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Theoretical Study on Electronic Gain-and-loss Properties of TEMPO and Its Derivates in Charge/Discharge Processes

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(Dated: Received on November 30, 2011; Accepted on February 12, 2012)

Theoretical study on the electronic structures and related properties of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its cationic lipid derivates in the charge/discharge processes has been carried out using the density functional theory (DFT) at the (U)B3LYP/6-31G(d,p) or 6-31+G(d,p) level. The changes and regularities of geometric and electronic properties of these compounds in the charge/discharge processes were revealed in detail. The computational results show that the substitute group plays a very important role in the electronic structures and related properties of TEMPOs during the charge/discharge processes. It is very interesting to find that after getting an electron, TEMPO is more stable in singlet state but the lipid is more stable in triplet state. For TEMPO, both the charge and the discharge processes greatly influence the electronic properties of N and O atoms of the radical part. For the cationic lipid, the discharge process mainly influences the pyridinium head and the charge process mainly influences the free radical head. Moreover, the solvent effect plays an important role in some bond lengths and the charge population of the free radical head. In addition, the UV-Vis absorption spectra of TEMPO and the lipid were calculated and simulated using TDDFT at the 6-31G(d,p) or 6-31+G(d,p) level, in satisfying agreement with the experimental ones.

Key words: 2,2,6,6-tetramethyl-1-piperidinyloxy, Charge/discharge process, Electronic structure, Density functional theory calculation

I. INTRODUCTION

2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), the known stable organic radical, has attracted much attention due to its wide applications. TEMPO and its derivates are used as antioxidants [1], light-stabilizers [2], radical reaction controllers [3], spin labeling agents [4], catalysts [5], and so on. Therefore, they are widely researched in medicine, plastic, water treatment, agriculture, biology, and other fields. Recently, a series of new compounds containing TEMPO units have been reported and many academician's interest was greatly attracted because these compounds have very important potential applications in the photo-responsive materials [6], magnetic materials [7], liquid crystal materials [8], energy conversion materials [9], or charge-storage devices.

As well-known, lithium-ion batteries are widely used

as power in portable electronic devices at present, but in future the power may be used in vehicles, which will demand the batteries with better quality and performance. Current cathode materials of lithium-ion batteries are based on cobalt components. They are toxic and unfriendly to surrounding, in particular, so far their recycling problem has not been solved yet. So new active materials based on organic compounds are an attractive alternative and deserve deep investigation. In recent years, some different compounds containing TEMPO units have been reported as potential active cathode materials including poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-N-oxyl) (PTMA) [10], polyacrylamide [11], polyacetylene [12], polynorbornene [13], even some novel compounds binding to cellulose [14], or DNA [15]. Usually their ultraviolet spectra (UV), charging capacity, recharging times, and cyclic voltammetry curves were measured during experiments. When the charge/discharge processes were discussed, the redox process resembling TEMPO (R=H) (Fig.1) was generally cited as reference. However, so far the detailed research and discussion on the substitutive effect on the electronic

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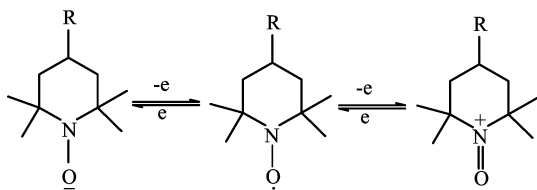


FIG. 1 The charge and discharge process of resembling TEMPO (R=H).

structures and related properties of this kind of compound in the charge/discharge processes has not been found yet. Therefore, it is very significant work to perform the theoretical study on the electronic structures and related properties of TEMPO, and its cationic lipid derivatives in the charge/discharge processes.

In this work, the pyridinium lipid containing TEMPO unit was chosen as a research molecule because it is a very special cation and can incorporate with DNA very easily [15]. The DNA-lipid complex demonstrates interesting reversible multi-stage charge/discharge processes. Here, the theoretical studies on TEMPO and the pyridinium cationic lipid in the charge/discharge processes were carried out. The substance of the charge/discharge processes at a level of molecular electronic structure were revealed. In particular, the substituent effect on the electronic structure and related properties of TEMPO in the charge/discharge processes was deeply discussed. This work will help to understand the substance in the charge/discharge processes at the microcosmic level and further to direct the functional molecular design of this kind of compound.

II. COMPUTATION AND METHOD

The calculated structural schematic diagrams and atoms number are shown in Fig.2. Figure 2(a) is TEMPO molecule marked as TEMPO(I), which is an open-shell system with one lone electron. When TEMPO(I) gets an electron, *i.e.*, after a discharge process, it will become the compound marked as TEMPO(II). This is very interesting that there are two possible states for this compound. One of them is the singlet state further marked as singlet-TEMPO(II) (close-shell system) if the exotic electron pair-match with its lone electron; and the other one is the triplet state further marked as triplet-TEMPO(II) if the exotic electron does not pair-match with its lone electron. Therefore it needs to confirm which state will be the most stable one via the calculations. On the other hand, when TEMPO(I) loses an electron, *i.e.*, after a charge process, it will become the compound marked as TEMPO(III) (close-shell system generally in the singlet state). Figure 2(b) is the cationic lipid molecule marked as lipid(I) (open-shell system). When it gets an electron, lipid(I) will become lipid(II) in singlet state

(close-shell system) further marked as singlet-lipid(II) or become lipid(II) in triplet state (open-shell system) further marked as triplet-lipid(II), according to whether exotic electron pair-match or not. When it loses an electron, lipid(I) will become lipid(III) in singlet state (close-shell system).

Full geometry optimizations of these molecules were carried out using the DFT method, at the B3LYP/6-31G(d,p) level for the close-shell systems and at the UB3LYP/6-31G(d,p) level (unrestricted B3LYP method) for all the open-shell systems. Meanwhile, for TEMPOs, 6-31+G(d,p) was used because diffuse basis set is usually essential for negatively charged systems. In addition, the time-dependent DFT (TDDFT) was used for the calculations of the UV-Vis spectra [16] using the above-mentioned methods and basis sets in order to perform the reasonable discussion. TEMPO(III) (close-shell system) was calculated by both UB3LYP/6-31G(d,p) and B3LYP/6-31G(d,p) method, and the results of two methods were coincident totally, so the close-shell systems were all calculated by the B3LYP method. In addition, considering that the molecules contain acyl radical moieties and BHandHLYP level was appreciated for calculating acyl radical [17], (U)BHandHLYP/6-31G(d,p) calculations were also carried out for comparison.

In this work, the results of the (U)B3LYP method will be discussed in detail, and the results of (U)BHandHLYP method will be only mentioned if necessary. All the optimized stationary points were verified by vibrational frequency analysis and the stabilities of all the wavefunctions were checked. All the calculations were performed by Gaussian03 program-package (revision D.01) [18]. In addition, in order to clearly depict the details of some frontier molecular orbitals, their stereographs were also drawn based on the DFT computational results.

Actually above mentioned compounds are used in solvents, so the calculations in solvents were also carried out by the polarizable conductor calculation model (CPCM), and the results obtained in methanol are discussed in detail.

III. RESULTS AND DISCUSSION

A. Energy and stability

The calculated energies of TEMPOs and the lipids are shown in Table I. From Table I, we can see the following: First, the energies based on B3LYP/6-31G(d,p) method are all respectively lower than those based on BHandHLYP/6-31G(d,p) method, whether zero-point corrections or not, but the trends obtained by these two methods are accordant. Secondly, it is notable that for TEMPOs in vacuum, the trend in energies based on 6-31+G(d,p) is different from that based on 6-31G(d,p), however, they are in agreement with that in methanol,

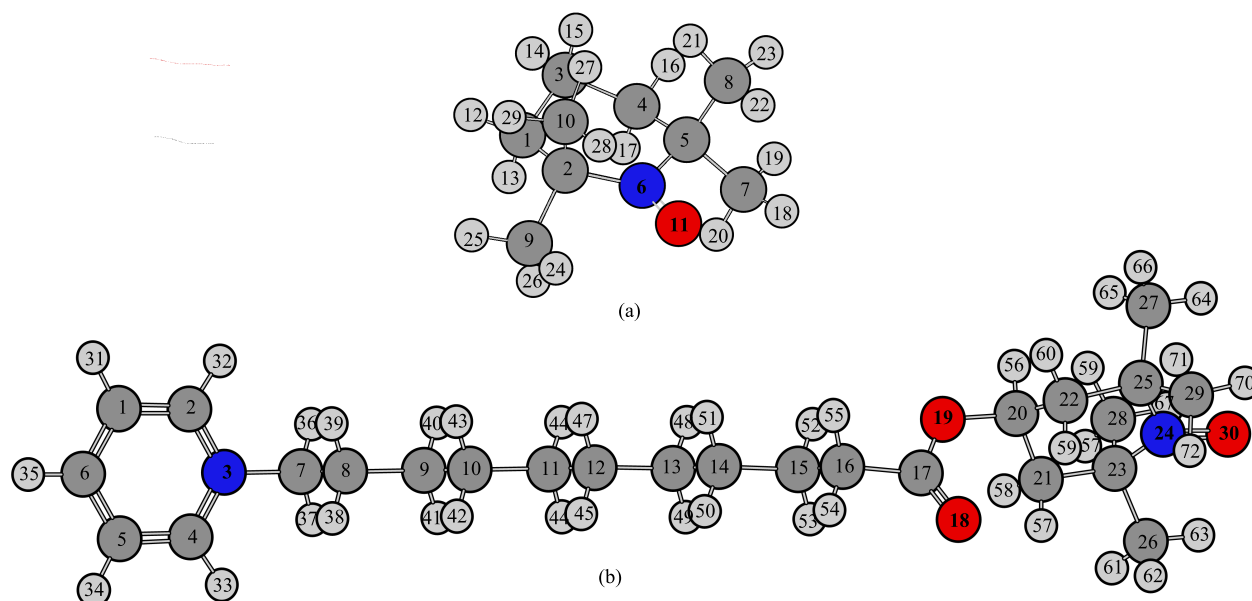


FIG. 2 Structural schematic diagrams of (a) TEMPO and (b) the pyridinium lipid containing TEMPO.

TABLE I Molecular energies (in a.u.) of the TEMPOs and the lipids.

	I		Singlet-II		Triplet-II		III	
	E_{Scf}	$E_{\text{Scf+zpc}}^{\text{a}}$	E_{Scf}	$E_{\text{Scf+zpc}}$	E_{Scf}	$E_{\text{Scf+zpc}}$	E_{Scf}	$E_{\text{Scf+zpc}}$
BHandHLYP ^b	-483.4439	-483.1719	-483.4242	-483.1554	-483.2989	-483.0360	-483.1897	-482.9164
B3LYP ^b	-483.7451	-483.4826	-483.7334	-483.4744	-483.6226	-483.3702	-483.4963	-483.2327
B3LYP ^c	-483.7593	-483.4977	-483.7677	-483.5102	-483.7243	-483.4648	-483.5029	-483.2399
B3LYP ^d	-483.7511	-483.4891	-483.8189	-483.5594	-483.6898	-483.4383	-483.5640	-483.3008
B3LYP ^e	-483.7668	-483.5057	-483.8592	-483.6005	-483.7827	-483.5230	-483.5712	-483.3087
BHandHLYP ^f	-1312.1445	-1311.4756	-1312.2112	-1311.5467	-1312.3111	-1311.6472	-1311.8570	-1311.1871
B3LYP ^f	-1312.9454	-1312.3003	-1313.0636	-1312.4228	-1313.1127	-1312.4719	-1312.6621	-1312.0158
B3LYP ^g	-1313.0347	-1312.3916	-1313.1083	-1312.4679	-1313.1310	-1312.4922	-1312.8408	-1312.1968

^a $E_{\text{Scf+zpc}}$: the energies after zero-point correction.

^b TEMPO in vacuum at 6-31G(d,p).

^c TEMPO in vacuum at 6-31+G(d,p).

^d TEMPO in methanol at 6-31G(d,p).

^e TEMPO in methanol at 6-31+G(d,p).

^f Lipid in vacuum at 6-31G(d,p).

^g Lipid in methanol at 6-31G(d,p).

showing that the solvent effect plays an important role and thus the solvent effect should be considered for the calculations of these compounds. Thirdly, for the lipid derivatives, the trends in energies both in vacuum and in methanol are accordant. Fourthly, according to the energy analysis, singlet-TEMPO(II) is more stable than triplet-TEMPO(II), however, triplet-lipid(II) is more stable than singlet-lipid(II). These conclusions are also in good agreement with the frontier molecular orbital energy analysis as follows.

The energies of some frontier molecular orbitals of TEMPOs in methanol from orbital 41 to orbital 48 are shown in Fig.3, based on the B3LYP/6-31+G(d,p)

calculations. TEMPO(I) and triplet-TEMPO(II) are open-shell systems and their orbitals are distinguished by the occupation of α or β electrons. For TEMPO(I), the SOMO (singly occupied molecular orbital) is 44α , simply marked as O beside the orbital. 44β orbital is unoccupied molecular orbital, simply marked as V beside it. When TEMPO(I) is discharged (*i.e.* gets one electron), there are two possible states, singlet-TEMPO(II) and triplet-TEMPO(II). Since the energies of the frontier molecular orbitals of triplet-TEMPO(II) show that the SOMO energy of orbital 45α is higher than the energy of unoccupied orbital 44β , the triplet-TEMPO(II) is not a stable state. That is to say, the

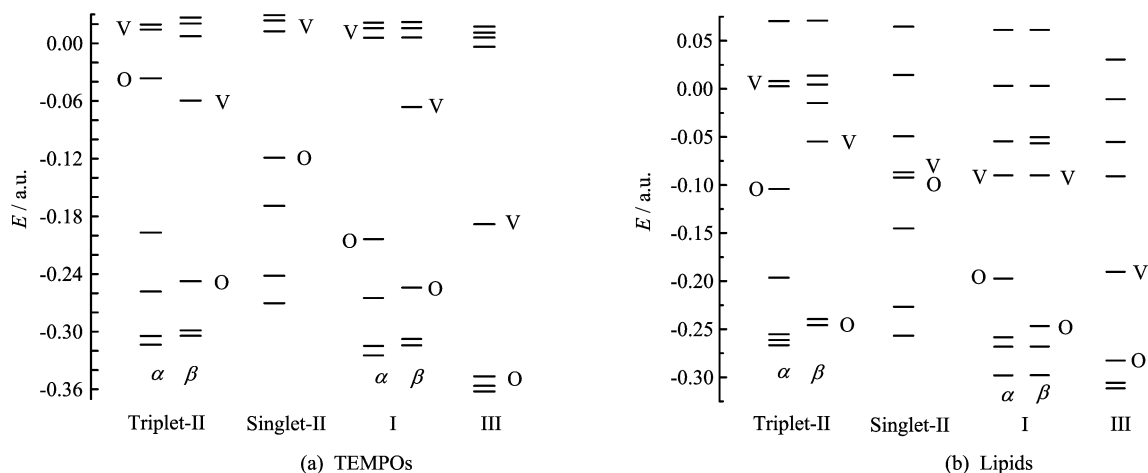


FIG. 3 Schematic diagram of the energies of some frontier MOs of TEMPOs and lipids in methanol.

TABLE II Natural charge population (in a.u.) of the key atoms of TEMPOs in methanol calculated at B3LYP/6-31+G(d,p).

Atom	I	Singlet-II	III
C1	-0.4780	-0.4651	-0.4920
C2	0.0885	0.0861	0.0939
N6	0.0191	-0.2866	0.3179
O11	-0.4918	-0.9137	-0.1439
C9	-0.6926	-0.6797	-0.7196
C10	-0.6985	-0.7117	-0.7021
H24	0.2576	0.2509	0.2727
C3	-0.4805	-0.4740	-0.4931
H14	0.2610	0.2408	0.2890

exotic electron trends to fill in orbital 44β , resulting in all electrons to be pair-matched and becoming the singlet state. The energies of the frontier molecular orbitals of singlet-TEMPO(II) also show the same conclusion. Such a conclusion is in good agreement with the energy result in Table I. So, we will mainly discuss the singlet-TEMPO(II) when discharge of TEMPO(I).

The orbital energies of the lipids in methanol from orbital 112 to orbital 119 are also shown in Fig.3 based on the B3LYP/6-31G(d,p) calculations. For lipid(I), the SOMO (marked as O beside it) is 115α , and the energy of 116α is almost same as that of 115β . When getting an electron, the diagram of triplet-lipid(II) shows that the energy of 116α (marked as O beside it) is lower than that of 115β (marked as V). Comparing the diagrams of the singlet and the triplet states, we can find that the energy gap ΔE (LUMO-HOMO) of the singlet-lipid(II) is quite small (0.0054 a.u. or 0.1478 eV), which means that the electron at the HOMO easily transfers to the LUMO, resulting in the compound to be an excited state. So it can be expected that triplet-lipid(II) be more stable than the singlet-lipid(II), such a prediction

is in good agreement with the total energies in Table I. So triplet-lipid(II) will be discussed in detail below. In addition, lipid(I) loses the electron of orbital 115α in charge process to become lipid(III) which is generally accepted to be a singlet state as shown in Fig.3.

In order to visualize the orbitals, some key frontier molecular orbitals are also exhibited in Fig.4. From Fig.4, we can clearly see what changes of the electronic structures of TEMPOs and the lipids in methanol are in charge/discharge processes.

B. Natural charge populations of TEMPOs and lipids

The natural charge populations of some typical atoms of TEMPOs in methanol are shown in Table II. When TEMPO gets an electron in discharge, the populations of N6 and O11 become more negative, especially that of O11. The total change of N6 and O11 is -0.7276 a.u. On the other hand, when TEMPO loses an electron in charge, their charge populations become more positive, and the total change is 0.6467 a.u. In short, whether TEMPO gets or loses an electron in charge/discharge process, the N6 and O11 atoms (in the radical part) are the most influenced ones, the appropriate expression of the charge/discharge processes is shown in Fig.2 (R=H).

The natural charge populations of some typical atoms of the lipids in methanol are shown in Table III. Generally, the changes of the natural charge populations of the lipids are less than those of TEMPOs, but there are still some rules. First, besides H the atoms are all positive, the most positive atom is C17 (the C of ester), and its charge reaches 0.85 a.u. N3 is more negative than other C atoms of the pyridinium ring although the molecule is a quaternary ammonium salt. Secondly, the electron-getting process greatly affects the charge distribution of the pyridinium head, which can be seen from

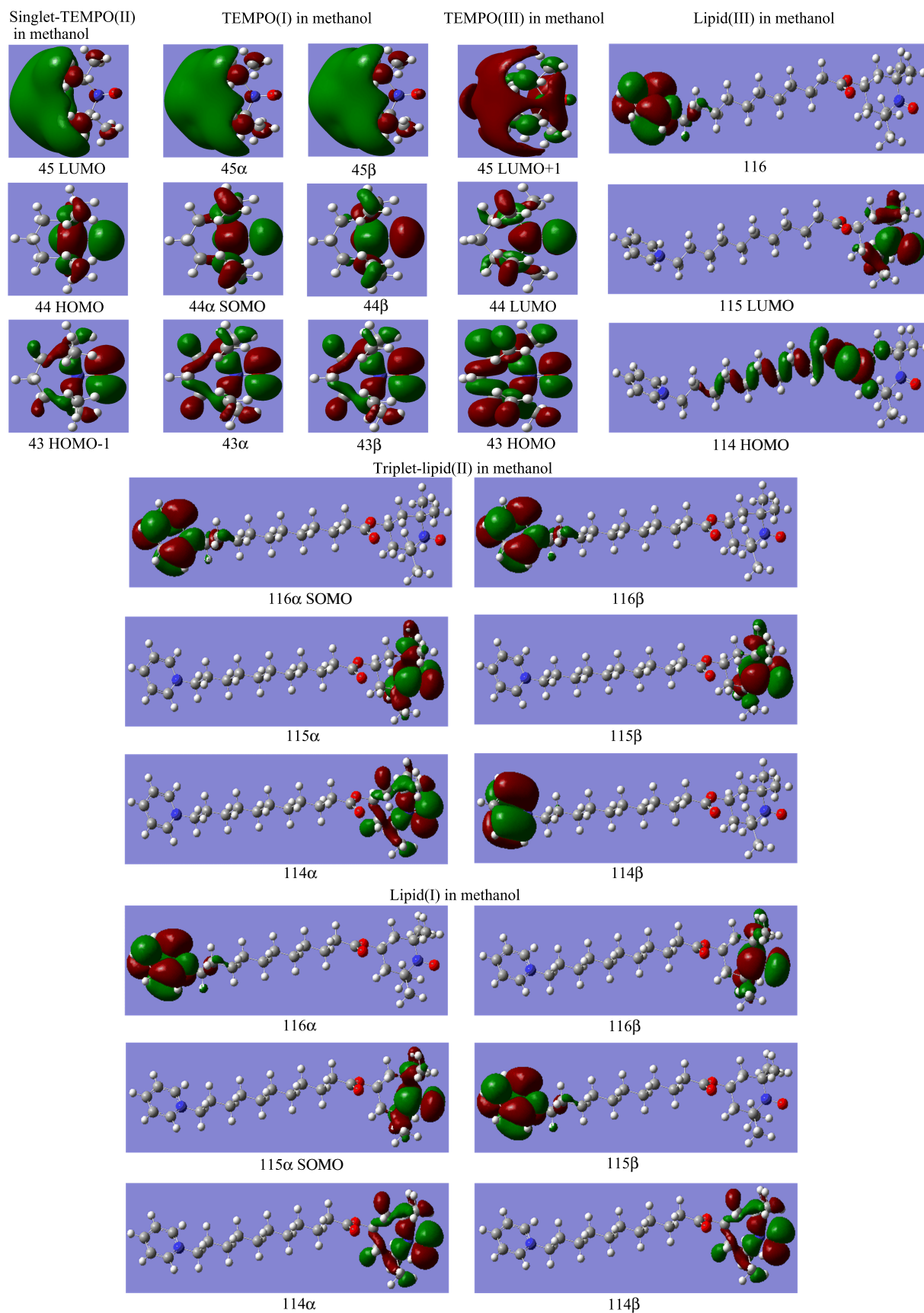


FIG. 4 Stereograph of some key orbitals of TEMPOs and lipids.

TABLE III Natural charge population (in a.u.) of the key atoms of the lipids in methanol calculated at B3LYP/6-31G(d,p).

Atom	I	Triplet-II	III
C2	0.0651	-0.0747	0.0651
N3	-0.2962	-0.4071	-0.2962
C7	-0.2626	-0.2564	-0.2627
C16	-0.5610	-0.5612	-0.5621
C17	0.8500	0.8502	0.8508
O18	-0.6443	-0.6446	-0.6335
O19	-0.5583	-0.5584	-0.5521
N24	0.0232	0.0235	0.3297
O30	-0.4633	-0.4636	-0.1326

TABLE IV Computational bond lengths (in Å), and bond angles (in °) of TEMPOs in methanol calculated at B3LYP/6-31+G(d,p).

	I	Singlet-II	III
C1-C2	1.543	1.546	1.548
C1-C3	1.529	1.529	1.528
C2-N6	1.508	1.502	1.539
N6-O11	1.289	1.430	1.196
C2-C9	1.538	1.541	1.530
C2-C10	1.545	1.550	1.551
O11, H24	2.549	2.573	2.573
O11, H28	2.678	2.460	3.015
N6-C2-C9	107.72	106.79	107.55
N6-C2-C10	109.09	114.82	106.74
C2-N6-O11	115.99	109.95	117.85

the charge change of C2, N3, and C7. The charge population changes become less with the atoms departing far away. So, it can be described that the radical head almost keeps its form after the lipid getting an electron. Thirdly, when losing an electron, the main charge population changes occur on the atoms of the free radical head. The charge population changes of N24 and O30 are obvious, and the charge population changes of the middle atoms such as C16, C17, O18, and O19 are moderate, but the change in charge population of the pyridinium head is only slight. In general, the discharge process greatly influences the pyridinium head and the charge process greatly influences the free radical head.

C. Structure change in the charge/discharge processes

The calculated geometrical parameters of TEMPOs in methanol are selectively listed in Table IV. The bond length of N6-O11 of TEMPO(I) is 1.289 Å, which is in good agreement with the experimental data 1.283 Å [19]. After getting/losing an electron, the biggest bond change occurs on N6-O11. Getting an electron makes

TABLE V Computational bond lengths (in Å), bond angles (in °), and dihedral angles (in °) of the lipids in methanol calculated at B3LYP/6-31G(d,p).

	I	Triplet-II	III
C1-C2	1.384	1.368	1.384
C2-N3	1.354	1.405	1.354
N3-C7	1.491	1.460	1.491
C17-O19	1.349	1.349	1.358
C23-N24	1.506	1.506	1.540
N24-O30	1.287	1.286	1.194
O30, H63	2.500	2.512	2.561
O30, H68	2.629	2.617	2.966
C2-N3-C4	121.04	118.15	121.03
C1-C6-C5	119.30	116.88	119.29
N3-C7-C8	111.69	113.97	111.71
O18-C17-O19	124.71	124.63	123.97
C23-C24-O30	115.72	115.63	117.92
N6-C1-C2-N3	0.074	1.719	0.085
C1-C2-N3-C4	-0.161	-3.662	-0.164
C1-C2-N3-C7	-177.56	-166.21	-177.64
C15-C16-C17-O18	-121.42	-121.84	-106.78
C15-C16-C17-O19	59.06	57.82	72.03
C21-C23-N24-O30	169.00	169.86	142.64
C26-C23-N24-O30	50.55	51.37	22.15

it increase and losing an electron makes it reduce. Other bond length changes are only slight. In addition, the distances of O11-H24 and O11-H28 of TEMPOs (symmetrically on the other half) are all in the range of 2.45–3.02 Å. These distances mean that some intramolecular interactions may exist although there are not covalent bonds between these atoms. These intramolecular interactions help to make the molecules more stable, especially for singlet-TEMPO(II). From Table II, we can see that the charge population of O11 and N6 of singlet-TEMPO(II) are -0.9137 and -0.2866 a.u. respectively. Both are negative and the most negative-charged O11 is on the terminal, which should result in the molecule unstable, but the molecule is stable from the energy analyses. The reason may be partly attributed to these intramolecular interactions. In addition, comparing the data in vacuum and in methanol (Table IV) based on the same basis set 6-31+G(d,p), we find that the distances of O11-H24 (2.514 Å in vacuum) and O11-H28 (2.650 Å in vacuum) change obviously, moreover, the populations of N6 (0.0013 a.u. in vacuum) and O11 (-0.4378 a.u. in vacuum) change obviously too, it further shows that the solvent effect has greater influence for the radical head.

The calculated geometric parameters of the lipids in methanol are selectively listed in Table V. Just as the charge population changes in the charge/discharge processes, the changes of geometric parameters show the same regularity. The geometric data of pyridinium head

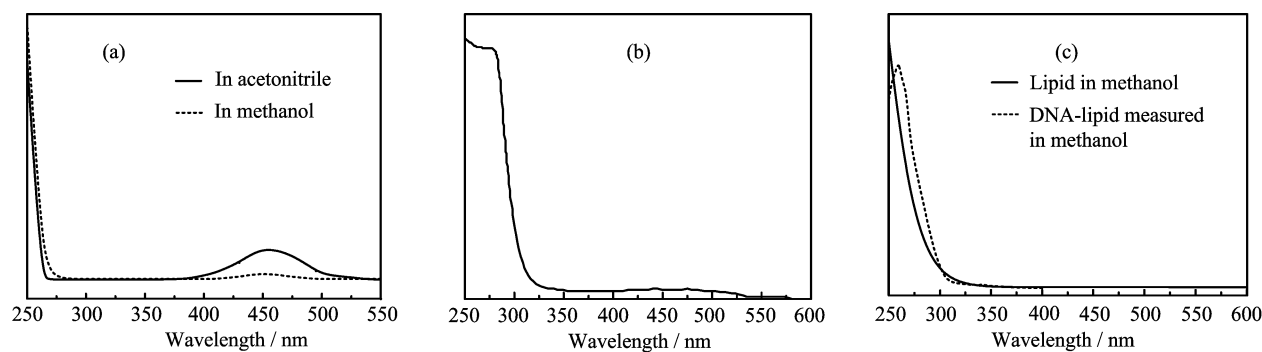


FIG. 5 UV-Vis spectra of TEMPO and lipid. (a) The simulated absorption spectra of TEMPO based on the calculation results. (b) The experimental absorption spectra of 0.01 mol/L TEMPO solution. (c) The simulated and the experimental absorption spectra of lipid.

greatly change after it gets an electron. The bond lengths change become less with departing far away from the pyridinium head. On the contrary, the bond lengths of C1–C2, C2–N3, and N3–C7 almost keep unchanged after the lipid loses an electron. With departing far away from the pyridinium head, the bond lengths change become great. This can be seen from C17–O19, C23–N24, and N24–O30. In a word, the discharge process influences the geometric parameters of pyridinium head much and the charge process influences the free radical head much. Meanwhile, the corresponding changes happen on the bond angles and dihedral angles too (some listed in Table V). In addition, for triplet-lipid(II), the distances of O30–H63 and O30–H68 (symmetrically on the other half) are in the range of 2.50–3.00 Å. Corresponding to that the charge populations of N24 and O30 do not greatly change, the distances of O30–H63 and O30–H68 almost keep still too. Since the crystal structures of the lipids have not been determined yet, the direct comparison between the computational results and the corresponding experimental data can not be performed. However, the comparison between the calculated results and experimental data of the analogs can show that the computational results are reasonable. We find that the N24–O30 bond length of substituted neutral TEMPO radicals are within the range of 1.27–1.30 Å [20]; the bond lengths of C1–C2 and C2–N3 of pyridine are 1.395 and 1.340 Å respectively, according to CRC Handbook of Chemistry and Physics [21]; and the C17–O19 of 4-acetyloxy TEMPO measured by X-ray diffraction is 1.338 Å [22]. Therefore, the calculated parameters in Table V as well as the related discussion should be reliable.

D. UV spectra

Time-dependent density functional theory (TDDFT) has recently become one of the most popular methods for the calculations of electronic spectra and excited

states of medium-sized and large molecules [23], and to our best knowledge, there may be some disagreement on calculating open-shell system by the TDDFT method, but some correlative papers have been published [24]. In order to indicate the validity of our calculation by TDDFT method, we compare the calculational UV spectra with the experimental ones. Figure 5(a) shows the simulated absorption spectra of TEMPO based on the calculation results in acetonitrile or in methanol at the used basis set level, and the experimental spectra of a 0.01 mol/L TEMPO solution (Fig.5(b)) measured in acetonitrile [9]. They are basically accordant. The absorption of TEMPO was very weak in the visible region and peaked around 460 nm. We have not found the experimental spectra of the cationic lipid, but found that of the lipid binding to DNA in methanol (Fig.5(c)) [15]. Accordingly Fig.5(b) shows the simulated absorption spectrum of the lipid without DNA in methanol. They are semblable too. That is a reason that the B3LYP method is adopted in this work.

IV. CONCLUSION

The electronic structures and related properties of TEMPOs and the cationic lipids with pyridium head and free radical head in the charge/discharge processes have been studied by using DFT method. The changes and regularities of geometric and electronic properties of these compounds in the charge/discharge processes were revealed in detail. The computational results show that substitute group plays a very important role in the electronic structures and related properties of TEMPOs during the charge/discharge process. It is very interesting to find that after getting an electron, TEMPO becomes the singlet state but the lipid becomes the triplet state. There are very obvious difference in the redox process between TEMPO and the lipid. For TEMPO, both the charge and the discharge processes greatly influence the electronic properties of N and O atoms of the radical part. For the cationic lipid, the discharge

process mainly influences the pyridinium head and the charge process mainly influences the free radical head. In addition, the solvent effect plays an important role in some bond lengths and the charge population for the free radical head. The UV-Vis absorption spectra of TEMPO and the lipid were calculated and simulated using TDDFT at the 6-31G(d,p) or 6-31+G(d,p) level, the simulated results are in satisfying agreement with the experimental ones.

V. ACKNOWLEDGMENTS

We heartily thank the Information & Network Center, Sun Yat-Sen University for offering the High Performance Computing Clusters (HPCC).

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