Role of Intramolecular and Intermolecular Hydrogen Bonding in Both Singlet and Triplet Excited States of Aminofluorenones on Internal Conversion, Intersystem Crossing, and Twisted Intramolecular Charge Transfer†

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Time-dependent density functional theory method was performed to investigate the intramolecular and intermolecular hydrogen bonding in both the singlet and triplet electronic excited states of aminofluorenones AF, MAF, and DMAF in alcoholic solutions as well as their important roles on the excited-state photophysical processes of these aminofluorenones, such as internal conversion, intersystem crossing (ISC), twisted intramolecular charge transfer (TICT), and so forth. The intramolecular hydrogen bond C═O···H−N can be formed between the carbonyl group and amino group for the isolated AF and MAF. However, no intramolecular hydrogen bond for DMAF can be formed. At the same time, the most stable conformation of DMAF is out-of-plane structure, where the two dihedral angles formed between dimethyl groups and fluorenone plane are 163.1° and 41.74°, respectively. The formation of intramolecular hydrogen bond for AF and MAF is tightly associated with the intersystem crossing of these aminofluorenones. Furthermore, the ISC process can be dominantly determined by the change of intramolecular hydrogen bond between S_1 and T_1 states of aminofluorenones. Since the change of hydrogen bond between S_1 and T_1 states of AF is stronger than that of MAF, the rate of ISC process for AF is faster than that for MAF. Moreover, the rate constant of the ISC process of DMAF is nearly close to zero because of the absence of intramolecular hydrogen bond. On the other hand, the intermolecular hydrogen bond C═O···H−O can be also formed between all aminofluorenones and alcoholic solvents. The internal conversion process from S_1 to S_0 state of these aminofluorenones is facilitated by the intermolecular hydrogen bond strengthening in the electronic excited state of aminofluorenones because of the decrease of energy gap between S_1 and S_0 states. At the same time, the change of intermolecular hydrogen bond between S_1 and T_1 states for AF is much stronger than that for MAF, which may also contribute to the faster ISC process for AF than that for MAF in the same solvents. The TICT process plays an important role in the deactivation of the photoexcited DMAF, since the TICT process along the twisted dihedral angle is nearly barrierless in the S_1 state of DMAF. However, the TICT cannot take place for AF and MAF because of the presence of the intramolecular hydrogen bond.

1. Introduction

The photophysics and photochemistry of fluorenone and its derivatives were widely investigated in past decades.[1−7] Fluorenone is very sensitive to both the intramolecular and intermolecular interactions, such as hydrogen bonding, polarity, steric interaction, and so forth.[8−25] The photophysical properties of fluorenone with various substitutes at different sites of molecule can be changed markedly. Moreover, their photophysical properties in aprotic and protic solvents are also drastically different from each other.[26−39] It has been demonstrated that fluorenone derivatives are excellent model compounds for the investigation of the intramolecular and intermolecular hydrogen bonding induced deactivation of photoexcited molecules, and details of the quenching processes for the excited state have been revealed.[1−39]

Aminofluorenone was successfully utilized to study the hydrogen-bonding effects on the photophysics and photochemistry of fluorenone derivatives, since both the intramolecular and intermolecular hydrogen bonds can be formed and are able to be distinguished by different substitutes.[26−39] When the substitute group is $-NH_2$, the intramolecular hydrogen bond can be formed and the compound is denoted as AF. If the non-hydrogen-bonded H atom of $-NH_2$ is replaced by a methyl group, the compound is denoted as MAF. If the two H atoms are replaced by two methyl groups, one can denote the compound as DMAF.[26−31] Moreover, the deactivation process of aminofluorenones was observed to be strongly dependent on the type and substitution at the amino group.[32−39] The internal conversion (IC) from the fluorescent state to the ground state and intersystem crossing (ISC) from the singlet excited state to the triplet excited state are dominant deactivation processes that are completed with the fluorescence emission of the fluorenone derivatives.[33−36] For AF in acetonitrile, the deactivation of photoexcited AF is dominated by the ISC process.[33,34] For AF in ethanol, the rate constant of ISC is slightly decreased, while the IC process is enhanced.[35,36] This indicates that the formation of intramolecular hydrogen bond in aminofluorenones is very helpful for the ISC, while the intermolecular hydrogen bonding can facilitate the IC.[33−36] Furthermore, the case of MAF in acetonitrile and ethanol is similar to that of AF.[36] However, it is noted that the rate constant of ISC continues to be decreased in comparison with that of AF.[35,36] At the same time, the rate

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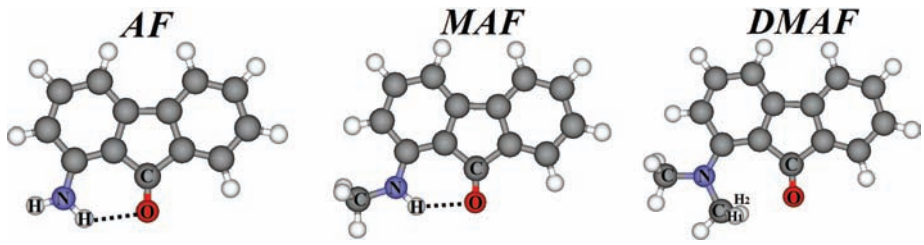


Figure 1. Optimized geometric conformations of the isolated AF, MAF, and DMAF.

constant of IC for MAF is also gradually increased and comparable with that of the ISC.[36] Interestingly, for the DMAF in both acetonitrile and ethanol, the IC is drastically enhanced and is the dominant process.[33−36] However, the rate constant of the ISC process is nearly close to zero. It is confirmed that the intramolecular hydrogen bonding is the determining factor for the deactivation by use of ISC.[32−37]

Many studies have demonstrated that the excited states of aminofluorenones are intramolecular charge transfer (ICT) states.[38,39] In addition, the conformational relaxation by the dimethylamino group was also found to play an important role in the deactivation of the photoexcited DMAF. The twisted intramolecular charge transfer (TICT) mechanism was proposed to explain the conformational relaxation of DMAF.[38] However, there have been no TICT states for the AF and MAF molecules due to the presence of the intramolecular hydrogen bonding.[38] Hence, the intramolecular hydrogen bonding can inhibit the occurrence of TICT.

The intermolecular hydrogen bonding in the singlet electronic excited states of fluorenone and some other important systems in hydrogen-bonding environments has been theoretically and experimentally investigated in our previous work.[40−52] The role of hydrogen bonding in some of the important processes in the electronic excited states of chromophores has been reported. To the best of our knowledge, detailed theoretical information on the intramolecular and intermolecular hydrogen bonding in the singlet excited states of aminofluorenones and their role in the photophysics of these compounds has not been presented. Moreover, the triplet electronic excited states of aminofluorenones are strongly referred to during the deactivation of the photoexcited aminofluorenones, since the ISC from the S_1 state to the T_1 state is a very important process for these compounds.[26−39] Therefore, the intramolecular and intermolecular hydrogen bonding in the triplet excited states are also theoretically studied in this work. The TICT mechanism for DMAF and the influence of intramolecular hydrogen bonding on the TICT for AF and MAF are theoretically mentioned. The potential energy curves with the twisted dihedral angles for DMAF, MAF, and AF, as well as their hydrogen-bonded complexes, are calculated in the present work.

2. Theoretical Methods

As we know, the ground-state electronic structures for these chromophores can be conveniently obtained using various quantum chemistry computation methods. However, it is difficult to calculate the electronic structures of the electronic excited state for complex molecular systems. Nowadays, the configuration interaction with single substitute (CIS)[53,54] and complete active space self-consistent field (CASSCF)[55,56] methods are very popular computational methods for the excited-state electronic structures. It is noted that the CIS method is less expensive but gives less accurate results.[53,54] On the contrary, the CASSCF methods can give very accurate results but are quite expensive for the large molecular systems.[55,56] Hence, the time-dependent density functional theory (TDDFT) method becomes a good candidate for computing the electronic excited states of complex molecular systems because of its moderate efficiency and accuracy.[40−52]

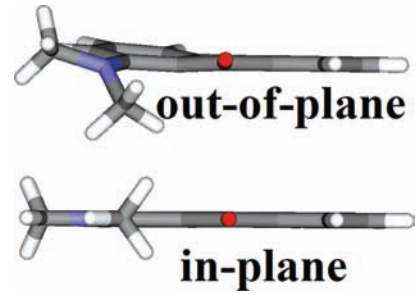


Figure 2. Optimized different geometric conformations for DMAF.

The geometry optimizations of the isolated monomers and the hydrogen-bonded solute−solvent complexes considered here for the ground state were performed, using density functional theory with Becke's three-parameter hybrid exchange function with Lee−Yang−Parr gradient-corrected correlation functional (B3-LYP functional).[57] The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets throughout.[58] The excited-state electronic structures were calculated using TDDFT with B3-LYP hybrid functional and the TZVP basis set. Fine quadrature grids 4 were also employed.[59] The convergence thresholds for both the ground-state and excited-state optimization were reset to 10^{-8} (default settings are 10^{-6}). The excited-state Hessian was obtained by the numerical differentiation of analytical gradients using central differences and default displacements of 0.02 b.[60] The infrared intensities were determined from the gradients of the dipole moment. All the electronic structure calculations were carried out using the Turbomole program suite.[57−61]

3. Results and Discussion

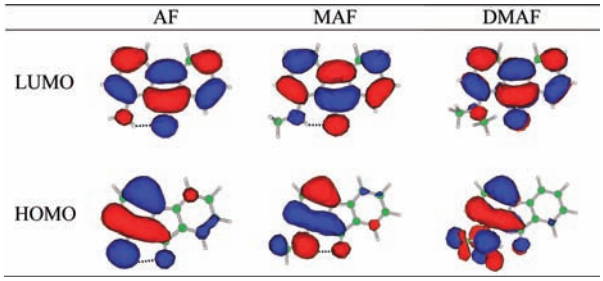
Figure 1 shows the optimized geometric conformations of isolated AF, MAF, and DMAF. The geometric conformations of AF and MAF are similar to each other. The amino group moiety is coplanar with the fluorenone moiety.[26−39] At the same time, an intramolecular hydrogen bond C═O···H−N can be formed between the carbonyl group and amino group.[33−36] Thus, one six-membered ring structure is stabilized by the intramolecular hydrogen bond. For DMAF, there is no stable six-membered ring structure because of the absence of the intramolecular hydrogen bond C═O···HN.

Figure 2 gives two possible geometric conformations of DMAF. One is the in-plane conformation, in which both the dimethylamino group and fluorenone moieties are coplanar. The other is the out-of-plane conformation, in which the dimethylamino group resides out of the plane. At the same time, one benzo ring is also turned outside the original plane because of

TABLE 1: Calculated Electronic Excitation Energies (Electronvolts) for Both the Singlet and Triplet Excited States of the Isolated AF, MAF, and DMAF

	AF		MAF		DMAF	
state	singlet	triplet	singlet	triplet	singlet	triplet
1	3.147	2.382	2.976	2.249	2.903	2.263
	H → L	H → L	H → L	H → L	H → L	H → L
	95.3%	96.1%	93.6%	96.1%	93.4%	95.5%
2	3.234	2.526	3.201	2.498	3.243	2.535
3	3.345	2.915	3.336	2.911	3.252	2.792
4	4.324	3.397	4.301	3.390	4.149	3.365
5	4.435	3.568	4.314	3.530	4.289	3.435
6	5.026	3.911	4.981	3.890	4.859	3.868

TABLE 2: LUMO and HOMO of the Isolated AF, MAF, and DMAF



the steric effect.[33−39] Both these geometric conformations of DMAF were optimized by use of the same method. From our computational results, the total energy of out-of-plane conformation is lower than that of the in-plane conformation. Thus, the out-of-plane conformation of DMAF is more stable than the in-plane conformation. This is consistent with previous results.[33−39] Furthermore, the two dihedral angles formed between dimethyl groups and fluorenone are calculated to be 163.1° and 41.74°, respectively.

The electronic excitation energies for both the singlet and triplet excited states of the isolated AF, MAF, and DMAF molecules are presented in Table 1. One can note that the calculated excitation energies of the S_1 state are 3.147, 2.976, and 2.903 eV for AF, MAF, and DMAF, respectively. It is distinct that the excitation energy is gradually decreased in the order of AF, MAF, and DMAF because of the introduction of the methyl group. This may be induced by the strengthened charge transfer (CT) property of the methylamino group.[26−39] Moreover, the calculated excitation energies of the T_1 state are also gradually decreased in the order of AF, MAF, and DMAF. Our calculated data are in good agreement with the experimental results reported in previous studies.[33−37]

From Table 1, one can also note that both the S_1 and T_1 states correspond to the molecular orbital transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Therefore, only the HOMO and LUMO orbitals are presented in Table 2. The CT property from the amino group moiety to the fluorenone moiety is very distinct. Hence, it is confirmed that the excited states of aminofluorenones are ICT states.[33−39] In addition, the LUMO orbitals of AF, MAF, and DMAF are nearly the same, while the HOMO orbitals of AF, MAF, and DMAF are somewhat different from one another. It should be noted that some HOMO electron density is localized in the methyl group. That is to say, the methyl groups are good electron donors in the ICT state of these molecules. As a result, the strength of ICT is gradually enhanced in the order of AF, MAF, and DMAF. This is in accordance with our above explanation for the lowered excited-state energy level of MAF and DMAF.

As discussed above, the deactivation of photoexcited AF and MAF is dominated by ISC, while the IC process is dominant for the deactivation of the photoexcited DMAF.[26−39] This indicates that the intramolecular hydrogen bonding is the determining factor on the deactivation by use of the ISC process for AF and MAF. To understand how the intramolecular hydrogen bond is changed in the electronic excited state, the calculated bond lengths and angles of the intramolecular hydrogen bond in the S_0, S_1, and T_1 states of AF and MAF are listed in Table 3. The calculated hydrogen bond length between O and H atoms is 2.198 and 2.136 Å for the ground-state AF and MAF, respectively. Thus, the intramolecular hydrogen bond C═O···H−N can be strengthened because of the introduction of a methyl group. At the same time, the angle of O···H−N in MAF is increased in comparison with that of AF. It can be noted that the hydrogen bond length between O and H atoms in the S_1 state is calculated to be 2.059 and 1.883 Å for AF and MAF, respectively. The intramolecular hydrogen bond C═O···H−N in the S_1 state of both AF and MAF is strengthened significantly. Furthermore, the hydrogen bond in MAF is enhanced more strongly than that in AF. This may be closely related to the ICT property of the S_1 state of AF and MAF. In addition, the case in the T_1 state resembles that in the S_1 state.

Since the ISC process is related to both the S_1 and T_1 states, it is very valuable to get the information on the intramolecular hydrogen bonding changes in the S_1 and T_1 states. The calculated hydrogen bond length is changed by 0.093 Å between the S_1 and T_1 states of AF. For MAF, the hydrogen bond length is slightly changed by 0.020 Å. As discussed above, the rate constant of ISC of AF is faster than that of MAF in the same solvents.[33−36] Therefore, the ISC process can be determined by the change of intramolecular hydrogen bond between the S_1 and T_1 states of aminofluorenones. In addition, the rate constant of the ISC process of DMAF is nearly close to zero because of the absence of intramolecular hydrogen bond.[33−36] At the same time, it is also confirmed that the intramolecular hydrogen bonding is the determining factor on the deactivation via ISC.

All the rate constants of the IC process for AF, MAF, and DMAF in ethanol solvent are correspondingly enhanced in comparison with those in acetonitrile solvent.[26−39] This suggests that the formation of an intermolecular hydrogen bond facilitates the IC process from the fluorescent state to ground state.[32−36] In our previous work, we demonstrated that the IC enhancement of fluorenone in alcoholic solvents can be attributed to the intermolecular hydrogen bond strengthening in the electronic

TABLE 3: Calculated Hydrogen Bond Lengths (Angstroms) and Hydrogen Bond Angles (Degrees) in Different Electronic States for Isolated AF and MAF

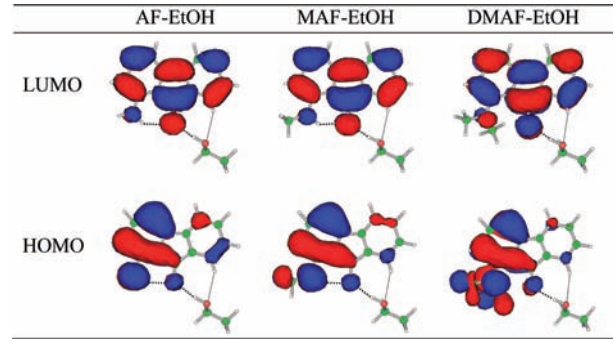
	AF				MAF			
	$L_{C=O}$	$L_{O\cdots H}$	L_{H-N}	A_{OHN}	$L_{C=O}$	$L_{O\cdots H}$	L_{H-N}	A_{OHN}
S_0	1.224	2.198	1.010	128.4	1.226	2.136	1.011	133.1
S_1	1.260	2.059	1.016	134.1	1.253	1.883	1.030	142.6
T_1	1.246	2.152	1.013	130.4	1.267	1.863	1.036	143.5

Figure 3. Optimized geometric conformations of the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes. Dotted lines denote the intramolecular and intermolecular hydrogen bonds.

TABLE 4: Calculated Electronic Excitation Energies (Electronvolts) for Both the Singlet and Triplet Excited States of the Hydrogen-Bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH Complexes

	AF−EtOH		MAF−EtOH		DMAF−EtOH	
state	singlet	triplet	singlet	triplet	singlet	triplet
1	3.074	2.316	2.937	2.186	2.857	2.187
	H → L	H → L	H → L	H → L	H → L	H → L
	59.6%	95.7%	91.3%	96.6%	95.8%	96.4%
2	3.129	2.445	3.070	2.412	3.112	2.452
3	3.457	3.086	3.451	3.083	3.358	2.952
4	3.727	3.331	3.731	3.326	3.801	3.332
5	4.218	3.581	4.193	3.557	4.169	3.418
6	5.520	3.694	4.405	3.700	4.222	3.782

TABLE 5: LUMO and HOMO of the Hydrogen-Bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH Complexes



excited state of hydrogen-bonded complexes formed by fluorenone and alcohols.[41] This mechanism may also be applicable to the aminofluorenones in alcoholic solvents. To delineate the intermolecular hydrogen bonds between aminofluorenone and alcohols, the hydrogen-bonded aminofluorenone−EtOH complexes are also fully optimized here.

Figure 3 shows the optimized geometric conformations of the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes. One can note that the intermolecular hydrogen bond C═O···H−O is formed between aminofluorenones and ethanol molecules. Furthermore, the hydroxyl group of ethanol is in the plane of aminofluorenone, while the ethylic group resides outside of the molecular plane. The intermolecular hydrogen bond resembles that of the hydrogen-bonded fluorenone−methanol complex reported in a previous study.[41] At the same time, a relatively weak intermolecular hydrogen bond C−H···O−H is also formed between the hydroxyl group of ethanol and adjacent benzo ring of aminofluorenones. Hence, a stable seven-membered ring structure can be constructed by two intermolecular hydrogen bonds.

Table 4 lists the electronic excitation energies for both the singlet and triplet excited states of the intermolecular hydrogen-bonded complexes AF−EtOH, MAF−EtOH, and DMAF−EtOH. It can be noted that all the electronic excitation energies for both the singlet and triplet excited states of these intermolecular hydrogen-bonded complexes AF−EtOH, MAF−EtOH, and DMAF−EtOH are lowered in comparison with those of isolated aminofluorenones. That is to say that the intermolecular hydrogen bonding induces the electronic spectral shift to the red. The relationship between electronic spectral shifts and the excited-state hydrogen-bonding dynamics has been clarified in our previous studies.[40−50] Hydrogen bond strengthening can lower the excitation energy of a related excited state and therefore induce an electronic spectral red-shift.[50] On the other hand, hydrogen bond weakening can heighten the excitation energy of a related excited state and induce an electronic spectral blue-shift.[50] Thus, we can conclude that intermolecular hydrogen bonds in both the singlet and triplet excited states of the intermolecular hydrogen-bonded complexes AF−EtOH, MAF−EtOH, and DMAF−EtOH are strengthened in comparison with those in ground states.

Table 4 shows that the S_1 and T_1 states of the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes also correspond to the orbital transition from HOMO to LUMO. Thus, the formation of intermolecular hydrogen bond does not influence the orbital transitions. Table 5 presents the HOMO and LUMO orbtials of all the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes. It is distinct that they resemble those of the isolated AF, MAF, and DMAF, respectively. In addition, the electron density at the site of the carbonyl group is evidently increased in LUMO in comparison with that in HOMO. This also indicates that the intermolecular hydrogen bond would be strengthened in the S_1 and T_1 states of the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes.

The calculated intramolecular and intermolecular hydrogen bond lengths and angles of both hydrogen-bonded AF−EtOH and MAF−EtOH complexes in S_0, S_1, and T_1 states are listed in Table 6. It can be noted that the intramolecular hydrogen bond C═O···H−N is slightly influenced by the formation of intermolecular hydrogen bond C═O···H−O. Moreover, the intermolecular hydrogen bond C═O···H−O is much stronger than the intermolecular hydrogen bond O···H−C for both the hydrogen-bonded AF−EtOH and MAF−EtOH complexes. Therefore, the intermolecular hydrogen bond C═O···H−O determines the intermolecular interaction between aminofluorenones and ethanol molecules. One can note that the intermolecular hydrogen bond length of C═O···H−O is strongly shortened in the S_1 state of both the hydrogen-bonded AF−EtOH and MAF−EtOH complexes. Thus, it is confirmed that the intermolecular hydrogen bond length of C═O···H−O can be significantly strengthened in the S_1 state. The intermolecular hydrogen bond strengthening induces the energy gap between the S_1 and S_0 states to be decreased, which contributes to the enhanced IC from S_1 to S_0 state for AF and MAF in protic

TABLE 6: Calculated Intramolecular and Intermolecular Hydrogen Bond Lengths (Angstroms) and Angles (Degrees) of Both Hydrogen-Bonded AF−EtOH (a) and MAF−EtOH (b) Complexes in the S_0, S_1, and T_1 States

(a)	$L_{C=O}$	$L_{O\cdots H}$	L_{H-N}	A_{OHN}	$L_{O\cdots H}$	L_{H-O}	A_{OHO}	$L_{O\cdots H}$	L_{H-C}	A_{OHC}
S_0	1.232	2.195	1.010	127.8	1.920	0.973	169.6	2.424	1.085	149.9
S_1	1.270	2.095	1.014	132.8	1.800	0.981	171.4	2.338	1.085	148.1
T_1	1.257	2.142	1.013	130.4	1.828	0.979	171.6	2.368	1.085	148.8
(b)	$L_{C=O}$	$L_{O\cdots H}$	L_{H-N}	A_{OHN}	$L_{O\cdots H}$	L_{H-O}	A_{OHO}	$L_{O\cdots H}$	L_{H-C}	A_{OHC}
S_0	1.234	2.134	1.011	132.6	1.917	0.973	169.8	2.426	1.085	149.7
S_1	1.269	1.969	1.020	138.9	1.831	0.979	171.2	2.352	1.084	148.5
T_1	1.275	1.875	1.034	142.7	1.839	0.978	174.0	2.539	1.084	146.7

solvents compared with that in aprotic solvents. Moreover, the intermolecular hydrogen bond C═O···H−O in the T_1 state is also stronger than that in ground state, while weaker than that in S_1 state. It is distinct that the intermolecular hydrogen bond length is changed by 0.028 Å between the S_1 and T_1 states of the AF−EtOH complex. However, the intermolecular hydrogen bond length is only changed by 0.008 Å between the S_1 and T_1 states of the MAF−EtOH complex. Therefore, the change of intermolecular hydrogen bond between the S_1 and T_1 states for AF is much stronger than that for MAF. The stronger change of intermolecular hydrogen bond between the S_1 and T_1 states may also contribute to the faster ISC process for AF than that for MAF in the same solvents.[32−39]

Since the TICT mechanism was proposed to explain the conformational relaxation by the dimethylamino group of DMAF, which was also found to play an important role in the deactivation of the photoexcited DMAF, the potential energy curves of different electronic states along the twisted dihedral angles for isolated aminofluorenones and their intermolecular hydrogen-bonded complexes are calculated in this work. Figure 4 presents the calculated potential energy curves of the S_0, S_1, and T_1 states along the twisted dihedral angles for isolated AF, MAF, and DMAF. One can note that the potential energy curves of different electronic states for AF have good symmetry. The most stable conformation of the ground-state AF is the planar geometric conformation with the twisted dihedral angle of 0° or 180°. In both the ground and T_1 states, the energy barrier of the conformational twist is very high at the perpendicular conformation. At the same time, there is no stable geometric conformation at the dihedral angle of 90°. Moreover, there is a stable position at the perpendicular geometric conformation in the S_1 state of AF. However, the energy barrier of the conformational twist from planar to perpendicular geometries is too high to get there. As a result, the TICT process cannot take place for AF in both S_1 and T_1 states.

The potential energy curves of different electronic states for MAF have no symmetry. In the range from 0° to 90°, the potential energy curves of MAF are similar to those of AF. In addition, their energy levels are somewhat lowered in comparison with those of AF because of the stronger ICT property of MAF. It is distinct that the TICT process can also not occur because of high twist energy barrier in the presence of intramolecular hydrogen bonding in MAF. Moreover, it is noted that the energy levels of the electronic states for MAF are significantly increased with the conformation twist from 90° to 180°. This may be induced by the steric effects of the methyl group of MAF during the twisting process.

The potential energy curves of various electronic states for DMAF are different from those of AF and MAF. As discussed above, the most stable geometry of DMAF in ground state is not the planar conformation but the twisted conformation with twist angle of 41.74°. There is a marked energy barrier along the conformational twist coordinate in the ground state. The potential energy curves of the T_1 state resemble those of the ground state. That is to say the conformational twist is not easy to take place in the T_1 state because of the high energy barrier at the dihedral angle of 90°. For the potential energy curves of the S_1 state, it should be noted that there is a stable geometric conformation of the minimum energy at the dihedral angle of

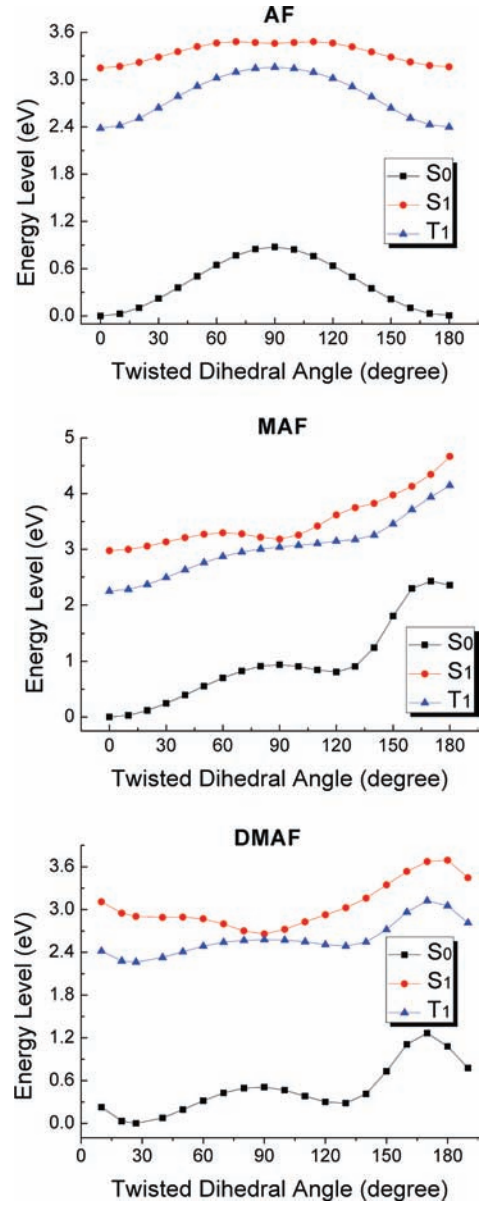


Figure 4. Calculated potential energy curves of different electronic states along the twisted dihedral angles for isolated AF, MAF, and DMAF.

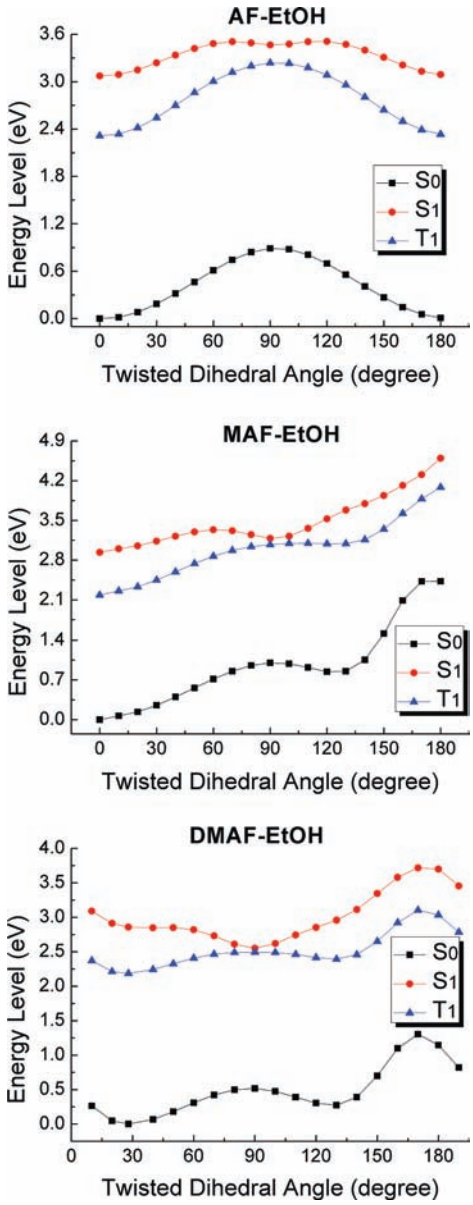


Figure 5. Calculated potential energy curves of different electronic states along the twisted dihedral angles for the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes.

90°. Furthermore, there is nearly no barrier for the conformational twist from the ground-state geometry to the perpendicular geometry in the S_1 state. Hence, the conformation twist is easy to occur in the S_1 state of DMAF. Consequently, the S_1 state of DMAF is theoretically confirmed to be a TICT state via the calculated potential energy curves with the twist angle.

The calculated potential energy curves of different electronic states along the twisted dihedral angle for the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes are given in Figure 5. One can note that all the potential energy curves of the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes are correspondingly lowered in comparison with those of the isolated AF, MAF, and DMAF. However, their main characters are similar to those of the isolated AF, MAF, and DMAF. It is indicated that the intermolecular hydrogen bonds cannot significantly influence the conformational twist in the excited states of these aminofluorenones. Consequently, the TICT process for these molecules is dominantly determined by the intramolecular hydrogen bonds.

4. Conclusions

Excited-state intramolecular and intermolecular hydrogen bonding of different aminofluorenones in alcoholic solvents was theoretically investigated using the TDDFT method. Furthermore, the role of the intramolecular and intermolecular hydrogen bonding on the internal conversion, intersystem crossing, and twisted intramolecular charge transfer in both the singlet and triplet electronic excited states of these aminofluorenones was also discussed in the present work. The geometric conformations of the ground state and the S_1 and T_1 states for AF, MAF, and DMAF as well as their hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes were fully optimized. There is an intramolecular hydrogen bond C═O···H−N formed between the carbonyl group and amino group for the isolated AF and MAF. Moreover, their amino group moiety is coplanar with the fluorenone moiety. However, the most stable conformation of DMAF is the out-of-plane structure, where the two dihedral angles formed between dimethyl groups and fluorenone plane are 163.1° and 41.74°, respectively. Furthermore, there is no formation of intramolecular hydrogen bond for DMAF. We found that the intersystem crossing of these aminofluorenones is tightly associated with the intramolecular hydrogen bond. At the same time, the ISC process can be determined by the change of intramolecular hydrogen bond between the S_1 and T_1 states of aminofluorenones. Since the change of hydrogen bond between the S_1 and T_1 states of AF is stronger than that of MAF, the rate of the ISC process for AF is faster than that for MAF. In addition, the rate constant of the ISC process of DMAF is nearly close to zero because of the absence of intramolecular hydrogen bond. On the other hand, the intermolecular hydrogen bond C═O···H−O can be also formed between carbonyl group of all aminofluorenones and the hydroxyl group of alcoholic solvents. We also found that the formation of intermolecular hydrogen bond can facilitate the internal conversion process from the S_1 to S_0 state of the aminofluorenones. It has been theoretically demonstrated that the intermolecular hydrogen bond can be significantly strengthened in the S_1 state in comparison with that in ground state. Therefore, the energy gap between the S_1 and S_0 states for these compounds is drastically decreased because of the intermolecular hydrogen bond strengthening. Consequently, the IC from the S_1 to S_0 state of the aminofluorenones is enhanced by the intermolecular hydrogen bond strengthening in the excited state. Moreover, the intermolecular hydrogen bond C═O···H−O in the T_1 state is also stronger than that in the ground state, while weaker than that in the S_1 state. At the same time, the change of intermolecular hydrogen bond between the S_1 and T_1 states for AF is much stronger than MAF. The stronger change of intermolecular hydrogen bond between the S_1 and T_1 states may also contribute to the faster ISC process for AF than that for MAF in the same solvents. The TICT was found to play an important role in the deactivation of the photoexcited DMAF. From the calculated potential energy curves of different electronic states along the twisted dihedral angle for the hydrogen-bonded AF−EtOH, MAF−EtOH, and DMAF−EtOH complexes, we demonstrated that the TICT cannot take place for AF and MAF because of the presence of the intramolecular hydrogen bond. However, the TICT process is nearly barrierless in the S_1 state of DMAF. Moreover, it was noted that the intermolecular hydrogen bonding can lower the energy levels of all the potential energy curves, but cannot change the main character of the calculated potential energy curves of different electronic states along the twisted dihedral angle. All the calculated results are in good agreement with the spectral results recorded in experiments.

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