pentagon, are easy to be added by oxygen. The other 6−6 bonds surrounded by four hexagons are uneasy to be added by oxygen. The first absorption in the electronic spectrum of 73,78-$C_{78}O$ is blue-shifted, relative to that of C_{78} with group C_{2v}, owing to the wider energy gap.

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