

Bending effect on the stabilities of quadruple hydrogen bonding systems: theoretical study of a series of self-constituted quadruple hydrogen bonded complexes ($C_9H_9N_5O_2$)₂

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Received 5th August 2005, Accepted 12th September 2005

First published as an Advance Article on the web 26th September 2005

A series of self-constituted quadruple hydrogen bonded (QHB) complexes ($C_9H_9N_5O_2$)₂ has been designed and studied systematically using density functional theory (B3LYP/6-31G**) and the Morokuma energy decompose method (HF/6-31G**). Despite very similar structures of these systems, the interaction energies fluctuate significantly from 22.33 to 88.30 kcal mol⁻¹. To explain this somewhat unexpected observation, several doubly hydrogen bonded (DHB) systems were designed and a “bending effect” hypothesis was presented. According to the hypothesis, the spatial arrangement of hydrogen bonds is less important than their intensity arrangement.

1. Introduction

It is well known that hydrogen bonds play a very important role in forming the double helix of DNA¹ and the secondary structure of proteins.² Multiple-hydrogen bonded systems, in which several hydrogen bonds act together, exhibit a stability that is larger than the sum of the single hydrogen bonds.³ This kind of cooperativity has been demonstrated in the base pairs of DNA. In these base pairs, the arrangement of the hydrogen bond donor (D) and acceptor (A) determines the total stability as well as the cooperative contribution to the total stability. Many hypotheses and theories have been proposed to explain the reason why different arrangements of D and A cause different stabilities.

One notable theory in doubly hydrogen bonded (DHB) systems, proposed by Gilli *et al.*, is resonance-assisted hydrogen bonding (RAHB).⁴ It can be simply described as a cyclic arrangement of hydrogen bonds that allows each to strengthen the other (Fig. 1). Another is Jorgenson's secondary interaction hypothesis (SIH),⁵ which correlates with the stability of many synthesized QHB. This theory mainly considers electrostatic interactions between neighboring hydrogen bond sites, and it puts forward that, for a given approximate strength of primary attractive interactions, secondary electrostatic interactions usually determine the stabilities of complexes (Fig. 1). However, the two theories are incompatible in nature: a complex with cyclic arrangement of hydrogen bond will automatically have a pair of repulsive secondary interactions.

The former theory (RAHB) was proved by Guerra *et al.*,⁶ and further work even estimated its contribution to the total stabilization of base pairs.⁷ As for quadruple hydrogen bonded (QHB) systems, Jorgenson's SIH can only rationalize part of them, and it was criticized by Popelier *et al.*⁸ Therefore, we turned our attention to QHB complexes and tried to find a reasonable hypothesis to fit them. Based on this thought, a series of self-constituted quadruple hydrogen bonded (QHB) complexes ($C_9H_9N_5O_2$)₂ are designed in light of the AADD and ADAD models. These systems have very similar structures but large interaction energy (IE) differences. A rational explanation is presented to account for the significant difference in IE between them.

2. Models and methods

Nine self-constituted QHB isomers of ($C_9H_9N_5O_2$)₂ (Fig. 2) are designed, with little structural difference to each other. All the QHB systems are controlled with C_{2h} symmetry based on the following two considerations: (1) systems are self-constituted, which should have C_2 axis; (2) all the QHB complexes are conjugated and the existence of intra-molecular hydrogen bonds will ensure all the atoms are on the same plane (except for the hydrogen atoms in the methyl groups). (Fig. 2)

Considering the size of the systems to be analyzed, it is appropriate to use the B3LYP/6-31G** method.^{9,10} The GAUSSIAN 98 program¹¹ is used for structural optimization and energy calculation for all QHB complexes. In order to further analyze the component of the IE between these molecules, the Morokuma method with the same basis sets is used to decompose the total IE into five parts: electrostatic interaction (ES); exchange repulsion (EX); polarization interaction (PL); charge transfer or electron delocalization interaction (CT); and coupling term (MIX). All the energy decomposition calculations were done using the GAMESS 94 program.^{12–14} Moreover, because most of these QHB complexes can be considered as an assembled system with two equal DHB complexes (see Fig. 3), the corresponding DHB complexes are also studied to explore the reason why these QHB systems with similar structures have different interaction energies. In order to ensure the energy data of corresponding QHB and DHB complexes are comparable, the structures of DHB complexes are optimized using the same method and basis set as used in QHB complexes, as well as the same methods for evaluating interaction energies and decomposed energy sites.

In addition, the interaction energies of all the DHB complexes with substructures are calculated in order to approximately evaluate the IEs of a single hydrogen bond using the same method and basis set.

3. Results and discussion

All self-constituted QHB complexes of ($C_9H_9N_5O_2$)₂ are optimized by the B3LYP/6-31g** method except for one of these isomers, ADAD-6. The ADAD-6 structure can not be obtained by optimization because the complex with the less stable

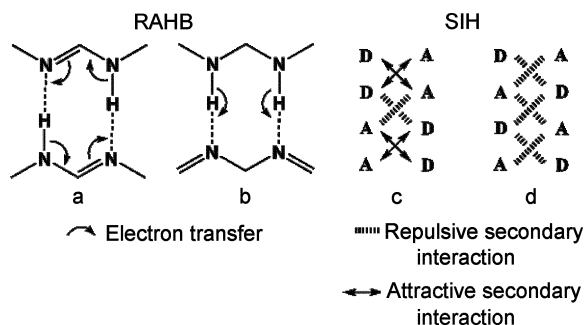


Fig. 1 RAHB: DHB complexes with different HB orientation will be energetically favorable (a), or else unfavorable if with the same HB orientation (b). SIH: QHB complexes with the same HB orientation will be energetically favorable (c), or else unfavourable if with different HB orientation (d).

enol configuration always shifted to its tautomer with a more stable keto configuration, which results in the transformation from ADAD-6 to ADAD-1. The total energies (E) and interaction energies (IE) of the eight self-constituted QHB isomers are listed in Table 1. The lengths (d) and angles (A) of the hydrogen bond of these systems are also tabulated.

From Table 1, we find that the IE increases with the shortening of the hydrogen bond length in the AADD group, and the same phenomenon is also observed in the ADAD group. However, if we mix all eight isomers together and perform a similar analysis, the aforementioned observation no longer holds. For example, ADAD-4 has a shorter bond length and less IE than AADD-1 and AADD-2. It seems to show that the IE varies not only with hydrogen bond length but also the arrangement of hydrogen bonds. Coincidentally, these results apparently support Jorgenson's SIH theory. Given the similar structures, AADD complexes with approximately equal hydrogen bond lengths usually have larger IEs than ADAD complexes.

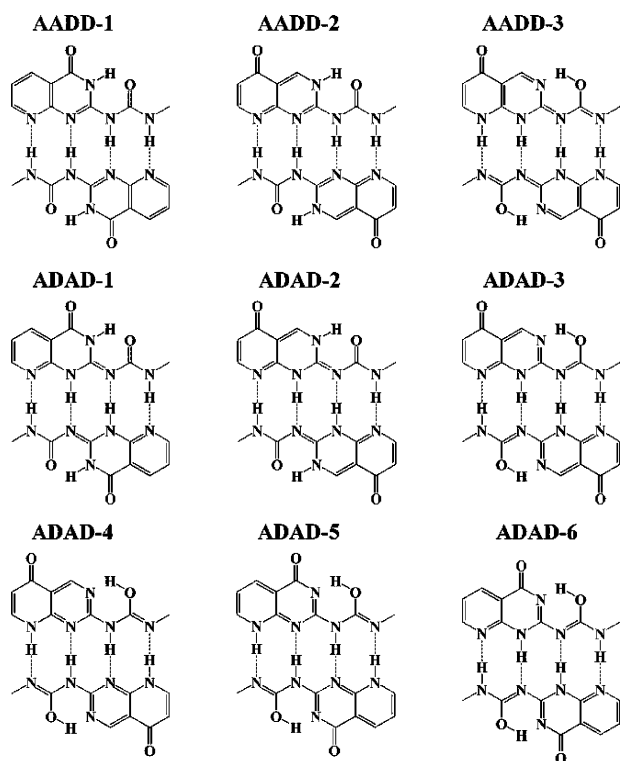


Fig. 2 Structures of nine designed QHB complexes: the first three are AADD-DDAA complexes, and the rest are ADAD-DADA complexes.

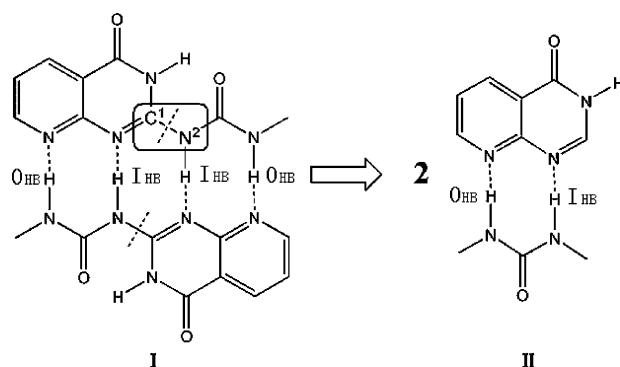


Fig. 3 Schematic diagram of QHB complexes divided into two identical DHB complexes. IHB: inside intermolecular hydrogen bond. OHB: outside intermolecular hydrogen bond.

3.1. Observation of cooperativity in QHB complexes

To discover why these similar systems have large IE differences, we first place several of these compounds in two equivalent groups of DHB complexes (AADD-1, -2 and ADAD-3, -4, -5) to study the cooperativity caused by the two groups with identical approaches (see Fig. 3). Optimized structural and energy data of the DHB complexes are listed together with those of their original QHB complexes in Table 2.

Obviously, the cooperativity is very significant (20.14 and 28.99 kcal mol⁻¹) when AA is built into AADD. But AD complexes, when they are included in their corresponding ADAD complexes, exhibit either non-cooperativity (E_{coop} of ADAD-4 and -5 is -1.26 and 2.24 kcal mol⁻¹, respectively) or even negative cooperativity (E_{coop} of ADAD-3 is -20.32 kcal mol⁻¹). We attempt to use both Jorgenson's SIH⁵ and Gilli's RAHB⁴ to explain the three different behaviors of cooperativity, but neither could rationalize all the instances completely. Jorgenson's SIH theory could only explain the negative cooperativity process of AD to ADAD—each process increases a pair of secondary repulsive forces—but only ADAD-3 exhibits negative cooperativity. Gilli's RAHB theory could explain the process of AA to AADD only—each process increases a so-called “resonance assistant” structure in the midst of full hydrogen bonds—but only AADD complexes exhibit cooperativities.

3.2. Observation of cooperativity in DHB complexes

Given the difficulties of rationalizing cooperativity, we further calculate the energy of two substructures of DHB complexes, whose substructures are obtained by rotating 90° around one of the hydrogen bonds, respectively (for better visualization, see Fig. 4). The IEs of the resulting substructures are approximated as the single hydrogen bond energy, shown in Table 3.

The interaction energies of DHB complexes are further compared to the sum of two single hydrogen bond energies. This method proved useful in showing the cooperative contributions to the total stabilities of Asensio *et al.*³ The difference between AA and AD complexes in cooperativity is striking: AD complexes exhibit cooperativity, while AA complexes exhibit negative cooperativity. The cooperativity in AD complexes can be well explained by Gilli's RAHB theory,⁴ for the conjugated cyclic arrangement of hydrogen bonds in AD complexes allows each to strengthen the other. As for AA complexes, because they don't have a conjugated cyclic arrangement of hydrogen bonds, the rotations won't result in the loss of cooperative energy.

Table 4 lists the charge properties of DHB complexes. We draw the same conclusion from these—the charge densities (which are the sum of two Mulliken charge densities, one between the acceptor atom and H atom and the other between

Table 1 The energy and structural data of QHB complexes

System	E/E_h	IE/kcal mol ⁻¹	$d_1/\text{\AA}$ ^a	$d_2/\text{\AA}$ ^b	$A_1/^\circ$ ^a	$A_2/^\circ$ ^b
AADD-1	-1545.38 9554	-36.48	1.861	2.122	170.5	178.9
AADD-2	-1545.326 2958	-45.99	1.811	2.040	173.7	178.6
AADD-3	-1545.286 7393	-88.30	1.504	1.859	175.8	176.3
ADAD-1	-1545.377 6732	-17.38	1.940	2.134	169.8	177.1
ADAD-2	-1545.314 0365	-22.54	1.899	2.035	172.2	178.0
ADAD-3	-1545.312 6675	-28.54	1.819	2.027	173.4	177.2
ADAD-4	-1545.315 9638	-33.72	1.742	2.069	174.7	178.3
ADAD-5	-1545.328 2287	-53.50	1.581	1.943	174.1	177.4

^a d_1 and A_1 are the bond length (distance between atom H and atom N on the other side) and bond angle of the outside intermolecular hydrogen bond (Fig. 3 I), respectively. ^b d_2 and A_2 are the bond length and bond angle of the inside intermolecular hydrogen bond, respectively.

Table 2 Structural data of DHB and QHB complexes

	IE _{DFT} /kcal mol ⁻¹ ^a	ΔE_{coop} /kcal mol ⁻¹ ^b	$d_1/\text{\AA}$ ^c	$d_2/\text{\AA}$ ^d	$A_1/^\circ$ ^c	$A_2/^\circ$ ^d
AA-1	-8.17	20.14	2.204	2.220	176.5	176.3
AADD-1	-36.48		1.861	2.122	170.5	178.9
AA-2	-8.50	28.99	2.160	2.259	176.8	175.9
AADD-2	-45.99		1.811	2.040	173.7	178.6
AD-3	-24.43	-20.32	1.913	1.634	177.2	176.7
ADAD-3	-28.54		1.819	2.027	173.4	177.2
AD-4	-17.49	-1.26	1.765	2.025	176.2	177.9
ADAD-4	-33.72		1.742	2.069	174.7	178.3
AD-5	-25.63	2.24	1.643	1.886	176.1	177.1
ADAD-5	-53.50		1.581	1.943	174.1	177.4

^a IEs with DFT method. ^b Cooperative energies, which are equal to twice IE_{DFT} of DHB – IE_{DFT} of the corresponding QHB. ^c d_1 and A_1 are the bond length (distance between atom H and atom N on the other side) and bond angle of the outside intermolecular hydrogen bond, respectively. ^d d_2 and A_2 are the bond length and bond angle of the inside intermolecular hydrogen bond respectively.

the acceptor atom and heavy atom on the donor site) of hydrogen bonds in AD complexes are weakened remarkably (0.0070 to 0.0136), which can be considered as the cooperativity being destroyed because one of the hydrogen bond was broken; but the same changes for AA complexes only slightly affect the charge densities (0.0011 to 0.0019). We hence consider that AA complexes lack cooperativity.

3.3. Energy decomposition

We are interested in the origin of large differences in the IE caused by small structural differences. Therefore, the energy-decomposition method based on the *ab initio* molecular orbital theory is used to analyze the components of IE. The five components of decomposed IE sites of all of the QHB com-

plexes and some of their combinations are listed in Table 5. The following conclusions can be drawn from Table 5. (1) ΔE , is the difference between the total IEs calculated by Morokuma's energy decomposition and DFT methods. They are just a small proportion in the total IE. (2) The electrostatic interaction (ES) is the most important attraction interaction (AI) and it is relatively larger for ADAD systems than AADD systems. The magnitudes of the exchange repulsion (EX) are comparable to those of ES. The sum of the ES and EX may be a reference indicator because ES and EX make significant positive and negative contributions to the total IE, respectively. (3) The polarization interaction (PL) is large for AADD systems relative to ADAD systems, contrarily the electron delocalization interaction (CT) is more important for ADAD systems than AADD systems.

Given the results of DHB complexes, we focus our attentions on AA and AADD complexes again. If cooperativity in AADD complexes resulted from increments of structure of cyclic arrangement of hydrogen bonds, the hydrogen bond length of AA complexes on the right (Fig. 3 (I)) would be longer than that of their corresponding AADD complexes. In fact, the hydrogen bond length on the right in each AA complex indeed shortens (bond lengths of AA-1 and AA-2 shorten by 0.219 and 0.098 Å, respectively) compared with those in AADD complexes. The hydrogen bond length on the left, in comparison, becomes even shorter than the one on the right (left bond lengths of AA-1 and AA-2 shorten by 0.349 and 0.343 Å, respectively). These results account for the cooperativity that stems from the cyclic arrangement structure of hydrogen bonds, which play a partial, but certainly not dominant, role in the total cooperativity in AADD complexes. This conclusion can be well supported by the results of the energy decomposition. For AADD-1 and AADD-2, in

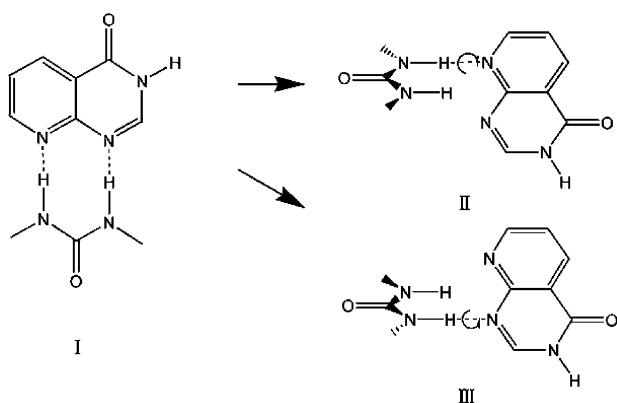


Fig. 4 Schematic diagram of the DHB complexes to two substructures by rotating 90° around one of the hydrogen bonds.

Table 3 IEs of optimized DHB complexes and their single hydrogen-bond substructures

	IE/kcal mol ⁻¹ ^a	IE ₁ /kcal mol ⁻¹ ^b	IE ₂ /kcal mol ⁻¹ ^c	E _{coop} /kcal mol ⁻¹ ^d	E _{coop} /IE (%)
AA-1	-8.17	-5.38	-5.43	-2.64	-32.3
AA-2	-8.50	-4.77	-6.72	-2.99	-35.2
AD-3	-24.43	-4.63	-14.89	4.91	20.1
AD-4	-17.49	-11.22	-3.43	2.84	16.2
AD-5	-25.63	-14.92	-5.43	5.28	20.6

^a IEs of DHB complexes with structures shown in Fig. 4 (I). ^b IEs of DHB complexes with structures shown in Fig. 4 (II). ^c IEs of DHB complexes with structures shown in Fig. 4 (III). ^d E_{coop} = IE - IE₁ - IE₂.

Table 4 Charge density on hydrogen bond of DHB complexes and sub-structure complexes

	C ₁ ^a	C _{1s} ^b	ΔC ₁ ^c	C ₂ ^d	C _{2s} ^e	ΔC ₂ ^f
AA-1	0.0305	0.0288	0.0017	0.0216	0.0197	0.0019
AA-2	0.0271	0.0257	0.0014	0.0243	0.0232	0.0011
AD-3	0.0480	0.0359	0.0121	0.0538	0.0402	0.0136
AD-4	0.0518	0.0434	0.0084	0.0396	0.0321	0.0075
AD-5	0.0568	0.0432	0.0136	0.0476	0.0350	0.0126

^a Charge density of the left hydrogen bond (its counterpart is the outside HB of QHB) of DHB complexes (Fig. 4). ^b Charge density of the hydrogen bond in substructure II complexes (Fig. 4 (II)). ^c ΔC₁ = C₁ - C_{1s}. ^d Charge density of the right hydrogen bond (its counterpart is the inside HB of QHB) of DHB complexes (Fig. 4). ^e Charge density of hydrogen bond in sub-structure III complexes (Fig. 4 (III)). ^f ΔC₂ = C₂₁ - C_{2s}.

comparison with AA-1 and AA-2, CT increases by 7.93 and 10.35 kcal mol⁻¹, respectively. However, the increments of PL in AADD-1 and AADD-2 are 10.79 and 15.40 kcal mol⁻¹, with both being more than that of CT. The ratios PL : AI and CT : AI also illustrate the same idea: CT is not the major contributor to the total cooperativity as well as stability in AADD complexes. Meanwhile, the positive contribution of AI to the total stability increases by 6.80 and 9.30 kcal mol⁻¹ in AADD-1 and AADD-2, respectively. Thus, the cooperativity in AADD complexes is the collective consequence of polarization, charge transfer and electrostatic interaction.

3.4. Bending effect

We divided the ADAD complexes into two types: (1) ADAD-4 and ADAD-5 with non-cooperativity and (2) ADAD-3 with negative cooperativity. In the previous analysis of the cooperativity of DHB complexes, there is an important comparison we ignored. Through observing the energies of single hydrogen bonds in AD complexes (Table 3 and 4) with their structures shown in Fig. 2, it is not difficult to find that the energy of the hydrogen bond with the arrangement of D (donor) on the heterocycle is more stable than that of A (acceptor) on the heterocycle. In order to express the two types of hydrogen bonds conveniently, we define the former type as “strong HB” and latter as “weak HB”.

Fig. 5 shows the process of different kinds of DHB complexes assembling into QHB complexes. As it can be readily seen, QHB complexes bend in the middle of each monomer. Table 3 lists the comparison of bonding lengths and angles between DHB and QHB complexes. These data account for the fact that there is a bend in every QHB complex. When AD-4 and AD-5 build into their corresponding QHB complexes, there are only minor changes in the structure of each DHB complex. The length of the left hydrogen bond of AD-4 and AD-5 (strong HB) decreases by 0.023 and 0.062 Å, respectively, whereas the one on the right (weak HB) increases by 0.044 and 0.062 Å, respectively (Fig. 5 (II)). However, when AD-3 builds into its corresponding QHB complexes, there are sharp changes in the structure of each DHB complex. The length of the left hydrogen bond (weak HB) of AD-3 decreases

by 0.094 Å, while the one on the right (strong HB) increases by 0.393 Å (Fig. 5 (III)). Obviously, the strong HB of AD-3 is considerably weakened by the effect of “bending”, while a similar effect does not act on AD-4 and AD-5. We consider that “bending” is an effect that should not be neglected because it influences the cooperativity in QHB complexes remarkably.

The results of the energy decomposition indicate the origin of the two different behaviors in cooperativity. Unlike AADD complexes, CT makes the most contribution to the total stabilities of ADAD complexes. It can be considered as having more conjugated cyclic arrangements of hydrogen bonds than AADD complexes. CT and PL of ADAD-4 and ADAD-5

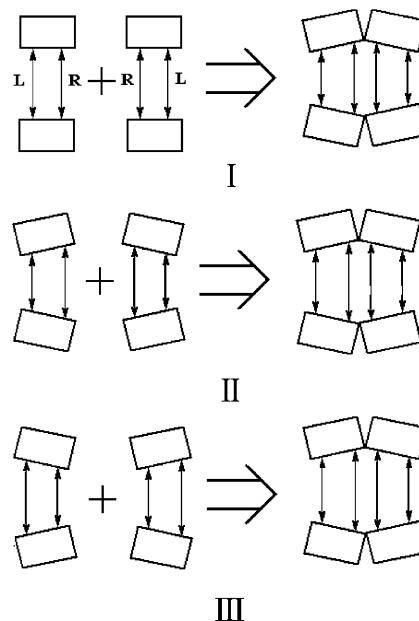


Fig. 5 Sketch map of “bending”: long arrowheads denote weak hydrogen bonds and short arrowheads denote strong hydrogen bonds. L: left hydrogen bond; R: right hydrogen bond. I: cooperativity type (AADD-1 and -2) II: non-cooperativity type (ADAD-4 and -5) III: negative cooperativity type (ADAD-3).

Table 5 Decomposed energy sites of QHB and DHB complexes

	IE _{HF} / kcal mol ⁻¹	ΔE/ kcal mol ⁻¹ ^a	ES/ kcal mol ⁻¹	EX/ kcal mol ⁻¹	PL/ kcal mol ⁻¹	CT/ kcal mol ⁻¹	MIX/ kcal mol ⁻¹	ES+EX/ kcal mol ⁻¹	PL/AI ^b (%)	CT/AI (%)	ES/AI (%)
AADD-1	-31.48	-5.00	-51.34	40.69	-12.88	-10.20	2.25	-10.65	17.3	13.7	69.0
AA-1	-7.50	-0.67	-12.40	8.55	-2.09	-2.27	0.71	-3.85	12.5	13.5	74.0
AADD-2	-40.97	-5.02	-62.95	49.60	-17.57	-12.63	2.57	-13.35	18.9	13.6	67.6
AA-2	-7.79	-0.72	-12.65	8.60	-2.17	-2.28	0.71	-4.05	12.7	13.3	74.0
AADD-3	-85.01	-3.29	-122.0	120.4	-45.95	-44.82	3.18	-1.60	21.6	21.1	57.3
ADAD-1	-11.73	-5.65	-34.90	33.07	-4.66	-9.29	0.89	-1.83	9.5	19.1	71.4
ADAD-2	-16.05	-6.49	-43.11	40.78	-6.91	-11.37	1.20	-2.33	11.3	18.5	70.2
ADAD-3	-21.85	-6.69	-47.04	41.46	-8.75	-10.48	2.97	-5.58	13.2	15.8	71.0
AD-3	-20.74	-3.70	-42.12	42.76	-10.66	-13.06	2.34	0.64	16.2	19.8	64.0
ADAD-4	-27.96	-5.76	-59.85	57.12	-12.82	-15.65	3.25	-2.73	14.5	17.7	67.8
AD-4	-13.73	-3.76	-29.81	28.40	-6.23	-7.51	1.42	-1.41	14.3	17.2	68.5
ADAD-5	-48.34	-5.16	-91.79	93.96	-24.80	-31.29	5.59	2.17	16.8	21.1	62.1
AD-5	-22.04	-4.08	-43.01	42.57	-10.94	-12.91	2.25	-0.44	16.4	18.3	64.3

^a ΔE is the difference between the interaction energies calculated by the HF and DFT methods. ^b AI is the sum of ES, PL and CT (all three attractive sites).

exhibit cooperativity, while ADAD-3 does not (Table 5). We can describe ADAD-4 and ADAD-5 as having the arrangement strong-weak-weak-strong (SWWS), and ADAD-3 has the arrangement WSSW. Of course, the “bending” effect will mainly impact on the complexes with arrangement WSSW and be less effective on the complexes with the SWWS arrangement. Moreover, we envisage that if the structure of ADAD-6 could be optimized, this complex would be likely to exhibit negative cooperativity, because its arrangement is also WSSW.

Because AA-1 and AA-2 do not have any cooperativity and their hydrogen bonds are relatively weak, we consider AADD-1 and AADD-2 to have the arrangement WWW. When DHB complexes build into QHB complexes, the “bending” effect will strengthen outside hydrogen bonds, and the increment in the conjugated cyclic arrangement of the hydrogen bonds will strengthen inside hydrogen bonds also. That is why significant cooperativity is exhibited when AA complexes assemble into AADD complexes.

Finally, we are interested in whether the “bending effect” would be applicable for other QHB complexes. For AADD-3, all of its four intermolecular HBs are strong HBs, so its IE is consequentially much larger than that of other AADD complexes. ADAD-1 and ADAD-2 have the arrangement WSSW, just like ADAD-3, and are energetically unfavorable as a result of the “bending effect”.

4. Conclusion

After systematically analyzing the energetic and structural data of QHB complexes, we have found three different behaviors of cooperativity in QHB complexes. Jorgenson’s SIH theory partly accounts for some stabilities of QHB complexes, however it lacks a theoretic basis.⁸ Gilli’s RAHB theory can explain the origin of cooperativity very well in DHB complexes, but it can not rationalize the different behaviors of cooperativity in QHB complexes effectively. We have found an important phenomenon where each QHB monomer “bends” when forming the QHB complex, which strengthens outside hydrogen bonds and weakens inside hydrogen bonds. This effect results in QHB complexes with different strength arrangements of hydrogen bonds that differ in interaction energy. To conclude, the “resonance-assistant” structure, along with a “bending effect”, accounts for the high stability of the QHB complexes.

Acknowledgements

The work is supported by Science Foundation of NSFC (grant number 20271009 and 20231010) and the Major State Basic Research Development Programs (grant number G2000078100 and G2004CB719900).

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