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COOPERATIVITY IN CHAIN-LIKE AND RING-LIKE NETWORKS OF THREE-CENTERED HYDROGEN BONDS

Dayessi Rivero*, Daniel Madock*, Miguel Montero*, Ruben D. Parra†

Department of Chemistry and Biochemistry, DePaul University, Chicago, IL 60614

Abstract

Hydrogen bond cooperativity in chain-like and ring-like networks of bifurcated or three-centered hydrogen bonded systems is examined via density functional and ab initio methods. Up to twelve molecules of diformamide are considered to model three-centered hydrogen bond interactions of the A_1…H…A_2 type in which one unit donates one hydrogen bond while an adjacent unit has two acceptors of the hydrogen bond. Similarly, up to twelve molecules of carbonic acid are considered to model three-centered hydrogen bonds of the H_1…A…H_2 type in which one unit donates two hydrogen bonds while an adjacent unit has one acceptor of the two hydrogen bonds. Changes in the average dissociation energies with increasing size of the networks are used as one indicator of hydrogen bond cooperativity. Other indicators of cooperativity used here include the hydrogen bond distances, and the N-H or O-H stretching and bending vibrational frequency modes. It is found that cooperative enhancement tends to be larger for the H_1…A…H_2 network over its A_1…H…A_2 counterpart. For example, for n = 12, there is a 58% increase in the dissociation energy per bifurcated H bond in the DFA ring-like network compared with a 77% increase in its CA counterpart. Similarly, for n = 12, there is a 50% increase in the average dissociation energy in the DFA chain-like network compared with a 62% increase in its CA counterpart.

†corresponding author: rparral@depaul.edu

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Introduction

Hydrogen bond (H bond) cooperativity is typically understood as the non-additive enhancement of an H bond upon the formation of an additional H bond with either the proton donor or proton acceptor of the first H bond[1-4]. Given the ubiquitous and influential role that hydrogen bonds play in nature, researchers have devoted considerable amount of efforts to investigate systematically the nature and extent of H bond cooperativity in a great variety of molecular systems[5-12]. Most of this research has been on intermolecular systems containing the more common two-centered H bonds with one proton donor and one proton acceptor. Examples of cooperative effects in intramolecular two-centered H bonds have also been reported[13].

Some attention to H bond cooperativity on intermolecular as well as intramolecular three-centered H bonds has also been given, especially over the last two decades[14-19]. One type of three-centered H bonds involves a hydrogen atom and two acceptor atoms, A_1…H…A_2, while another type involves two hydrogen atoms and an acceptor atom, H_1…A…H_2. For example, cooperative enhancement of a three-centered H bonds of the A_1HA_2 type was computationally investigated in linear chains of molecules of diformamide, DFA, each in the trans-trans conformation[18]. This work demonstrated significant cooperativity as revealed for example in a 47% increase of the average electronic dissociation energy from 9.88 kcal/mol in the dimer to 14.57 kcal/mol in the DFA decamer. The DFA dissociation energies were corrected for basis set superposition error (BSSE-corrected) and calculated at the MP2/6-31+G(d)//B3LYP level. An examination of cooperative enhancement of a three-centered H bond of the H_1AH_2 type was reported for ring-like networks of up to nine carbonic acid, CA, molecules each in its trans-trans conformation[19]. For the CA ring-like system, the electronic dissociation energy per bifurcated hydrogen bond increases from 12.93 kcal/mol in the dimer to 22.52 kcal/mol in the nonamer which reveals a substantial 74% cooperative increase in this H_1AH_2 three-centered H bond interaction. The CA dissociation energies were BSSE-corrected and calculated at the MP2/6-31+G(d)//B3LYP/6-311+G(d) level.

In this paper, we expand upon the previous work on DFA chain-like and CA ring-like H bond cooperativity by examining the cooperative enhancement in the corresponding DFA ring-like and CA chain-like three-centered H bond networks. All calculations in this study are carried out at the same levels of theory as those in the previous studies to facilitate comparison[18, 19].

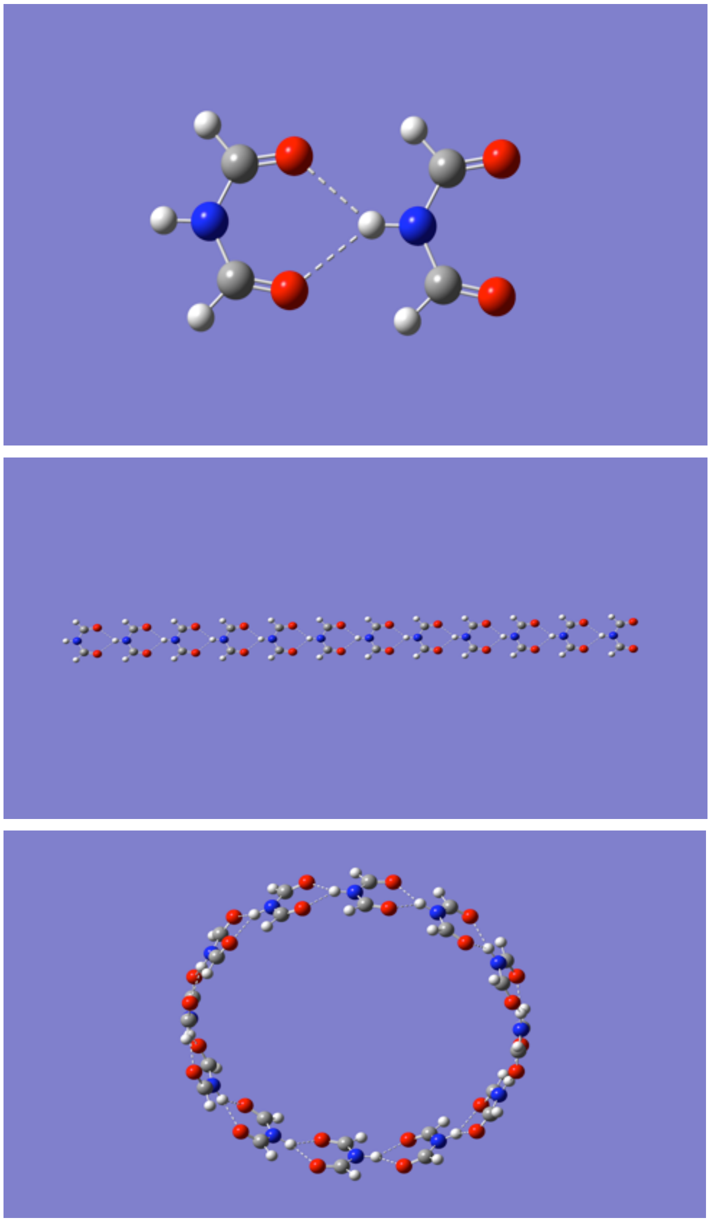
Methodology

All computations were performed with the Gaussian 16 program[20]. Visual representation and animation of the results were made using the Gaussview software[21]. Specifically, the geometries and vibrational frequencies of the various diformamide, DFA, ring-like networks were optimized with the B3LYP/6-31+G(d) model. The optimized geometries were used to compute the electronic interaction energies at the MP2/6-31+G(d) level of theory. Similarly, the geometries and vibrational frequencies of the various carbonic acid, CA, chain-like networks were optimized with the B3LYP/6-311+G(d) model. The optimized geometries were then used to compute the corresponding electronic interaction energies at the MP2/6-31+G(d) level of theory. Interaction energies were corrected for basis-set superposition error (BSSE) using the counterpoise method[22]. The levels of theory used in this paper were chosen to facilitate comparison with the previously published work on the pertinent systems. In particular, prior work showed that the interaction energies calculated at the MP2/6-31+G(d) level were very close to those obtained at the MP2/6-311++G(2d,2p) for both DFA and CA systems[18, 19]. In particular, the MP2/6-31+G(d) interaction energy for the DFA dimer was also remarkably close to that obtained at the MP4(SDTQ)/6-31+G(d) level.

Results and Discussion

In general, the strength of a given hydrogen bond, D-H…A, can be gauged with the help of several indicators. On geometric grounds, for example, the covalent D-H distance in the H bond donor tends to lengthen while the intermolecular separation between the H bond donor, D-H, and the acceptor, A, tends to shorten with increasing strength of the H bond. On spectroscopic grounds, for instance, the vibrational D-H stretching frequencies tends to shift to lower frequencies (red shift), while the corresponding D-H bending frequencies tend to shift to higher frequencies (blue shift). A red shift of the D-H stretching frequencies correlates with an elongation of the D-H bond length requiring less energy for stretching. A blue shift of the D-H bending frequencies can be traced down to the deviation from the H bond interaction line brought about by the bending modes, effectively breaking the interaction and thus requiring more energy as the H bond gets stronger. Lastly, one direct indicator of H bond strength is the energy required to break the H bond interaction itself. Accordingly, the larger the dissociation energy, then the stronger the H bond is. In this study, we use the aforementioned geometric, spectroscopic, and energetic indicators to gauge the strength of the three-centered H bonds in the DFA and CA networks as a function of both the number of molecules in a given network and the nature of the network, chain-like or ring-like.

Figure 1: B3LYP/6-31+G(d) optimized geometries for DFA networks: dimer (top); chain-like dodecamer (middle); ring-like dodecamer (bottom).



Diformamide Networks

A DFA molecule in its trans-trans conformation may interact with another DFA molecule via a three-centered H bond interaction of the $A_1 \ldots H \ldots A_2$ type as shown in Figure 1. Here the two acceptor groups are the two carbonyl groups in the H bond acceptor molecule, while the hydrogen comes from the N-H group in the H bond donor molecule. In a previous work, the chain-like networks of DFA were each shown to belong to the C_{2v} point group[18]. In this work, the optimized ring-like networks of DFA belong to the C_{nh} point group, with n representing the number of molecules in the ring. In this study, also, the number of molecules in the ring-like or the chain-like structures varies in even numbers from n = 4 to n = 12. Cooperative enhancement of the three-centered H bond in each case is examined relative to the strength of the H bond in the DFA dimer. The optimized structures for n = 12 are shown also in Figure 1 for each network type.

The H bond distances are shown in Table 1 for the dimer and the two types of DFA networks. Because of symmetry, the two H bond distances in a given three-centered H bond have the same values. It should be noted, however, that the strength of a dimer interaction in a chain-like DFA network depends on the position of the dimer itself in the network. Consequently, three H bond distances are reported in Table 1 for a chain-like network of size n to better capture the variety of dimer interaction strengths present: a) the longest H bond distance (Chain-Longest NH…O) corresponding to the rightmost dimer interaction in Figure 1 ($DFA_{n-1} \rightarrow DFA_n$); b) the shortest H bond distance (Chain-Shortest NH…O) corresponding to the dimer interaction at the middle of the DFA network; and c) the average H bond distance (Chain-Average NH…O) corresponding to the H bond distance averaged over all n-1 distinct H bond distances in the DFA chain-like network of size n. Evidence of cooperative strengthening of the H bond interaction in the DFA chain-like network is seen in the shortening of the corresponding H bond distances. The extent of the shortening appears much more substantial for the shortest H bond distances than in the longest ones. Similarly, cooperative strengthening of the H bond interaction in the DFA ring-like network is seen in the shortening of the H bond distance in each network. The exception is the tetrameric ring, which shows a minor H bond distance elongation that can be thought of as resulting from the relatively small size of the ring. Indeed, the folding of the chain-like network into

Table 1: B3LYP/6-31+G(d) H bond distances, N-H…O, in chain-like or ring-like networks of up to twelve molecules of diformamide, DFA. Distances in Angstroms, Å.*

	DFA Network					
	2	4	6	8	10	12
Chain-Longest NH…O	2.279	2.210	2.201	2.199	2.197	2.196
Chain-Shortest NH…O	2.279	2.159	2.124	2.108	2.101	2.097
Chain-Average NH…O	2.279	2.187	2.155	2.138	2.128	2.122
Ring NH…O	2.279	2.282	2.163	2.129	2.115	2.106

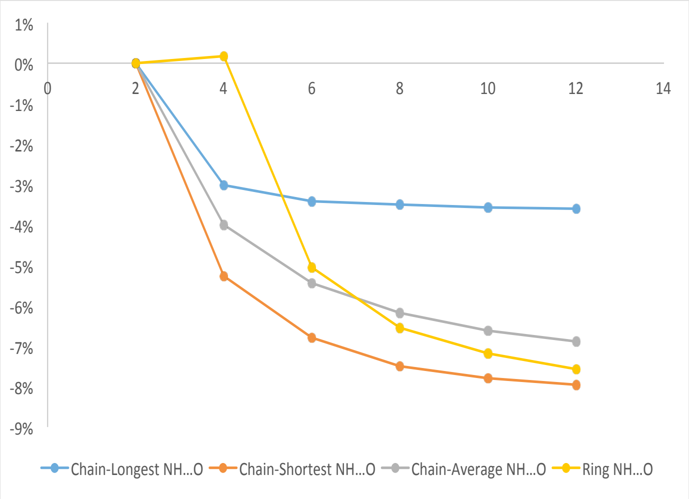
* Chain data from reference 18.

the corresponding ring-like network allows for the formation of an additional H bond upon ring closure. Ring formation also brings more closely all individual units, which would increase repulsive or steric interactions among themselves. Such increase in steric interactions is expected to be more prominent in the small-size ring networks. For example, the N…N distance in the ring-like DFA tetramer (3.934 Å) is 14.4% smaller than that in the DFA dimer (4.595 Å). For the largest ring-like DFA dodecamer, the N…N distance (4.316 Å) is only 6.1% smaller than that in the DFA dimer. Accordingly, the cooperative enhancement of the H bond interaction in the DFA ring-like network should counteract the steric interactions resulting upon ring formation. In the case of the tetrameric ring, however, the noted H bond distance elongation suggests that the H bond cooperativity in this system is unable to completely offset the steric strain.

The percent changes in the H bond distances are shown in Figure 2 for the two types of DFA networks. Inspection of Figure 2 reveals that the longest H bond distance in the chain-like network exhibits the smallest contraction (-3.6%) and converges much more quickly with network size. The percent contractions of the average H bond distance are closer to those of the shortest H bond distances indicating greater cooperative enhancement for the interior dimers in the chain-like network. Indeed, each interior molecule acts simultaneously as H bond donor and acceptor, while the leftmost can act only as H bond donor, and the rightmost molecules as H bond acceptor. The percent contractions for the shortest H bond distances in the chain-like networks are consistently larger than those in the ring-like networks, although the changes in the ring-like networks tend to approach those of the chain-like counterparts to the point that for n = 12, both contractions seem to converge to a decrease of about 8% in the H bond distances.

Evidence of cooperative strengthening of the H bond may also be revealed in the elongation of the covalent N-H bond length relative to its value in the DFA donor molecule in the dimer (1.019 Å). Interestingly, the corresponding N-H bond length in both kinds of networks varies little with network size exhibiting a maximum elongation (for n = 12) of less than 1% relative to its value in the dimer. In particular, the N-H bond length in the ring-like dodecamer is 1.027 Å (a 0.78% N-H lengthening). The same result is calculated for the N-H bond length of the DFA molecule in the middle of a chain-like network.

Figure 2: Percent changes in the H bond distances (N-H…O) as a function of DFA network size.



Further evidence of H bond cooperativity can be seen in the N-H stretching and bending frequencies listed in Table 2 for the two types of DFA networks considered. It is important to note that in the previous work for the chain-like DFA structures[18], the N-H bending frequencies were not listed, so we carried out the calculations to be able to present the results in this work. In particular, Table 2 lists the most intense N-H stretching and bending frequencies. The N-H stretching frequencies shift to the red with increasing size of the networks and essentially to the same extent for both the chain-like and the ring-like structures although the rate of change decreases with the size of the network. The ring-like tetramer actually exhibits a smaller shift to the red by about 15 cm^{-1} suggesting a somewhat weaker H bond interaction than that in the chain-like tetramer. The largest shifts occur for the networks of size n = 12, with a shift to the red of 122 cm^{-1} (chain-like) and of 121 cm^{-1} (ring-like). These shifts to the red amount to an absolute change of about 3.5% in the N-H stretching frequency relative to the dimer. In contrast, the N-H bending frequencies exhibit a shift to the blue with increasing network size for both the chain-like and the ring-like structures although the rate of change decreases with the size of the network. The shifts to the blue of the N-H bending frequencies are smaller than the N-H stretching counterparts, with the largest shifts to the blue seen in the networks of size n = 12, with a shift to the blue of 36 cm^{-1} (chain-like) and of 39 cm^{-1} (ring-like). These shifts to the blue amount to an absolute change of about 2.4% in the N-H bending frequency relative to the dimer. Interestingly, the blue-shifting of the N-H bending frequencies are slightly larger in the ring-like clusters. Graphical representations of the percent changes in the N-H stretching and bending frequencies are shown in Figure 3 and Figure 4 respectively for both types of DFA networks.

Cooperative enhancement of the three-centered H bonds in the DFA networks can be directly gauged by examining how the dissociation energy per bifurcated H bond changes with the size and type of network. Accordingly, for the chain-like network, the electronic dissociation energy averaged over all bifurcated H bonds in the system is defined as

$$\langle \Delta E \rangle_{chain} = \frac{\Delta E_n}{(n-1)}$$

Table 2: B3LYP/6-31+G(d) N-H stretching and bending frequencies, in chain-like or ring-like networks of up to twelve molecules of diformamide, DFA. Frequencies in cm^{-1}.

	DFA Network					
	2	4	6	8	10	12
N-H stretching						
Chain-like*	3530	3472	3441	3424	3414	3408
Ring-like	3530	3487	3442	3424	3415	3409
N-H bending						
Chain-like*	1540	1560	1568	1573	1575	1576
Ring-like	1540	1566	1574	1577	1578	1579

*N-H stretching chain-like network data from reference 18. However, N-H bending were not listed in reference 18, so they were obtained in this work.

Where ΔE_n is obtained as the negative of the BSSE-corrected interaction energy for the network containing n molecules, and (n-1) is the corresponding number of bifurcated H bonds present in the chain-like network. ΔE_n is then the electronic energy required to dissociate a network into its n molecular components by breaking all the (n-1) bifurcated H bonds that hold the system together. Consequently, $<\Delta E_n>$ may be understood as the energy required to dissociate a DFA dimer that represents an average of all the dimers in a DFA network. Similarly, for the ring-like network, the definition is as follows

$$\langle \Delta E \rangle_{ring} = \frac{\Delta E_n}{n}$$

Where in this case, the number of bifurcated H bonds, n, equals the number of molecules in the network. Table 3 shows the corresponding dissociation energies per bifurcated H bond for the chain-like and ring-like DFA networks considered. The three different values reported for the chain-like network in Table 3 corresponds to three different DFA dimers representing the three different H bond distances reported in Table 1. In particular, each of the $<\Delta E_n>_{chain}$ average values listed in Table 3 represents the dissociation energy of a dimer that is an average of all the dimers in the chain-like network of size n having a H bond conforming to the NH…O average distances listed in Table 1. A linear relationship is found for the DFA chain dissociation energies with a very high coefficient of determination, R^2, as displayed below.

$$\langle \Delta E \rangle_{chain} = -31.352 R_{NH...O} + 81.226 \qquad R^2 = 0.996$$

Although the equation above was obtained using the $<\Delta E_n>_{chain}$ average values and the corresponding chain-average NH…O distances in Table 1, this equation provides a convenient means to estimate the strongest and weakest $<\Delta E_n>_{chain}$ values using respectively the chain-shortest and chain-longest NH…O distances in Table 1. The estimated $<\Delta E_n>_{chain}$ values are also displayed in Table 3. Inspection of Table 3 reveals that $<\Delta E_n>_{chain}$ increases with n, and that the increases parallel the strength of the interaction. That is, the largest increases are seen for the strongest interactions, while the smallest increases are seen for the weakest interactions. The corresponding $<\Delta E_n>_{ring}$ increases with n follow closely those of the strongest chain network counterparts. This result demonstrates that a three-centered H bond in the DFA ring is generally stronger than its counterpart in the chain-like network. The percent changes in dissociation energy, relative to the dimer, for the two network types as a function of size are presented in Figure 5 which reveals the substantial enhancement of the three-centered H bond in either network as it increases in size. Figure 5 shows also that the increase in $<\Delta E_n>_{chain}$ weakest reaches plateau (a 25% increase for

Table 3: MP2/6-31+G(d)//B3LYP/6-31+G(d) electronic dissociation energy per bifurcated H bond in DFA chain-like $<\Delta E_n>_{chain}$ or ring-like $<\Delta E_n>_{ring}$ networks of size n. Energies in kcal/mol.

		DFA Network		
n	$<\Delta E_n>_{ring}$	$<\Delta E_n>_{chain}$ average[a]	$<\Delta E_n>_{chain}$ weakest[b]	$<\Delta E_n>_{chain}$ strongest[b]
2	9.88	9.88	9.88	9.88
4	12.17	12.47	11.89	13.34
6	14.24	13.59	12.17	14.67
8	15.03	14.20	12.24	15.31
10	15.40	14.57	12.29	15.65
12	15.62	14.83	12.31	15.84

[a] Data for size up to *n* = 10 from reference 18. Value for size *n* = 12 was not calculated in reference 18, so it
obtained in this work.

Figure 3: Percent changes in the N-H stretching frequencies as a function of DFA network size.

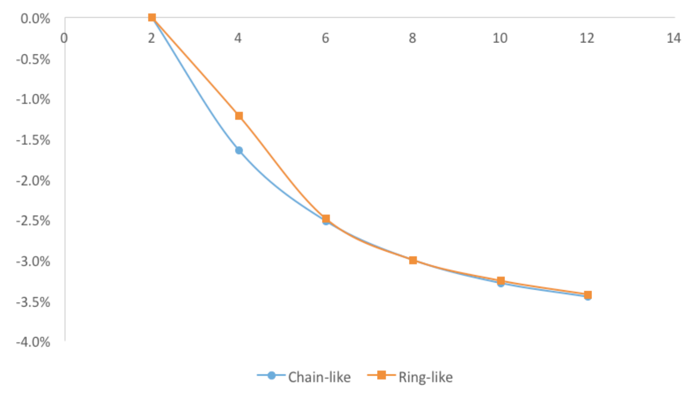


Figure 4: Percent changes in the N-H bending frequencies as a function of DFA network size.

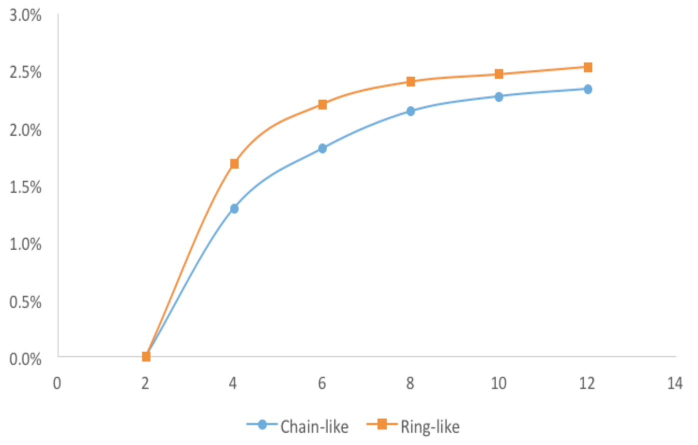
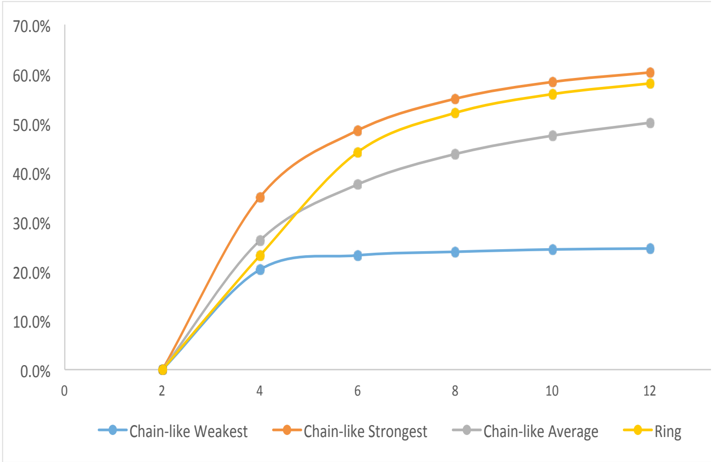


Figure 5: Percent changes in the electronic dissociation energies per bifurcated H bond (average dissociation energy) as a function of DFA network size.



n = 12) much more quickly than any of the other systems. For n = 12, there is a 58% increase in the $<\Delta E_n>_{ring}$ which is close to the 60% increase in the $<\Delta E_n>_{chain}$ strongest but well above the 50% increase in the corresponding $<\Delta E_n>_{chain}$ average.

Carbonic Acid Networks

A CA molecule in its trans-trans conformation may interact with another CA molecule via a three-centered H bond interaction of the H_1…A…H_2 type as shown in Figure 6. Here the two donor groups are the O-H groups in the H bond donor molecule, while the acceptor comes from the C=O group in the H bond acceptor molecule. In a previous work, the ring-like networks of CA were each shown to belong to the C_{nh} point group with n representing the number of molecules in the ring, while the minimum energy structure of the CA dimer was shown to be of C_s symmetry[19]. In fact, a CA dimer with C_{2v} symmetry was shown to be a saddle point of second order. In this study, it is found that all chain-like CA networks of C_{2v} are indeed saddle points (second order for dimer and tetramer, and first-order saddle points for the larger networks) at the B3LYP/6-311+G(d) theoretical model. Perturbing the small imaginary frequency and optimizing the geometries resulted in optimized chain-like CA networks of C_s symmetry and with no imaginary frequencies. As with the DFA networks, the number of molecules in the ring-like or the chain-like structures varies in even numbers from n = 4 to n = 12. Cooperative enhancement of the three-centered H bond in each case is examined relative to the strength of the H bond in the CA dimer. The optimized structures for n = 12 are shown also in Figure 6 for each network type. Moreover, the chain-like structure is also shown in Figure 6 to show the flattening of this type of CA network with increasing size.

The symmetric H bond distances are shown in Table 4 for the dimer and the two types of CA networks. Three H bond distances are reported in Table 4 for a chain-like network of size n to better capture the variety of dimer interaction strengths present: a) the longest H bond distance (Chain-Longest OH…O) corresponding to the rightmost dimer interaction in Figure 1 (CA_{n-1} à CA_n); b) the shortest H bond distance (Chain-Shortest OH…O) corresponding to the dimer interaction at the middle of the CA network; and c) the average H bond distance (Chain-Average OH…O) corresponding to the H bond distance averaged over all n-1 distinct three-centered H bond distances in the CA chain-like network of size n. Evidence of cooperative strengthening of the H bond interaction in the CA chain-like network is seen in the shortening of the corresponding H bond distances. The extent of the shortening appears much more substantial for the shortest H bond distances than in the longest ones. Similarly, cooperative strengthening of the H bond interaction in the CA ring-like network is seen in the shortening of the H bond distances even in the smallest tetrameric ring. Interestingly, the H bond cooperativity around the ring more than compensates for the unfavorable strain resulting from ring formation. For example, the C…C distance in the ring-like CA tetramer (3.679 Å) is 18.9% smaller than that in the CA dimer (4.528 Å). The steric strain tends to decrease with increasing network size as seen in the largest CA dodecamer with the C…C distance (4.192 Å) only 7.4% smaller than that in the dimer.

Table 4: B3LYP/6-311+G(d) optimized H bond distances, O-H…O, in chain-like or ring-like networks of up to twelve molecules of carbonic acid, CA. Distances in Angstroms, Å. *.

	CA Network					
	2	4	6	8	10	12
Chain-Longest OH…O	1.951	1.870	1.857	1.854	1.853	1.852
Chain-Shortest OH…O	1.951	1.825	1.784	1.765	1.756	1.750
Chain-Average OH…O	1.951	1.856	1.819	1.799	1.787	1.779
Ring OH…O	1.951	1.840	1.771	1.754	1.747	1.744

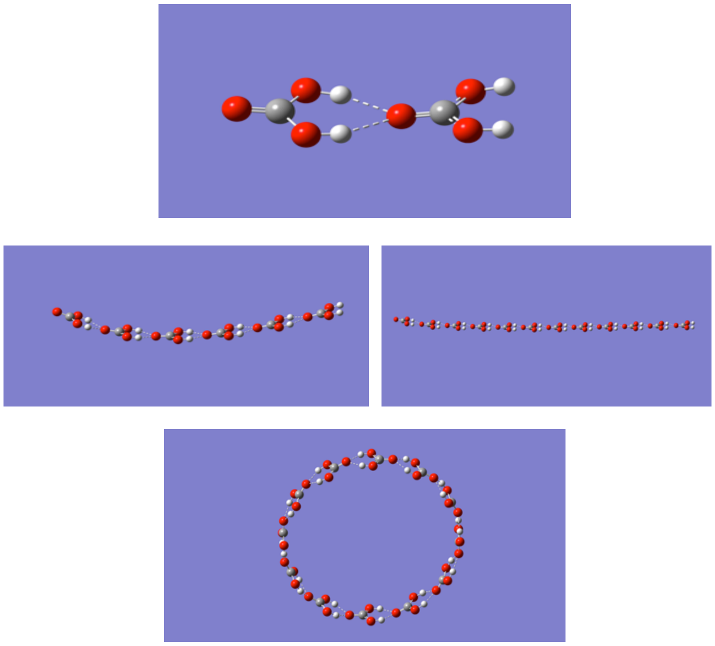
*Data for ring-like CA networks up to size n = 8 from reference 19; for larger sizes, n = 10 or 12, data obtained in this study.

The percent changes in the H bond distances are shown in Figure 7 for the two types of CA networks. Inspection of Figure 7 reveals that the longest H bond distance in the chain-like network exhibits the smallest contraction (-5.1%) and converges much more quickly with network size. The percent contractions of the average H bond distance are closer to those of the shortest H bond distances indicating greater cooperative enhancement for the interior dimers in the chain-like network. The percent contractions for the shortest H bond distances in the chain-like networks are consistently very close to those in the ring-like networks, and for n = 12, both contractions seem to converge to a percent decrease of about 11% in the H bond distances.

Evidence of cooperative strengthening of the H bond may also be revealed in the elongation of the covalent O-H bond length relative to its value in the CA donor molecule in the dimer (0.971 Å). The O-H bond elongations for the ring-like appear to converge to a maximum value of about 0.986 (a 1.5% increase). Essentially the same result is calculated for the O-H bond length of the CA molecule in the middle of a chain-like network.

Cross inspection of Figures 2 and 7 shows that the shortening of the H bond distances is larger in the CA networks than in their DFA counterparts suggesting a greater cooperative enhancement for the H_1…A…H_2 network over its A_1…H…A_2 counterpart.

Figure 6: B3LYP/6-311+G(d) optimized geometries for CA networks: dimer (top); chain-like hexamer and dodecamer (middle); ring-like dodecamer (bottom).



Moreover for the CA systems, the largest decreases in the H bond distances are seen in the CA ring-like networks, while for the DFA systems the largest decreases are those of the chain-like shortest NH…O H bond distances.

Table 5 lists the O-H stretching and bending frequencies for the two types of CA networks considered. It should be noted that in the previous work for the ring-like CA structures, the O-H bending frequencies were not listed, so we carried out the calculations to be able to present the results in this work. Moreover, the previous work considered ring-like clusters of up to nine molecules, so in this study we expanded the calculations to include ring-like systems of ten and twelve molecules. In particular, Table 5 lists the most intense O-H stretching and bending frequencies. The O-H stretching frequencies shift to the red with increasing size of the networks, although the rate of change decreases with the size of the network. Also, the ring-like structures consistently show the larger shifts even for the smallest tetramer structure. Thus, each of the three-centered H bonds in the tetramer appears to be strong enough to overcome the steric strain of bringing together the four CA molecules to form the ring. The O-H bending frequencies exhibit a shift to the blue with increasing network size for both the chain-like and the ring-like structures although the rate of change decreases with the size of the network. Interestingly, the blue-shifting of the O-H bending frequencies are slightly larger in the chain-like clusters of smaller size, n = 4 or n = 6, while for the larger sizes the blues shifts are virtually the same for both types of networks. Graphical representations of the percent changes in the O-H stretching and bending frequencies are shown in Figure 8 and Figure 9 respectively for both types of CA networks.

Figure 7: Percent changes in the H bond distances (O-H…O) as a function of CA network size.

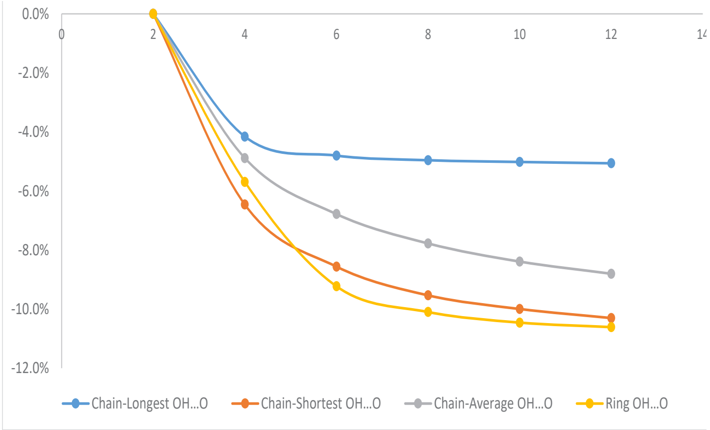


Figure 8: Percent changes in the O-H stretching frequencies as a function of CA network size.

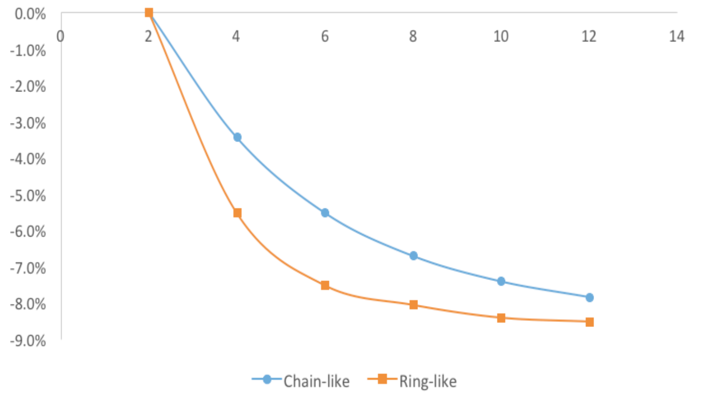


Table 6 shows the electronic dissociation energies per bifurcated H bond for the chain-like and ring-like CA networks considered. As in the DFA chain-like networks, a linear relationship is found for the CA chain dissociation energies with a very high coefficient of determination, R^2, as displayed below.

$$\langle \Delta E \rangle_{chain} = -46.791 R_{OH\ldots O} + 104.12 \qquad R^2 = 0.998$$

Although the equation above was obtained using the $<DE_n>_{chain}$ average values and the corresponding chain-average OH…O distances in Table 4, this equation is used to estimate the strongest and weakest $<\Delta E_n>_{chain}$ values using respectively the chain-shortest and chain-longest OH…O distances in Table 4. The estimated $<\Delta E_n>_{chain}$ values are displayed in Table 6. Inspection of Table 6 reveals that $<\Delta E_n>_{chain}$ increases with n, and that the increases parallel the strength of the interaction. That is, the largest increases are seen for the strongest interactions, while the smallest increases are seen for the weakest interactions. The corresponding $<\Delta E_n>_{ring}$ increases with n follow closely those of the strongest chain network counterparts. The percent changes in dissociation energy, relative to the dimer, for the two network types as a function of size are presented in Figure 10 which reveals the substantial enhancement of the three-centered H bond in either network as it increases in size. Figure 10 shows also that the increase in $<\Delta E_n>_{chain}$ weakest reaches plateau (a 31% increase for n = 12) much more quickly than any of the other systems. For n = 12, there is a 77% increase in the $<\Delta E_n>_{ring}$ which is close to the 78% increase in the $<\Delta E_n>_{chain}$ strongest but well above the 62% increase in the corresponding $<\Delta E_n>_{chain}$ average.

Cross inspection of Figures 5 and 10 corroborates the notion that cooperative enhancement tends to be larger for the H_1…A…H_2 network over its A_1…H…A_2 counterpart. For example, for n = 12, there is a 58% increase in the dissociation energy per bifurcated

Table 5: B3LYP/6-311+G(d) O-H stretching and bending frequencies, in chain-like or ring-like networks of up to twelve molecules of carbonic acid, CA . Frequencies in cm^{-1}.

	CA Network					
	2	4	6	8	10	12
O-H stretching						
Chain-like	3707	3579	3502	3458	3432	3416
Ring-like*	3707	3502	3428	3408	3395	3391
O-H bending						
Chain-like	1389	1423	1438	1445	1449	1451
Ring-like*	1389	1392	1432	1444	1448	1451

*O-H stretching ring-like network data from reference 19 for sizes up to n = 8. However, O-H bending were not listed in reference 19, so they were obtained in this work. Also obtained in this study are the data for the larger CA ring-like networks, n = 10 or 12.

H bond in the DFA ring-like network compared with a 77% increase in its CA counterpart. Similarly, for n = 12, there is a 50% increase in the average dissociation energy in the DFA chain-like network compared with a 62% increase in its CA counterpart. Moreover, the gap between the percent changes in $<\Delta E_n>_{ring}$ and $<\Delta E_n>_{chain}$ average tends to be much wider in the three-centered H bonds formed by CA.

Figure 9: Percent changes in the O-H bending frequencies as a function of CA network size.

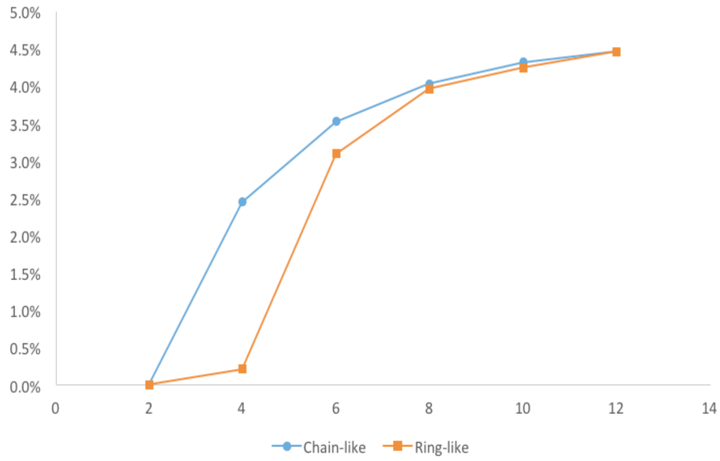


Figure 10: Percent changes in the electronic dissociation energies per bifurcated H bond (average dissociation energy) as a function of CA network size.

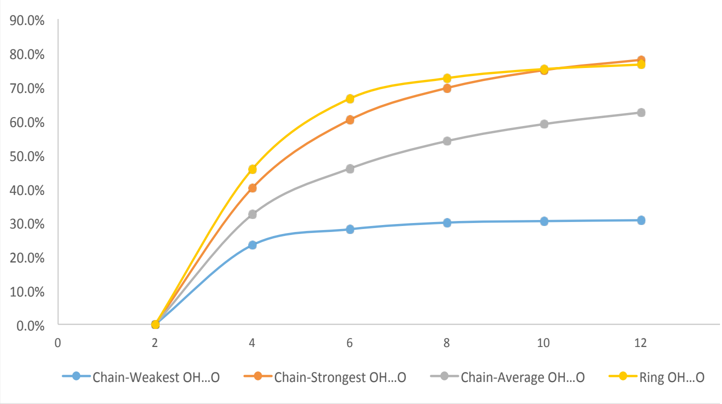


Table 6: MP2/6-31+G(d)//B3LYP/6-311+G(d) electronic dissociation energy per bifurcated H bond in CA chain-like $<\Delta E_n>_{chain}$ or ring-like $<\Delta E_n>_{ring}$ networks of size n. Energies in kcal/mol.

CA Network

n	$<\Delta E_n>_{ring}$ [a]	$<\Delta E_n>_{chain}$ average	$<\Delta E_n>_{chain}$ weakest[b]	$<\Delta E_n>_{chain}$ strongest[b]
2	12.93	12.93	12.93	12.93
4	18.85	17.12	15.95	18.13
6	21.53	18.86	16.55	20.72
8	22.31	19.91	16.81	21.94
10	22.66	20.56	16.86	22.62
12	22.83	21.00	16.90	23.01

[a] Data for size up to *n* = 8 from reference 19. Value for size *n* = 10 or 12 obtained in this work.

[b] Values estimated using the linear relationship between dissociation energies and H bond distances (see text).

It is worthwhile noting that the building dimer unit for the $H_1 \ldots A \ldots H_2$ network considered here (the CA dimer) exhibits a stronger three-centered H bond interaction than the building dimer unit for the $A_1 \ldots H \ldots A_2$ network (the DFA dimer). Therefore, cooperative enhancement of the three-centered H bonds appears to be larger for the system that has the stronger interaction to begin with. The stronger interaction in the CA dimer is evident from the calculated electronic dissociation energies of 12.93 kcal/mol (CA dimer) and 9.88 kcal/mol (DFA dimer). Also on geometrical grounds, in addition to the shorter H bond distance (1.950 Å in the CA dimer compared with 2.279 Å in the DFA dimer), the CA dimer has a much wider H bond angle (157° in the CA dimer compared with 141° in the DFA dimer). Furthermore, given the larger electronegativity of oxygen over nitrogen, the OH moiety in CA has a better H bond donor ability than the NH counterpart in DFA.

Conclusions

This paper reports on a comparative study of H bond cooperativity in chain-like and ring-like networks of three-centered H bonded systems formed by up to twelve molecules of either diformamide, DFA, or carbonic acid, CA. It is found that for both CA and DFA, the ring-like networks exhibit substantial cooperative enhancement with increasing network size. In contrast to the ring-like network, the strength of a dimer interaction depends on the position of the dimer itself in the network. Three distinct possibilities were considered, a dimer in the middle of the network (strongest), a terminal dimer (weakest), and an average of all (n-1) dimers in a chain-like network of size n. All these three possible dimers exhibit cooperative enhancement that is in proportion of their strength. It is found that when compared to the chain-like networks, the cooperative increase of the ring-like network H bonds follows closely the corresponding cooperative increase of the dimer in the middle of the network. Lastly, the extent of cooperative enhancement consistently appears larger for the CA ($H_1 \ldots A \ldots H_2$) network than it is for its DFA ($A_1 \ldots H \ldots A_2$) counterpart. The results presented here correspond to systems in the gas phase, therefore future studies that incorporate solvent effects are in order. Additional investigations including the many-body contributions to the binding energies are also in order. It is also in order to carry out a comprehensive comparison of the relative cooperativity in $H_1 \ldots A \ldots H_2$ and $A_1 \ldots H \ldots A_2$ networks (chain-like and ring-like) through many appropriate model systems to examine the generality of the results presented here.

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