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The Role of Charge Transfer in the Hydrogen Bond Cooperative Effect of *cis-N*-Methylformamide Oligomers

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Two accumulating molecular systems have been designed to investigate the cooperative effect of hydrogen bonding in theory. The first system included a series of linear oligomers of *cis-N*-methylformamide (*c*-NMF) molecules. Substantial cooperative effect has been confirmed in the electronic structures and energies of the hydrogen bonds in them as shown by the results obtained using the B3LYP method at the level of cc-pVTZ basis sets. Such a cooperative effect gradually increases with the growth of the *c*-NMF oligomer. The second system included a series of modified *c*-NMF trimers whose central *c*-NMF molecules contained insertion fragments of varying structural and electrical compositions. On the basis of an examination of the structures and charge populations of the *c*-NMF oligomers in these two systems, a mechanism of the cooperative effect of hydrogen bonding in these systems based on charge flow in the *c*-NMF molecules is proposed. The results from the second system of *c*-NMF trimers were particularly instrumental in formulating this mechanism, because the charge flows between the C═O and N─H groups in the modified *c*-NMF molecule of these trimers were dampened by the various molecular insertions. A clear correlation between the degree of charge flow dampening from each inserted fragment and the magnitude of the cooperative effect of hydrogen bonding was observed. On the basis of an analysis of the electronic structural characteristics of the molecular fragments, we conclude that the charge flow between the hydrogen bond donor and acceptor groups in the *c*-NMF molecule is the most important factor inducing the cooperative effect of hydrogen bonding.

Introduction

Many natural and artificial supramolecules are formed through intermolecular forces such as hydrogen bonding, van der Waals forces, and hydrophobic interactions. Among these interactions, hydrogen bonds play a pivotal role in biological systems because of their strength and directional characteristics. As has been well-established, hydrogen bonds are responsible not only for the stability but also for the functioning of many biomolecules and supramolecules. One need look no further than the elementary formation mechanisms of both DNA and proteins for an understanding of the importance of hydrogen bonds in biological systems: in the case of DNA, it is hydrogen bonding that links both DNA helices into the famous double helix, and in the case of proteins, it is hydrogen bonding between constituent amino acid residues that enables a protein to achieve its secondary structure, from which tertiary structure and ultimately protein function are derived. With regard to supramolecules, artificial synthesis of omnifarious supramolecular systems is one of the most important research fields for modern chemists. Among various strategies now available for molecular synthesis, the use of hydrogen bonds has proven to be very effective, with polypeptide nanotubes being good examples of supramolecules that are currently synthesized by processes driven by hydrogen bonding.[1−3] Self-assembling from the cyclic peptides formed by alternating D- and L-amino acid residues, these nanotubes exhibit remarkable long-term stability in many organic and inorganic solvents.[4] Interestingly, their particular stability appears to be greater than what one would expect from the hydrogen bonding between component cyclopeptides considered in isolation. Our previous work found that the cooperative effect resulting from cumulated hydrogen bonds could further strengthen the hydrogen bonds between two adjacent cyclic peptides in the tubular β^3-cyclopeptide.[5] Remarkably, this cooperative effect was found to be so strong that it appears able to dictate the structure and the stability of the peptide nanotube. Similar cooperative effects from theoretical calculations have also been reported for the hydrogen-bonding chains of formamide [6,7] and *N*-methylacetamide[8−10]. In contrast, the cooperative effect has not been detected in other systems containing multiple hydrogen bonds, such as a novel photoswitchable self-organized cyclic peptide system.[11] The uncertainty associated with the cooperative effect of systems of hydrogen bonds naturally leads to a number of questions concerning this phenomenon: What are the important conditions that induce the cooperative effect, and can these conditions be used to distinguish between those systems that display such an effect and those that do not? What determines the magnitude of this effect? Is this effect transferable, and if so, how is it transferred? These questions and others have motivated us to investigate the mechanism behind the cooperative effect of hydrogen bonding using computational methods by studying a series of designed systems containing *cis-N*-methylformamide.

Methods and Models

Because of its ready ability to form hydrogen bonds, the formamide molecule provides a good model to study the mechanism involved in the cooperative effect of hydrogen bonding. The amide group in the formamide molecule can simultaneously form two hydrogen bonds (its C═O can act as a hydrogen bond acceptor, while its N─H can act as a hydrogen bond donor), an ability that certainly seems conducive to

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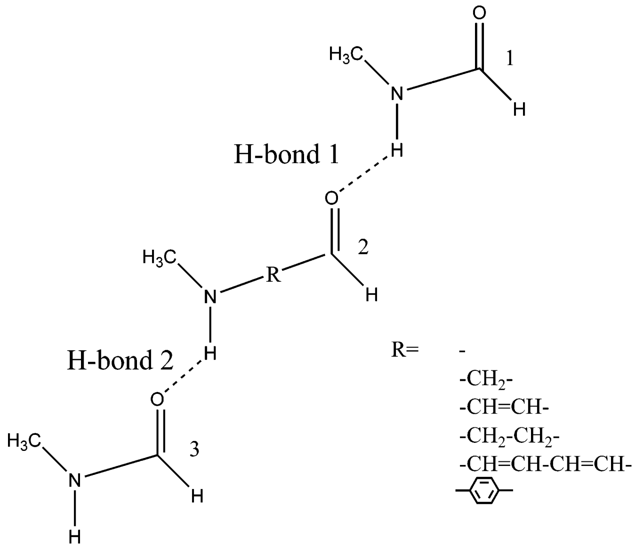
SCHEME 1: Modified *cis*-*N*-Methylformamide Trimer



initiating cooperative hydrogen-bonding effects. This molecule is also attractive as a model for study, because its amide group is the same basic structural unit found in all protein peptide bonds. By studying simple systems involving these relatively small molecules, we hope to gain some insight into the cooperative effect of hydrogen bonding that might occur in larger biomolecules and supramolecules, including proteins and DNA.

In this work, *cis*-*N*-methylformamide (*c*-NMF) was chosen instead of formamide to be the model molecule. Because methylation of the $-NH_2$ in formamide will limit it to forming at most one hydrogen bond at its N terminus, this choice was made to decrease the complexity of the resulting oligomers. Two distinct systems were designed and studied to investigate cooperative effects of hydrogen bonding in *c*-NMF oligomers. The first system included the linear oligomers of the *c*-NMF molecule from dimer to pentamer. Because the amount of hydrogen bonding within these molecules increases with the growth of the oligomers, this system provides a mechanism for studying the relationship between the number of hydrogen bonds and their cooperative effect by examining the hydrogen-bonding energies of each of the oligomers. The second system studied consisted of a series of *c*-NMF trimers, each of which had a modification to the second *c*-NMF molecule in the trimer (Scheme 1). In these trimers, the *c*-NMF molecules located at the beginning and end of each trimer functioned only as hydrogen bond donors or acceptors, but not both. The central *c*-NMF molecule was systematically modified by inserting a single molecular fragment between its N−H and C═O groups. The molecular fragments inserted included $-CH_2-$, $-CH_2-CH_2-$, $-CH{=}CH-$, $-CH{=}CH-CH{=}CH-$, and −Ph− (Scheme 1). For each such modified oligomers, the hydrogen-bonding energy was calculated and analyzed.

The geometrical structures of the oligomers in these two systems were optimized, and the energies as well as the electronic properties of the optimized supramolecules were calculated. Because the interactions under investigation are weak, the electronic correlation effect was taken into account by using both the density functional method B3LYP[12] and Dunning's correlation consistent basis sets with triple-ζ (cc-pVTZ)[13] in all calculations.

Throughout our analyses, the hydrogen bond energy of the mth hydrogen bond linking the mth monomer to the $(m + 1)$th monomer, E_{HBm}, was defined as the difference between the total energy of the linear *c*-NMF oligomer (containing n monomers) and the sum of the energies of the two components of the oligomer separated by the mth monomer. Symbolically, if $E_{j\cdots k}$ represents the energy of just the jth through kth monomers of the *c*-NMF oligomer, excluding its interaction energies with other monomers, then E_{HBm} is given by

$$E_{HBm} = E_{total} - E_{1,2,3\cdots m} - E_{m+1,m+2\cdots n} \quad m = 1, 2, ..., n - 1 \tag{1}$$

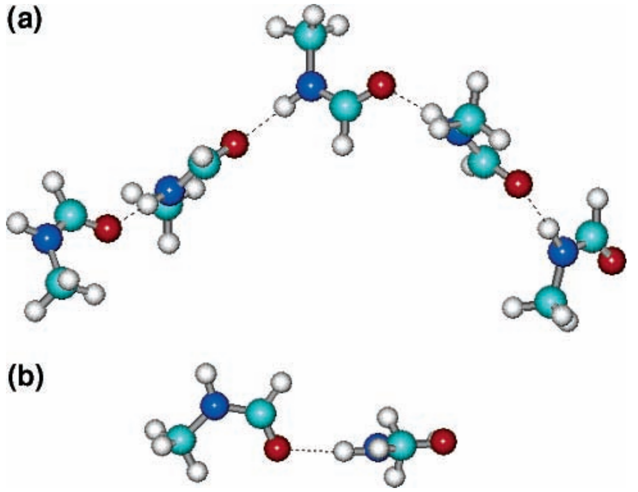


Figure 1. Optimized structures of the *c*-NMF pentamer and dimer. (a) The optimized structure of *cis*-NMF pentamer. (b) In the optimized oligomers, adjacent *cis*-NMF molecules were arranged with their molecule planes perpendicular to one other.

The cooperative energy of the mth hydrogen bond (E_{coopm}) is defined as the part of the hydrogen bond energy that excludes all interaction energies IE_{ij} between *c*-NMF and the two monomers i and j in the oligomer, where $i \leq m$ and $j > m$. The term IE_{ij} in eq 2 denotes the difference between the energies of individual monomers i, j and their total energy in the oligomer.

$$E_{coopm} = E_{HBm} - \sum_{i=1}^{m} \sum_{j=m+1}^{n} IE_{ij} \quad m = 1, 2, ..., n - 1 \tag{2}$$

E_{HBm}, then, represents the strength of the mth hydrogen bond, while E_{coopm} represents solely the magnitude of the cooperative effect of this hydrogen bond.

The energy terms were calculated with the basis set superposition error taken into account. All the calculation were performed with the *Gaussian 98*[14] software package on a PC equipped with an Intel P4 CPU operating at 3 GB clock frequency and 1 GB of memory.

Results and Discussions

1. Cooperative Effect of Hydrogen Bonding in *c*-NMF Systems. In the first system investigated, all the linear oligomers of *c*-NMF from dimer to pentamer were constructed and optimized. Because the optimization was done without constraints, every two adjacent *c*-NMF molecules in the optimized oligomers arranged themselves with their molecular planes perpendicular to one other (shown in Figure 1b) so as to minimize the electrostatic repulsion between them.

The lengths and energies (E_{HBm}) of the hydrogen bonds in all of the *c*-NMF oligomers are listed in Tables 1 and 2, respectively. The cooperative effect of cumulative hydrogen bonding is evident from these tables. First, the hydrogen bond lengths gradually decrease, while the bond lengths of the N−H and C═O bonds gradually increase, with the growth of the

TABLE 1: The Important Structural Features of the *c*-NMF Oligomers (Å)

	monomer	dimer	trimer		tetramer			pentamer			
		1−2	1−2	2−3	1−2	2−3	3−4	1−2	2−3	3−4	4−5
N···O		2.972	2.928	2.911	2.922	2.869	2.914	2.918	2.856	2.864	2.908
O···H		1.967	1.915	1.899	1.908	1.849	1.899	1.902	1.835	1.843	1.891
N−H	1.000	1.015	1.016	1.018	1.017	1.021	1.019	1.017	1.021	1.022	1.019
C═O	1.214	1.221	1.222	1.227	1.222	1.229	1.229	1.223	1.229	1.231	1.229

TABLE 2: E_{HBm} of the *c*-NMF Oligomers (kJ/mol)

	dimer	trimer		tetramer			pentamer			
m	1	1	2	1	2	3	1	2	3	4
E_{HBm}	−24.67	−32.36	−32.38	−34.24	−42.96	−35.11	−34.87	−45.26	−46.13	−35.86

TABLE 3: E_{coopm} of *c*-NMF Oligomers (kJ/mol)

	trimer	tetramer	pentamer
1	−4.57	−6.54	−7.00
2	−4.57	−11.62	−13.94
3		−6.45	−13.83
4			−6.84
avg	−4.57	−8.20	−10.40

oligomers. As expected, this leads to a gradual increase in the hydrogen bond energies from smaller to larger oligomers. Second, the hydrogen bonds located in the middle of these oligomers are stronger than those located at their termini. Both of these observations lead one to conclude that the more hydrogen bonding that occurs within a structure, the stronger the cooperative effect of these bonds in that structure will be.

In comparison to the hydrogen bond energies, the calculated E_{coopm} values provide better direct evidence of a correlation between the cooperative effect of hydrogen bonding and the number of hydrogen bonds within a structure. As can be seen in Table 3, the absolute value of E_{coopm} increases with the growth of the oligomer. For example, the average E_{coopm} of the hydrogen bonds in the pentamer is 10.40 kJ/mol, compared to only 4.57 kJ/mol in the trimer. Within any one oligomer, the cooperative energy of each hydrogen bond was found to vary consistently. Those hydrogen bonds located in the middle of the oligomers were found to have larger cooperative energies, which is consistent with the computational results from strained formamide oligomer structures[6,7] and from our previous results with β^3 peptide nanotubes.[5] When taken together, these results imply that the cooperative effect comes from the accumulation of hydrogen bonds and correlates well with the number of such bonds. This increase in the cooperative effect of hydrogen bonding will no doubt reach a ceiling as the *c*-NMF oligomers grow in length; indeed, as seen in Table 3, the measured increase in the cooperative effect from the tetramer to the pentamer is markedly less than the increase measured from the trimer to the tetramer. This upper bounding on the cooperative effect of hydrogen bonding is consistent with what has been reported in other studies,[5−7] suggesting that it is a common feature of this effect.

Harmonic vibrational frequencies for these *c*-NMF oligomers were computed to further substantiate the cooperative effects of hydrogen bonding. The vibrational frequencies of C═O and N−H bonds of the *c*-NMF in these oligomers are depicted in Figure 2. The red shift of the vibrational frequencies that occurs during the oligomerizing process is shown in this figure, and the trend in intensities provides further support for the existence of a cooperative effect between hydrogen bonds.

To further explore the mechanisms of the cooperative effect of hydrogen bonding in *c*-NMF oligomers, we constructed a second system of *c*-NMF oligomers, each one a trimer with an insertion modification in the second *c*-NMF molecule. As can be seen in Scheme 1, we chose to study the hydrogen bond between the first and second molecules of these trimers, HB1, because this bond is adjacent to the various fragments inserted into the second trimer molecules. Note that although the second hydrogen bond HB2 (between the second and third molecules of each trimer) was not directly examined, its importance should be reflected in the cooperative effect of HB1.

The geometries of each of these trimers were initially optimized. One of them is depicted in Figure 3. The hydrogen bond energy (E_{HB1}) and the cooperative energy (E_{coop1}) of the first hydrogen bond in these trimers were calculated and are listed in Table 4. The largest cooperative energy in the table

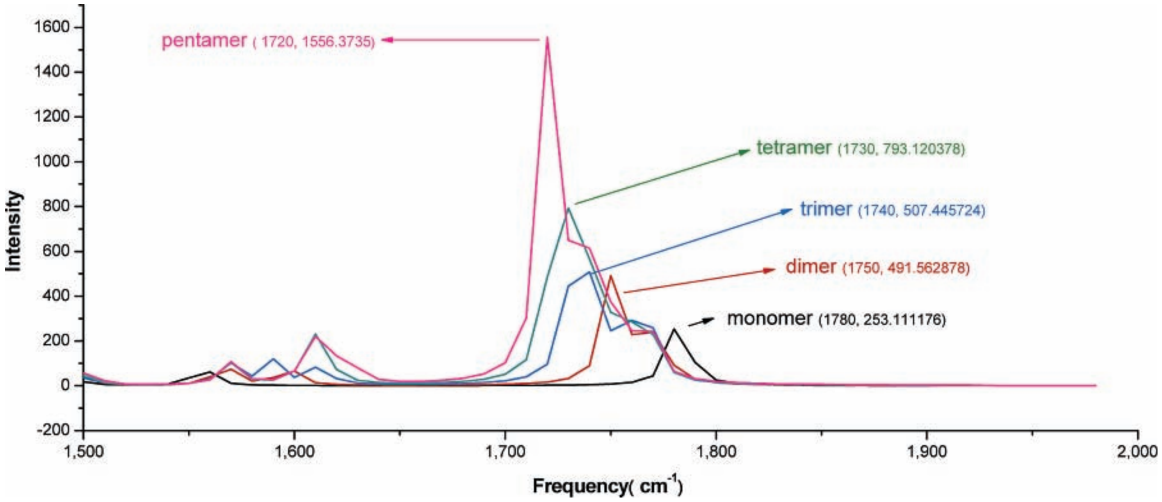


Figure 2. C═O Stretch Spectrum of the *c*-NMF Oligomers.

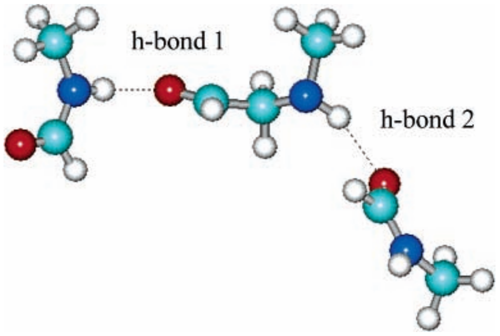


Figure 3. An optimized *c*-NMF modified trimer with an inserted $-CH_2-$ fragment.

belongs to the hydrogen bond in the original *c*-NMF trimer, which is −4.56 kJ/mol. Note that when the $-CH_2-$ fragment is inserted into the second *c*-NMF molecule of the trimer, E_{coop1} decreases to −1.49 kJ/mol, and it undergoes a further reduction to −0.95 kJ/mol when the $-CH_2-CH_2-$ is used as the insertion fragment. The natural conclusion that the cooperative effect of hydrogen bonding is decreased as the length of the intervening fragment increases is not, however, supported by the other three inserted fragments. When the inserted fragment is $-CH=CH-$, $-CH=CH-CH=CH-$, or $-Ph-$, the resulting cooperative energies (E_{coop}) are −3.52, −3.46, and −2.73 kJ/mol, respectively. These fragments result in considerably less dampening of the cooperative effects of hydrogen bonding than the alkyl fragments do. It appears, therefore, that the most important characteristic of the inserted molecular fragment that influences the cooperative effect in these trimers is not their length but their electronic configuration. When a fragment with conjugated π bonds is inserted between the N−H and C=O groups of a *c*-NMF molecule, the resulting reduction in the magnitude of the cooperative effect of hydrogen bonding is relatively small. On the other hand, inserted alkyl fragments, which do not have any conjugated π bonds, significantly reduce the cooperative effect of hydrogen bonding. The calculated harmonic vibrational frequencies of these trimers and their corresponding fore-dimers, tabulated in Table 5, strongly support this hypothesis. From dimer to trimer, clear red shifts are observed, consistent with the changes observed in cooperativity.

2. The Mechanism of the Cooperative Effect of Hydrogen Bonding. The hydrogen bond is akin to a donor−acceptor interaction. In the *c*-NMF molecule, the hydrogen bond donor group N−H and the acceptor group C=O can each form one hydrogen bond with another *c*-NMF molecule. When this has occurred, the two *c*-NMF molecules are directly connected by the conjugated amide bond so that electronic charge can flow freely between them. However, as we have reported above, if a molecular fragment is situated between N−H and C=O groups, it will interfere with this charge-flow process, resulting in a decreased cooperative effect between the two hydrogen bonds adjacent to the inserted fragment. This interference was found to be fragment-specific: When the molecular fragment inserted in the *c*-NMF molecule is $-CH=CH-$, $-CH=CH-CH=CH-$, or $-Ph-$, the hydrogen bond acceptor C=O and donor N−H groups in a *c*-NMF molecule are moved further apart, but the charge flow between them, though somewhat dampened, was not impeded; in contrast, when the inserted fragment is $-CH_2-$ or $-CH_2-CH_2-$, the charge flow between N−H and C=O is largely prohibited by their saturated hydrocarbon chains. We have thus concluded that the cooperative effect of hydrogen bonding is dictated by the charge flow between hydrogen bonds, and not by the spatial separation of the bonds. More precisely, we have found that a dampening or elimination of charge flow between hydrogen bonds results in a dampening or elimination of the cooperative effect. This conclusion would help to explain why the cooperative effect was not detected in some systems containing multiple hydrogen bonds, since the magnitude of the effect would now be dependent upon the specific electronic makeup of the systems in question. To confirm this explanation, we examined the charge carried by the O atoms in the central *c*-NMF molecules of the five trimers. We determined the charge on these O atoms without any cooperative effects of hydrogen bonding ($Ch_{ouncoop}$) by examining these modified monomers in isolation. We also included any cooperative effects of hydrogen bonding by determined the charge on these O atoms (Ch_{ocoop}) in dimers. The charge values are listed in Table 6. The ΔCh values indicate the differences in charges on these O atoms resulting from the cooperative effects of hydrogen bonding.

As can be seen in Table 6, when a dimer is formed via a hydrogen bond between the N−H component of these modified monomers and an unmodified *c*-NMF molecule, there is considerable variation in the resulting change to the charge carried by the O atoms in question (ΔCh). The ΔCh for O atoms from monomers with inserted $-CH_2-$ and $-CH_2-CH_2-$ alkyl groups is only −0.006 23 and 0.000 114, respectively. For the monomers with inserted fragments containing conjugated π bonds, however, the increases on the charges carried by the O atoms are more evident: For the $-CH=CH-$, $-CH=CH-CH=CH-$, and $-Ph-$ inserts, the changes in charges on the O atoms are −0.014 504, −0.013 868, and −0.008 496, respectively. Clearly, the alkyl groups, and especially the $-CH_2-CH_2-$ group, have significantly reduced any charge flow between the N−H and C=O in the *c*-NMF molecule. Figure 4 contains a graph of both the ΔCh and the changes in energy calculations for these five trimers. As is evident from this figure, the ΔCh from the various modified *c*-NMF molecules correlates well with the cooperative effects of hydrogen bonding measured for these molecules. When taken together, these results strongly support the conclusion that the charge flow between the donor and acceptor groups in the same molecule is primarily responsible for the cooperative effect of hydrogen bonding.

Using this conclusion, we returned to the analysis of *c*-NMF oligomers in general. A *c*-NMF oligomer can be considered as one whole donor−acceptor system. Within this system, the O, H, and N atoms at the two termini of an oligomer are the key atoms involved in the formation of hydrogen bonds with other *c*-NMF molecules. We performed detailed investigations of the electronic charge distributed in these three atoms. Our results are listed in Table 7.

From Table 7, it is clear that the positive charge on the H atom gradually increases with the growth of the *c*-NMF oligomer, while the negative charge on the adjacent N atom undergoes a concurrent decrease. These changes in charges indicate that the ability of the terminal N−H group to accept electronic charge is increasing. Thus, as a hydrogen bond donor, the larger *c*-NMF oligomers will form stronger hydrogen bonds with new hydrogen bond acceptors. Meanwhile at the other terminus of the oligomer, Table 7 shows that the negative charge carried by the O atom is also gradually increasing as the oligomers become longer. This implies that a larger oligomer will also be a stronger hydrogen bond acceptor. To summarize, then, our calculations show that hydrogen bonds formed at either end of the oligomer will become stronger as the *c*-NMF

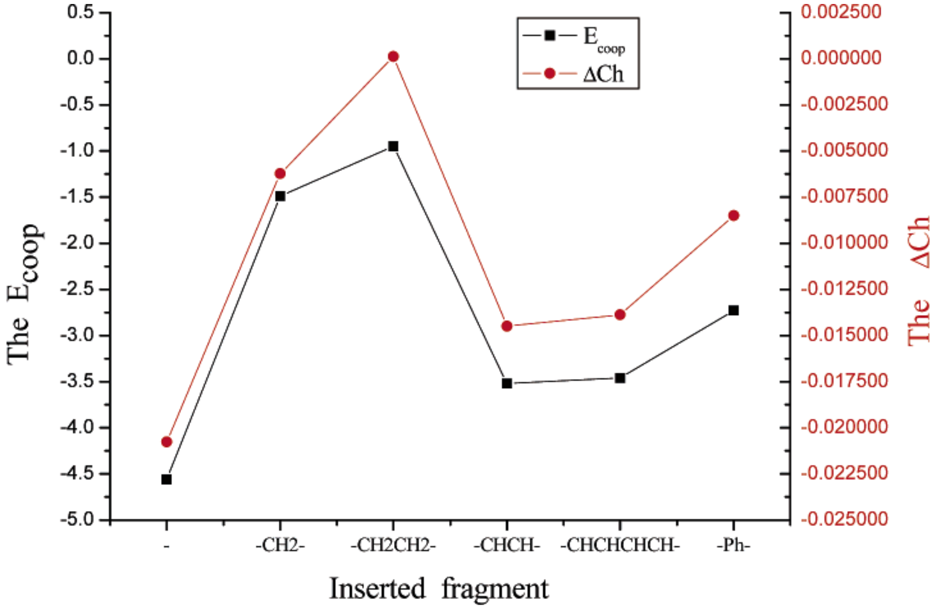


Figure 4. Graph of the cooperative energy and of the ΔCh in O atoms from *c*-NMF molecules with various inserted fragments.

TABLE 4: Energies of Hydrogen Bond 1 (E_{HB1}) in the Modified *c*-NMF Trimers and Their Cooperative Energies (E_{coop1})

inserted fragment		$-CH_2-$	$-CH_2-CH_2-$	$-CH=CH-$	$-CH=CH-CH=CH-$	$-Ph-$
E_{HB1} (kJ/mol)	−32.36	−20.04	−19.80	−34.02	−37.08	−28.56
E_{coop1} (kJ/mol)	−4.56	−1.49	−0.95	−3.52	−3.46	−2.73

TABLE 5: Calculated Harmonic Frequencies and Intensities of C=O and N−H Bonds in *c*-NMF Oligomers

inserted fragment	N−H frequencies/ intensities in the dimer	N−H frequencies/ intensities in the trimer	C=O frequencies/ intensities in the dimer	C=O frequencies/ intensities in the trimer
$-CH_2-$	3520.15	3512.32	1801.71	1748.14
	410.932	428.799	172.874	358.918
$-CH_2CH_2-$	3521.18	3509.077	1790.53	1787.42
	408.089	444.692	209.52	202.681
−CHCH−	3423.06	3382.2	1728.13	1723.89
	902.865	1537.23	114.545	65.8002
−CHCHCHCH−	3430.7	3308.29	1722.43	1711.15
	1099.14	2005.82	148.219	147.535
$-C_6H_4-$	3465.63	3434.97	1726.21	1718.16
	887.438	1156.74	424.979	401.697

TABLE 6: Electronic Charge on the O Atom at the Terminus of the Modified *c*-NMF Monomers (Ch_{ouncoop}) and Dimers (Ch_{ocoop})

inserted fragment		$-CH_2-$	$-CH_2-CH_2-$	$-CH=CH-$	$-CH=CH-CH=CH-$	$-Ph-$
Ch_{ouncoop}	−0.347492	−0.248809	−0.257372	−0.324427	−0.303839	−0.292249
Ch_{ocoop}	−0.368265	−0.255037	−0.257258	−0.338931	−0.317707	−0.300745
ΔCh	−0.020773	−0.00623	0.000114	−0.014504	−0.013868	−0.008496

TABLE 7: Electronic Charge Distributed on the H, N, and O Atoms at the Termini of the *c*-NMF Oligomers

	H	N	O
monomer	0.125222	−0.132567	−0.347492
dimer	0.154589	−0.129310	−0.368265
trimer	0.156291	−0.123638	−0.374948
tetramer	0.156803	−0.122758	−0.378074
pentamer	0.157327	−0.122784	−0.378815

TABLE 8: Energies of the Frontier Orbitals of the *c*-NMF Oligomers

	monomer	dimer	trimer	tetramer	pentamer
HOMO	−0.26302	−0.24014	−0.22971	−0.22657	−0.22265
LUMO	0.01873	−0.00672	−0.01594	−0.01981	−0.02324

oligomer grows larger. Thus, we find that the cooperative effect of hydrogen bonding in *c*-NMF oligomers is essentially an electronic inducing effect, and we posit the following mechanism as explanation. First, the electrostatic attractive force between two *c*-NMF molecules will pull them close to each other. After a hydrogen bond is formed between the C=O and N−H group, electronic charge will transfer from the C=O in one *c*-NMF molecule to the N−H in the other *c*-NMF through the hydrogen bond. Such a charge transfer process will influence the charge distribution in these two molecules themselves. In the *c*-NMF molecule that acts as the hydrogen bond acceptor, the charge lost from the C=O group will be partially compensated by a transfer of electronic charge from the N−H group of the molecule. This results in an N−H group with an increased positive charge, making it a better hydrogen bond donor, and a C=O group with an increased negative charge, making it a better hydrogen bond acceptor. Thus, the *c*-NMF dimer will be a more effective hydrogen bond acceptor and donor than the monomer. This result will generalize, so that larger *c*-NMF oligomers will be better acceptors and donors than smaller ones. The coopera-

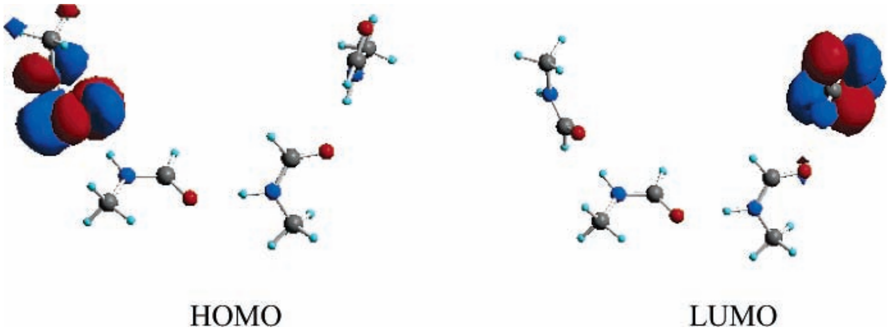


Figure 5. The HOMO and the LUMO of the tetramer of *c*-NMF.

tive effect of hydrogen bonding, then, is cumulative and results in stronger hydrogen bonds as the oligomers get larger. Note, however, that the intermolecular charge transfer brought about by hydrogen bond formation is relatively weak, and the intramolecular charge transfer process from the N—H group to the C═O group will gradually weaken. This will effectively limit the degree of the cooperative effect, as has been observed with β^3 nanotubes.[5]

Another factor that might influence the cooperative effect of hydrogen bonding is the frontier molecular orbitals of the *c*-NMF oligomers. The calculated energies of the frontier orbitals of the *c*-NMF oligomers are listed in Table 8. The energy of the highest occupied molecular orbital (HOMO) is gradually increasing and the energy of the lowest unoccupied (LUMO) is gradually decreasing with the growth of the oligomer. Furthermore, as shown in Figure 5, the HOMO of the supramolecule is primarily localized at the C═O terminus of the *c*-NMF molecule, while the LUMO is primarily localized at the other terminus. These characteristics of the frontier orbitals will make the larger oligomers form stronger hydrogen bonds than smaller ones, because the gap between HOMO and LUMO will be shortened for larger oligomers, thus facilitating the charge transfer process. Therefore, the variation of the supramolecular frontier orbitals will effectively strengthen the cooperative effect of hydrogen bonding.

Conclusion

The charge transfer mechanism of the cooperative effect of hydrogen bonding in *cis*-*N*-methylformamide oligomers is studied in this paper. The electronic structures and the energies of the hydrogen bonds in *c*-NMF oligomers were calculated using the B3LYP/cc-pVTZ method. Profound cooperative effect was observed in the computational results. By inserting molecular fragments into the *c*-NMF trimer, the charge flow between the N—H and C═O groups in the *c*-NMF molecule was found to be the essential driving force for the cooperative effect of hydrogen bonds. Further analysis of the frontier molecular orbitals of the *c*-NMF oligomers and the electronic distribution in O, H, and N atoms supported this conclusion. On this basis, we have detailed a charge-flow mechanism for the cooperative effect of hydrogen bonding.

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