Microenvironment Control of Methyl Rotation Induced by Proton Transfer

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Methyl rotation induced by proton transfer was found for *cis-N*-methylacetamide (NMA). More interestingly, it was found that the microenvironment could control the methyl rotation. The atom-centered density matrix propagation (ADMP) method, a recently developed ab initio molecular dynamics, was further carried out to depict the trajectories for methyl rotation of NMA. Moreover, trajectories for methyl rotation of NMA complexed with water molecules were also calculated, and water molecules at the two different sites of NMA were found to reverse or cease the rotational direction of the methyl groups of NMA. This finding that microenvironment can not only control rotational direction of methyl groups but can also cease the rotation may be of significant importance for the control of molecular machines.

1. Introduction

The field of molecular machines has experienced spectacular development in recent years because of their potential application in the creation of nanometer-scale molecular devices.[1,2] A wide variety of molecular machines such as shuttles,[3a] rotors,[3b] muscles,[3c] ratchets,[3d] pistons and cylinders,[3e] scissors,[3f] elevators,[3g] loop locks,[3h] and switches[3i] have been reported.

Although various motor molecules have been discovered to date, chemists are interested in far smaller elementary molecules that can potentially work as molecular machines or elements within one. Recently, the phenomenon that reciprocating motion of the proton can be mechanically transformed to intramolecular or interlocked intermolecular rotational motion is not only chemically surprising but also interesting for the study of molecular machines.[3b,4−6] A recent example of such a phenomenon is a molecule undergoing almost unidirectional methyl rotation, which was triggered by relevant proton-transfer processes in a mutually remote site. The mechanism of this long-range interaction was explained by quantum-mechanical interactions between hyperconjuction of the methyl group and tautomerization resulting from proton transfer.[7]

Herein, the proton-transfer process of a much smaller molecule, *cis-N*-methylacetamide (NMA) (Figure 1), was also found to induce methyl rotation. Therefore, the atom-centered density matrix propagation (ADMP) method was utilized to study the relevant dynamics. Since water molecules at different sites were found to influence the proton-transfer processes of molecules, trajectories for NMA complexed with water molecules were further investigated to find the effect of water molecules on methyl rotation of NMA. Corresponding mechanisms were also analyzed.

2. Computational Methods

As it is well-known that density functional theory (DFT) is an excellent compromise between computational cost and reasonable results, optimization of the structures of NMA/NMAts (the transition state)/(NMA)* (the enol form of NMA) with and without water molecules, energies, and frequency calculation, as well as zero-point energy (ZPE) correction, were all done at the B3LYP/6-311++G** level of theory using the *Gaussian 03* suite of programs.[8] Our results here agree well with the references.[9−11]

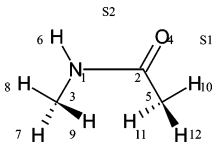

Figure 1. Sketch of the structure of NMA, and the preferential sites of water molecules in the vicinity of NMA, S1, and S2.

To study the relevant dynamics, the atom-centered density matrix propagation (ADMP) method was carried out at the B3LYP/6-31G(d) level of theory also using the *Gaussian 03* suite of programs to describe the trajectories for methyl rotation of NMA. The ADMP method is a recently developed ab initio molecular dynamics method. Reasonable energy conservation and adiabaticity may be maintained well during the trajectories, despite having hydrogen atoms in the system. This approach is well-suited for the dynamics of chemical systems such as clusters and gas-phase reactions,[12] while DFT methods have been validated to be well-implemented in ADMP.[13,14] Single trajectories were depicted as several trajectories starting from the same initial conditions that turned out to be identical. Single trajectories have also been approved to give reliable results.[12a,13,14] Ten thousand steps for each trajectory integrated with a step size of 0.1 fs were started from the optimized transition state and integrated toward the keto form of NMA, which is more stable than the enol form. The initial reaction coordinates were given at 27 *m*hartree (70.89 kJ/mol) nuclear kinetic energy (NKE), which was chosen to be much smaller than the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the system (Table 1) to ensure that the dynamics was simulated close to the Born−Oppenheimer ground-state surface, well below excited electronic state,[12b,15] and which was also chosen on the basis of an experiential initial kinetic energy of between 8 and 17 kcal/mol (12.75−27.09 *m*hartree).[16] The velocities of the individual atoms were generated randomly to simulate a Boltzmann distribution.[12,15]

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TABLE 1: HOMO−LUMO Gaps (in kJ/mol) of the Transition States

	NMAts	NMAts-W1	NMAts-W2	NMAts-W1-W2
HOMO−LUMO gap	221.22	218.15	208.18	178.09

To investigate the barriers of methyl rotation, we also carried out a methyl scan starting from the keto form, with one bond angle constrained to a sequence of given values but the other two bond angles varying correspondingly. So as to validate the availability of the DFT method in producing rotational barriers, the MP2 method was also utilized to calculate the methyl rotational barrier of NMA for comparison.

3. Results and Discussions

3.1. Isolated NMA. The proton-transfer process of isolated NMA was first studied (Figure 2). The transition state (NMAts) possesses an imaginary frequency 1733i cm^{-1} owing to the single-proton transfer of H6 (Figure 1). The relative free energy change of base tautomerism from the keto form NMA to its enol form (NMA)* is 50.97 kJ/mol. Thus, we can conclude that the keto form is more stable than the enol form. In other words, the transition state of this molecular (NMAts) tends to tautomerize to the ketone form. A remarkable phenomenon during this process is that the two methyl groups have both rotated. Therefore, the trajectories of methyl rotation were further studied below.

The time evolution of the dihedral angles 2−1−3−8 and 1−2−5−10 (Figure 1), which correspond to the rotation of the two methyl groups on atoms N and C, respectively, was presented in Figure 3. At about 17 fs, the proton H6 transferred to N (signed as $(NMA)_0$ in Figure 3). Around 60 fs, the methyl group on N began to rotate, followed by the rotation of the one on C, as can be seen from Figure 3. What was especially interesting was that the two methyl groups had rotated in opposite directions. In other words, the methyl group on N rotated anticlockwise, whereas the one on C rotated clockwise. It was further interesting to note, however, that after about 310 fs when it had rotated clockwise for 313° (indicated by$(NMA)_1$ in Figure 3), the methyl group on C began to reverse rotation, namely, it began to rotate anticlockwise, while around 405 fs when the one on N had rotated anticlockwise for 278° (indicated by $(NMA)_2$ in Figure 3), it also began to reverse rotation, viz., it began to rotate clockwise (Figure 3). Then, the two methyl groups repeated rotating with periodic changes in direction, but to a much lesser extent. Hence, we can conclude that the C-methyl rotation after 310 fs and the N-methyl rotation after 405 fs are general methyl rotation, whereas the C-methyl rotation before 310 fs and the N-methyl rotation before 405 fs with much larger amplitude are induced by proton transfer.

This was really an amusing and interesting phenomenon which led us to further investigate the mechanisms. First, why had the two methyl groups rotated during the proton-transfer process? It can be seen in Figure 3 that, when H6 transferred to N1 and tautomerized to be $(NMA)_0$ at 17 fs, the two methyl groups almost remained nonrotating. However, the two methyl groups had both rotated when comparing with NMA. Besides, the free energy of $(NMA)_0$ was 85.37 kJ/mol greater than that of NMA. Therefore, it can be concluded that $(NMA)_0$ was quite unstable, and methyl rotation was needed to stabilize the product of such a proton transfer. Second, why had the methyl group on N1 rotated before that on C2? It can be seen in Table 2 that the rotational barrier of the methyl bonded to N1 (4.53 kJ/mol) was smaller than that of the one bonded to C2 (8.15 kJ/mol). It indicated that methyl group on N1 was easier to rotate than that on C1 and it rotated before than the methyl group on C1. The MP2 calculation gave similar results.

The major contributor to the rotational barrier is charge transfer. The more charge transfers during the rotation, the larger the rotational barrier tends to be.[17] Charge transfer during the methyl rotation of cis-NMA has been calculated and listed in Table 3. It can be seen that charge shift on N1-methyl rotating clockwise is 0.035 e larger than that of N1-methyl rotating anticlockwise. Therefore, the potential barrier for the clockwise rotation of N1-methyl is higher than that of the anticlockwise rotation. Similarly, N1-methyl rotating anticlockwise gives 0.063 e smaller charge transfer than that of C2-methyl rotating clockwise, and therefore, the rotational barrier of N1-methyl is lower that of C2-methyl.

Third, why had the two methyl groups rotated in opposite directions? In fact, the rotational direction was decided by the initial energetic state of the methyl groups. Methyl scan starting from $(NMA)_0$ was studied as an example, and the rotational curves were depicted in Figure 4. As can be seen in Figure 4, if the methyl group on N1 rotated clockwise, though the barrier would decrease first, a much higher barrier would follow and the molecule may not able to overcome it. However, if it rotated anticlockwise, the energy barrier would be much lower, although the energy barrier would increase at the very start. Relatively, to be rotate anticlockwise was easier.

Fourth, why had the two methyl groups both changed rotational directions after rotating for some time? The free energies of $(NMA)_1$ and $(NMA)_2$ were both greater than that of NMA and were not stable yet. Therefore, they went on rotating for a more stable conformation. However, after 405 fs, the conformation had been very close to that of NMA, and the two methyl groups rotated or wiggled adjacent to the conformation of NMA, which may be induced by steric repulsion between the two methyl groups or the effect of electronic rearrangement or by some factor unknown, independent of proton transfer of NMA. After a long time, the conformation reached that of NMA, and the proton-transfer process was completed. Finally, the C-methyl and the N-methyl began normal rotation just like what occurred in the keto form of NMA.

3.2. NMA with Water Molecules. Furthermore, the factor influencing the process of proton transfer was taken into account. Microenvironments have been reported to influence the proton-transfer processes of molecules.[18−20] In our previous work, we theoretically studied the proton transfer of some model molecules with water molecules in the vicinity and found that there were two absolutely opposite regions in the vicinity of the model molecules. Water molecules in one of the regions can increase the barrier of proton transfer, whereas water molecules in the other region can decrease the barrier of proton transfer. The calculation results also indicate the assisting and protective role played by water for the model molecules.[20] As discussed above, microenvironments can influence the proton transfer greatly, while proton transfer can induce methyl rotation, and we speculated that such influence of microenvironments on proton transfer can be transferred to methyl rotation. To justify this point of view, further research was performed as follows.

There are two binding sites for water molecules in the vicinity of NMA/(NMA)*, S1, and S2[21,22] (Figure 1). Water is considered to be a H-bond acceptor and donor via the interactions occurring through its oxygen or hydrogen atoms, respectively, because the relevant structure is energetically favored over the alternative double-donor or double-acceptor hydrogen bonding.[23,24] Optimized structures of NMA, NMAts, and (NMA)* with water molecules in the vicinity of them were also calculated

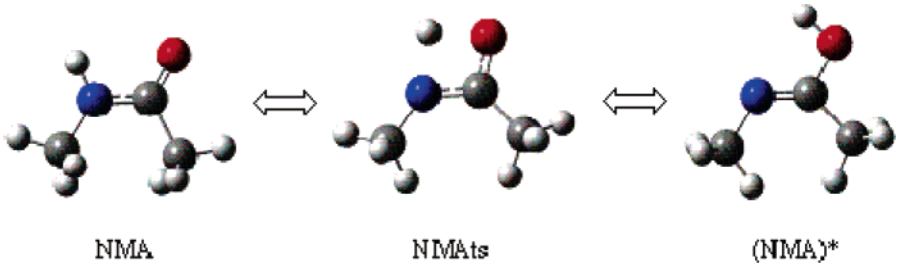

Figure 2. Optimized structures of NMA, NMAts, and (NMA)*, calculated at the B3LYP/6-311++G** level of theory.

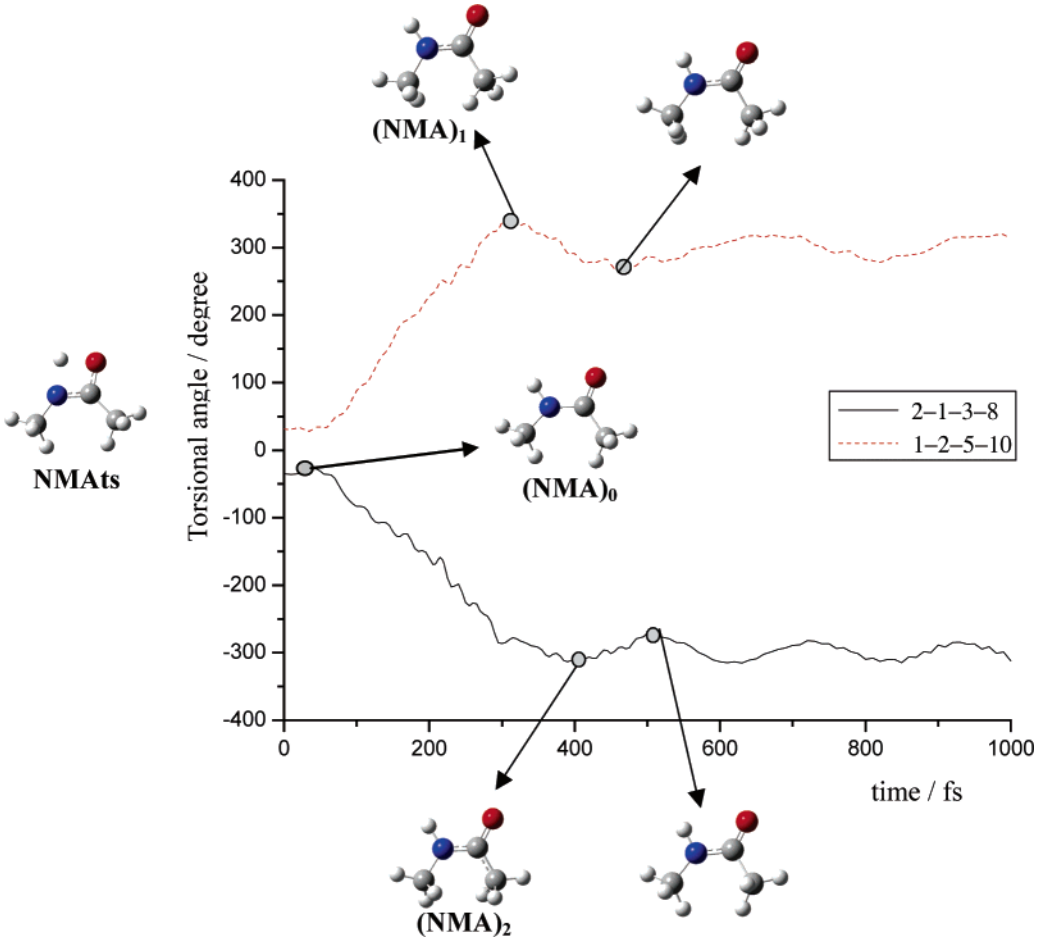

Figure 3. Variation of dihedral angles representing rotation of the two methyl groups of A with time in ADMP, starting from the transition state NMAts.

TABLE 2: Rotational Barriers (kJ/mol) for (A) Methyl Group on N1 and (B) Methyl Group on C2 of NMA, NMA-W1, NMA-W2, and NMA-W1-W2

computational method	NMA		NMA-W1	NMA-W2	NMA-W1-W2
	DFT	MP2	DFT	DFT	DFT
A	4.53	6.10	4.09	4.11	4.03
B	8.15	10.35	6.79	6.78	6.23

TABLE 3: Charge Shifts on a 90° Rotation of (a) N1-Methyl Rotating Clockwise, (b) N1-Methyl Rotating Anticlockwise, and (c) C2-Methyl Rotating Clockwise

	π, e	σ, e	net, e
a	−0.181501	−0.073375	−0.254876
b	−0.167796	−0.052018	−0.219814
c	−0.194054	−0.089014	−0.283068

(Figure 5). Trajectories of methyl rotation of complexes of NMA with water molecules at different binding sites were investigated also using the ADMP method. Figure 6 illustrated the variation of the two dihedral angles representing the rotation of the two methyl groups.

In the case of a water molecule in S1, the proton H6 transferred to N after about 19 fs. However, a surprisingly different trend was observed for the methyl group on N, which started rotating clockwise, entirely contrary to the case of isolated NMA. It was clearly seen from Figure 6a that, around 100 fs, the methyl group on N began to rotate clockwise. It kept rotating for 72°, when the curve reached the peak after about 300 fs, and almost remained there until 620 fs. Then, it also repeated rotating while changing the rotational direction. This suggests that water molecule in S1 can reverse the rotational direction of the methyl group on N. However, for the methyl group on C, it first rotated clockwise for 88° when the curve reached the maximum around 160 fs, and then began to reverse the rotational direction, namely, it went on rotating anticlockwise for 178° until the curve reached the minimum around 440 fs, followed by the repeating rotation in both directions.

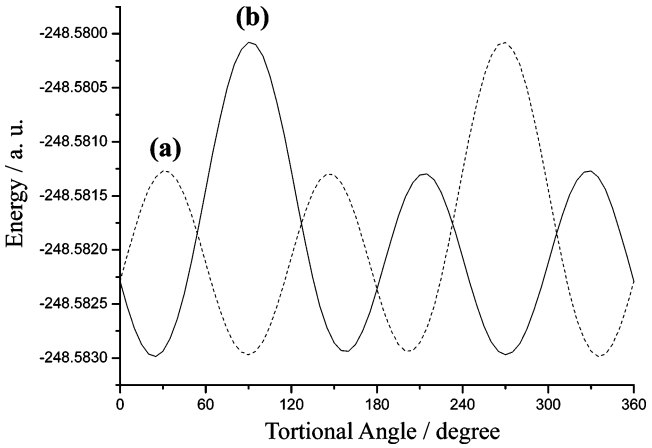

Figure 4. Rotational barriers of the methyl group on N1 starting from $(NMA)_0$: (a) rotating anticlockwise, (b) rotating clockwise.

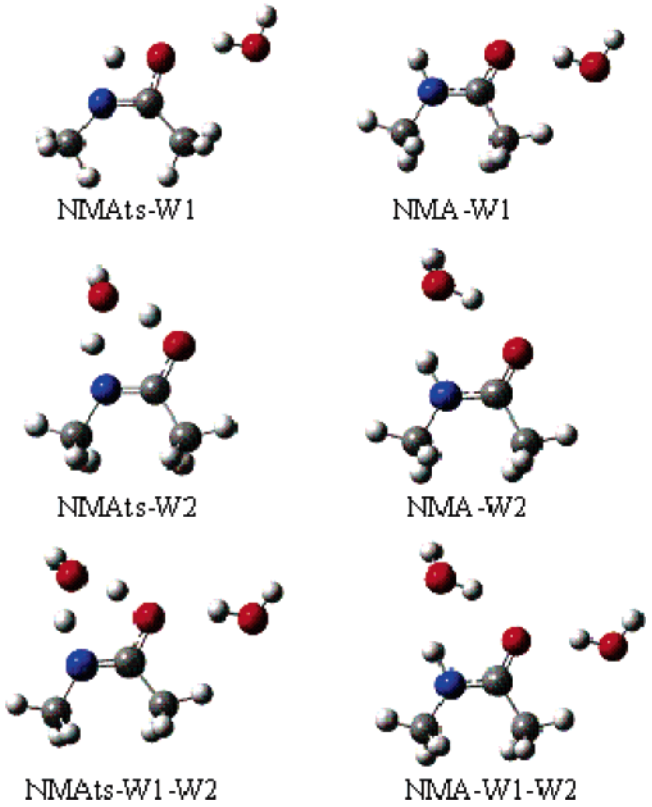

Figure 5. Optimized structures of NMAts-Wi and NMA-Wi (i = 1, 2), calculated at the B3LYP/6-311++G** level of theory.

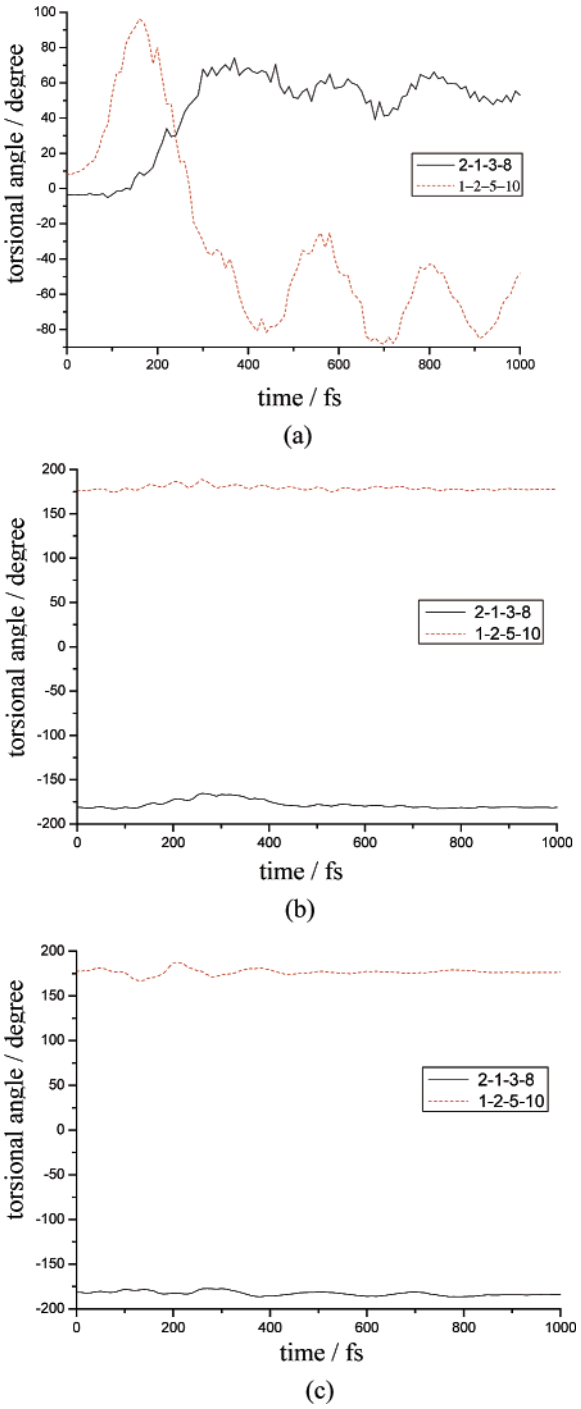

Figure 6. Variation of dihedral angles representing rotation of the two methyl groups of A-Wi (i = 1, 2) with time in ADMP, starting from the transition state: (a) NMAts-W1, (b) NMAts-W2, and (c) NMAts-W1-W2.

Moreover, water molecules were put in S2 and both in S1 and S2, and the trajectories of the methyl rotation were also depicted in Figure 6. The proton H6 transferred to atom N around 17 fs. Note that both of the two methyl groups in these two cases, however, had hardly rotated (Figure 6b,c). Even the normal methyl rotation of NMA is not observed. Therefore, it can be concluded that water molecules in S2 can cease the methyl rotation of NMA. While when there were water molecules in both S1 and S2, the one in S2 played a dominant role, and neither of the two methyl groups rotated for the total simulation time.

3.3. Discussions. Why could water molecules at different sites of NMA control methyl rotation? The question could be disassembled into two different ones. First, why could the methyl groups rotate in the case of water molecule in S1, while they could not rotate in the case of water molecules in S2 and both in S1 and S2? The basic nature of the electronic structure is reflected in the bond lengths.[7] It can be seen in Table 4 that, when the NMA molecule with and without water molecules tautomerized from the keto form to the transition state, the bond lengths of N1−C2 were all decreased, C2−O4 and N1−H6 increased, and the dihedral angle of N1−C2−O4 decreased. When a single water molecule (W1) is located in S1, W1 is only considered to hydrogen bonded to C2−O4, and it acts as an H-bond donor (Figure 5). During the tautomerism of NMA-W1 → NMAts-W1, the change of N1−H6 and N1−C2−O4 reduced, which made the tautomerism easier than that of NMA → NMAts. Moreover, the forming of the hydrogen bond

TABLE 4: Geometrical Changes of NMA, NMAts, NMA-W1, NMAts-W1, NMA-W2, NMAts-W2, NMA-W1-W2, and NMAts-W1-W2

	NMA	NMAts	NMA-W1	NMAts-W1	NMA-W2	NMAts-W2	NMA-W1-W2	NMAts-W1-W2
N1−C2	1.370	1.344	1.361	1.302	1.357	1.307	1.350	1.303
C2−O4	1.221	1.293	1.230	1.309	1.234	1.300	1.244	1.310
N1···H6	1.010	1.462	1.010	1.346	1.017	1.246	1.018	1.276
N1−C2−O4	121.22	102.51	120.33	106.31	121.64	119.45	120.75	118.61

O4···H−O (W1) changed the electron density around O4. It was also worth noticing that the N1···H6 bond in the transition state decreased, and the N1−C2 bond also decreased sharply. These factors may lead to the reduction of the activation energy of the proton-transfer process of NMA-W1 → NMAts-W1 because less energy was needed for the process, which can be seen in Figure 7. It was apparent that the processes of the transition state to the keto form were exothermic and the processes of NMAts → NMA and NMAts-W1 → NMA-W1 were much more exothermic. Though the energy given out from NMAts-W1 → NMA-W1 was less than that of NMAts → NMA, the energy given out was still sufficient to induce methyl rotation of NMA. Therefore, when the proton transferred to N1, there was still energy left for the rotation of the two methyl groups. Moreover, since the conformation was not stable yet, methyl rotation had to occur so as to reach the stable conformation.

However, when a single water molecule (W2) is located in S2, water acts as an H-bond acceptor and donor simultaneously. In the tautomerism, water in S2 accepts the hydrogen atom from the N1−H6 bond of A; at the same time, it donates its hydrogen atom to A, which is accepted by O4 (Figure 5). The geometrical change during the process of NMA-W2 → NMAts-W2 was similar to that of NMA-W1 → NMAts-W1, but the change was much more drastic. Notable was that there is a hexahydric ring in the NMAts-W2 state, in which water acts as a bridge. The formation of the hexahydric ring made the changes of N1−H6, N1−C2−O4, and C2−O4 more remarkable (Table 4). The N1···H6 and N1−C2 bonds in the transition state had also decreased sharply, which may make the tautomerism much easier. Moreover, the water molecule in S2 increased the partial electron density surrounding O4 significantly, which made O4 susceptible to proton attack. It may also lower the activation energy considerably compared with the case of isolated NMA (Figure 7). Therefore, for the processes of NMAts-W2 → NMA-W2, the lower energy given out could not provide sufficient energies to induce methyl rotation. Therefore, when H6 was transferred to N1, the conformation had almost reached the stable state just like that of NMA-W2, and the methyl groups need not rotate, and there was also not sufficient energy to induce the rotation. The case of water molecules in both S1 and S2 was similar to that of water in S2. That is why a water molecule in S2 and both in S1 and S2 could cease the methyl rotation of NMA.

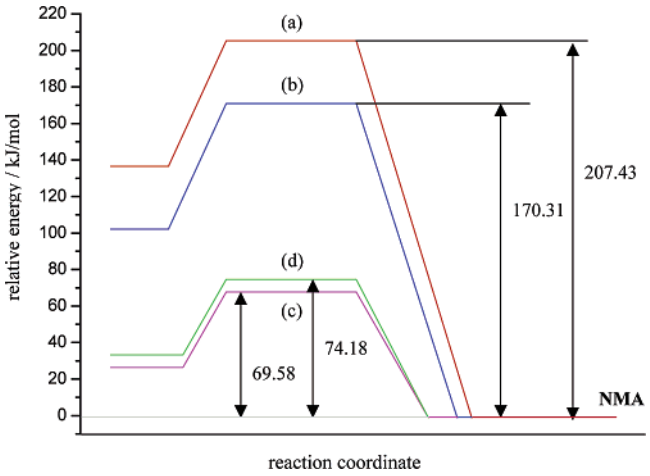

Figure 7. The reaction coordinate of (a) NMAts → NMA, (b) NMAts-W1 → NMA-W1, (c) NMAts-W2 → NMA-W2, and (d) NMAts-W1-W2 → NMA-W1-W2.

Second, why had the methyl group on N1 changed its rotational direction when a water molecule was put in S1, in comparison with the case of isolated NMA? The origin of rotational direction can also be explained from the viewpoint of rotational barriers, and the mechanism was similar to that of the methyl group on N1 of $(NMA)_0$ rotating anticlockwise, which has been discussed before.

Conclusions

In summary, the two methyl groups of *cis-N*-methylacetamide (NMA) were found to rotate in the reverse directions after proton transfer, which was of special interest. Trajectories of methyl rotation of NMA as well as complexes of NMA with water molecules were calculated using a recently developed ab initio molecular dynamics (ADMP) method. Water molecules at different binding sites of NMA, which were found to influence the proton transfer processes, were also found to have a great impact on the rotational direction of the two methyl groups. It was found that water molecules at different sites can not only reverse the direction of methyl rotation, but could also cease the rotation. The relevant mechanisms were also analyzed. This finding that microenvironment can control the direction of methyl rotation which is induced by proton transfer may be crucial for the control of molecular rotors.

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Supporting Information Available: The Z-MATRIX of calculated results and figures of methyl rotational barriers. This material is available free of charge via the Internet at http://pubs.acs.org.

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