

# Cooperativity effects in linear formaldehyde oligomers using density functional theory calculations

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**Abstract** This work reports hydrogen bonding interaction in linear formaldehyde oligomers using density functional theory method. Many-body analysis technique has been used to study the various interactions in these oligomers and to obtain % contributions from individual many-body energy terms to the binding energies of these oligomers. Co-operativity effects are studied using different indicators viz. hydrogen bond strength, inter- and intramolecular distances, dissociation energy, dipole co-operativity, energy per hydrogen bond, excess energy and non-additive energy. All these indicators show strong positive hydrogen bond co-operativity in linear formaldehyde oligomers. The dipole moment changes from 2.51 D in monomer to 20.92 D in formaldehyde heptamer.

**Keywords** Co-operativity effects · DFT method · Formaldehyde oligomers · Many-body interactions

## Introduction

Hydrogen bonding interactions, one of the very prevalent non-covalent interactions, play an important role in biological, chemical and physical processes [1]. They are also important

for the assembling of supramolecular structures. Hydrogen bonding interactions have attracted much attention and a significant amount of theoretical as well as experimental work has been carried out [2–4]. Hydrogen bonds also decide the shape of proteins and nucleic acids. Though there are several theoretical and experimental investigations on hydrogen bonding, it remains an area of active research. One of the important concepts in the theory of hydrogen bonding is the hydrogen bond co-operativity. It is the enhancement to the formation of additional hydrogen bonds as a result of an already formed hydrogen bond. The hydrogen bond co-operativity is also described as the nonadditive enhancement of hydrogen bond by the formation of another hydrogen bond with either proton donor or an acceptor of the first hydrogen bond. Hydrogen bond co-operativity effects play an important role in hydrogen bonded oligomers and hydrogen bonding chains [5].

The strong co-operativity effects are observed by King and Weinfeld in linear  $(\text{HCN})_n$  clusters [6]. Sum and Sandler through ab initio calculations have shown that hydrogen bond co-operativity effects were present in the formation of multimer hydrogen bonds in alcohol [7]. They studied clusters of methanol, ethanol, 1-propanol and methanethiol. Ludwig et al. have studied the hydrogen bonding of liquid N-methylacetamide using the quantum clusters equilibrium methodology and found strong co-operativity effects in linear clusters of trans-N-methylacetamide [8]. They suggested possibility of extending their methodology to broader spectrum of hydrogen bonded liquids. A high degree of cooperativity for hydrogen bonded chains of formamide has been observed by Nadya et al. and suggested its implications for protein-folding models [9]. Parra et al. have studied the co-operativity effects in one dimensional network of intermolecular bifurcated hydrogen bonded linear chain of diformamide using ab initio calculations [10]. In their system, the two proton acceptor atoms belong to the same molecule and they found significant co-operativity effects in

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the chain. Masunov and Dannenberg have studied the interactions in one dimensional bonding aggregates, chains and ribbons of urea and thiourea [11]. The cooperative interactions are found to be similar for urea and thiourea chains whereas the cooperative interactions for both ribbons were negligible. Parra et al. have compared co-operativity effects in two-center and three-center hydrogen bonded systems and found that the two-center hydrogen bond interactions are energetically superior to the mean three-center hydrogen bond interactions [12]. They considered diacetamide-HCN and diacetamide-CH<sub>3</sub>OH systems for their study. Solimannejad et al. have studied the co-operativity effects in HNO(H<sub>2</sub>O)<sub>n</sub> clusters and found strong co-operativity effects in these systems with blue shifting of NH vibrational mode upon hydrogen bonding [13]. Recently, Alkorta et al. have discussed the co-operativity effects in multiple unusual weak bonds [14]. A comparison of cooperativity effects in CH–O and O–H–O type hydrogen bonded systems is given by Kar and Scheiner [15]. They found reduction in co-operativity in these systems with an increase in dielectric constant of the surrounding solvent. Shivagal and Singh have studied the co-operativity effects in clusters of acetonitrile using semiempirical MO calculations and concluded that linear and antiparallel arrangement of molecules is more favorable [16]. Alkorta et al. have recently studied the co-operativity in the clusters up to tetramer of interhalogen derivatives of FCl, FBr and ClBr using ab initio and Density Functional Theory (DFT) methods and concluded that the main source of interactions in these clusters corresponds to the polarization term [17]. They considered linear and cyclic clusters for the study. Halogen bonding interactions in chlorides, bromides and nitrogen bases and cooperativity have been studied by Politzer et al. [18]. Hennemann et al. have explained the cooperativity by polarization [19]. The co-operativity effects in many other hydrogen bonded chains have also been examined previously [20–27].

The aim of this article is to study hydrogen bond co-operativity effects in linear chain of hydrogen-bonded formaldehyde oligomers using DFT method. We also studied the nature of interactions between different molecules in these oligomers. The manuscript is organized as follows: The next section gives the computational details. Results are presented and discussed in the Result and discussion section. Conclusions are inferred in the last section.

### Computational details

The geometries of formaldehyde oligomers (H<sub>2</sub>CO)<sub>n</sub> (n=1-7) are optimized using the BLYP and B3LYP functional with two different basis sets. The Gaussian 03 suit of program has been used for the calculations [28]. Many-body analysis technique [29–35] has been used to obtain various interaction energies in hydrogen bonded formaldehyde oligomers. The interaction energies are corrected for the basis set superposition error [36, 37].

### Many-body analysis

Many-body energies are calculated as follows : The decomposition of total energy of a complex can be written as

$$\begin{aligned} \Delta E &= E(\text{ijklmno}) - \{nE_1\} \\ &= \sum_{i=1}^5 E(i) - \{nE_1\} \quad (\text{relaxation energy}) \\ &+ \sum_{i=1}^{n-1} \sum_{j>i}^n \Delta^2 E(ij) \quad (\text{Two - body}) \\ &+ \sum_{i=1}^{n-2} \sum_{j>i}^{n-1} \sum_{k>j}^n \Delta^3 E(ijk) \quad (\text{Three - body}) \\ &+ \dots \dots \dots + \Delta^n E(\text{ijk} \dots n) \quad (n - \text{body}) \end{aligned} \quad (1)$$

where  $E(i)$ ,  $E(ij)$ ,  $E(ijk)$ ,  $E(ijkl)$  etc. are the energies of the various monomers, dimers, trimers, tetramer etc. in a complex and  $E_1$  is the energies of isolated formaldehyde monomer. The pairwise two-body interaction energies and higher three-body and four-body interaction energies are defined as :

$$\Delta^2 E(ij) = E(ij) - \{E(i) + E(j)\} \quad (2)$$

$$\begin{aligned} \Delta^3 E(ijk) &= E(ijk) - \{E(i) + E(j) + E(k)\} \\ &- \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\}, \end{aligned} \quad (3)$$

$$\begin{aligned} \Delta^4 E(ijkl) &= E(ijkl) - \{E(i) + E(j) + E(k) + E(l)\} \\ &- \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(il) \\ &+ \Delta^2 E(jk) + \Delta^2 E(jl) + \Delta^2 E(kl)\} \\ &- \{\Delta^3 E(ijk) + \Delta^3 E(ijl) + \Delta^3 E(ikl) \\ &+ \Delta^3 E(jkl)\} \end{aligned} \quad (4)$$

and so on. The BSSE-corrected energy of a subsystem ( $ijkl$ ) is evaluated in the full basis of a larger system ( $ijklm$ ), and denoted by the term  $E(ijkl|ijklm)$ . Accordingly, the  $n$ -body terms are substituted with the BSSE-corrected ones:

$$\Delta^2 E_C(ij) = E(ij|ijklm) - \{E(i|ijklm) + E(j|ijklm)\} \quad (5)$$

$$\begin{aligned} \Delta^3 E_C(ijk) &= E(ijk|ijklm) \\ &- \{E(i|ijklm) + E(j|ijklm) + E(k|ijklm)\} \\ &- \{\Delta^2 E(ij|ijklm) + \Delta^2 E(ik|ijklm) \\ &+ \Delta^2 E(jk|ijklm)\} \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta^4 E_C(ijkl) = & E(ijkl) - \{E(i|ijklm) + E(j|ijklm) + E(k|ijklm) + E(l|ijklm)\} - \{\Delta^2 E(ij|ijklm) + \Delta^2 E(ik|ijklm) \\ & + \Delta^2 E(il|ijklm) + \Delta^2 E(jk|ijklm) + \Delta^2 E(jl|ijklm) + \Delta^2 E(kl|ijklm)\} - \{\Delta^3 E(ijk|ijklm) \\ & + \Delta^3 E(ijl|ijklm) + \Delta^3 E(ikl|ijklm) + \Delta^3 E(jkl|ijklm)\} \end{aligned} \quad (7)$$

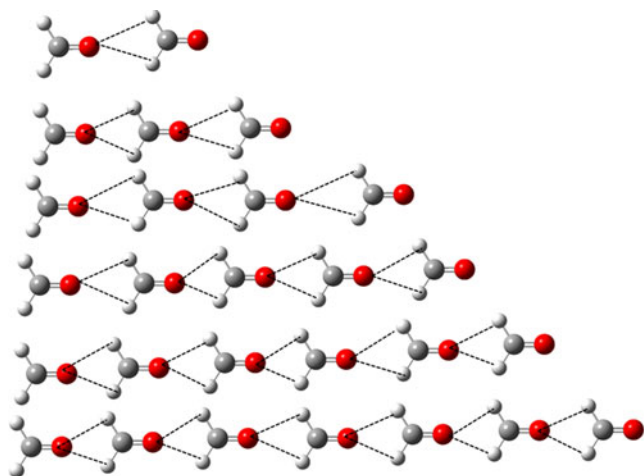
and so on.

The sum of relaxation energy, two-body energy, three-body energy, etc. gives the binding energy of a complex. All energies reported here are corrected for basis set superposition error.

## Results and discussion

### Geometrical parameters for oligomers

Figure 1 shows the structures of linear formaldehyde oligomers. The optimized geometries, dipole moment and total energy of formaldehyde monomer and dimer by DFT calculations along with available experimental data for the monomer are represented in Table 1. The theoretical values for the monomer from B3LYP calculations agree better with the experimental values than those from BLYP using the same basis set. The optimized geometries of monomer at B3LYP/6-31+G(d,p) level are in agreement with the experimental determinations. The calculated wavenumber for the C=O stretching vibration for monomer and dimer along with the available experimental data for the monomer is collected in Table 2. The dipole moment of monomer at B3LYP/6-31+G(d,p) level agrees with the experimental values within 0.2 debye. The scaling factor of 0.994 for BLYP and 0.961 for B3LYP has been used for the C=O stretching vibrational frequency [38, 39]. The theoretical value by B3LYP/6-31+G(d,p) is about 16 to 29  $\text{cm}^{-1}$  lower than the two experimentally reported values.



**Fig. 1** Linear formaldehyde oligomers

The linear formaldehyde dimer has two hydrogen bonds. The oxygen atom of first formaldehyde acts as a hydrogen bond donor for both the hydrogen bonds. The geometrical parameters for linear formaldehyde dimer are reported in Table 1. Table 3 gives the dipole moment, total energy and vibrational frequency for the C=O stretching mode of linear oligomers. As compared to the monomer, there is no large change in the C=O and C-H bond lengths for the linear oligomers. The O-H hydrogen bond distances of linear formaldehyde oligomers are distributed from 2.703 Å to 2.793 Å. The hydrogen bonds at both ends of linear oligomers are longer than those in the middle part. The change in  $\angle\text{H-C-H}$  is in a range of 1 to 0.6 degree in linear oligomers than the monomer. The dipole moment of oligomers increases from 2.51 to 20.92 debye with an increase in number of formaldehyde units in oligomer. The vibrational frequency for the C=O stretching mode of linear oligomers decreases with an increase in number of monomer units in oligomers.

### Many-body interaction energies for the linear oligomers

Table 4 gives many-body interaction energies for linear formaldehyde oligomers. It is found that, there is a strong attractive interaction between all the direct hydrogen bonded pairs for all the oligomers. There are one, two, three, four, five and six hydrogen bonded pairs in dimer, trimer, tetramer, pentamer, hexamer and heptamer respectively and interaction energies for all these pairs are higher than the non-hydrogen bonded pairs.

For the dimer, the two-body interaction energy is attractive and has about 93% contribution to its binding energy. The relaxation energy contributes about 7% to the binding energy of a dimer. The total two-body energies are attractive for all the structures from dimer to heptamer and have a major contribution to the binding energy of a respective cluster. However, the % contribution from total two-body energy decreases from dimer to heptamer. It decreases from 93% to 84.3%. For the total three-body interaction energy, the opposite is true viz. the % contribution from total three-body energies increases from trimer to heptamer. The total three-body energies are not negligible but also contribute significantly to the binding energy of a respective oligomer. The % contribution from total three-body energies increases from 5.5% in trimer to 21% in heptamer. The nature of total three-body energies is attractive for trimer to heptamer. The

**Table 1** Optimized geometries of a formaldehyde monomer and dimer

Method	Basis set	Bond length (Å)			Bond angle (deg)		Dipole moment (debye)	Energy (a.u.)
		C=O	C-H	O—H	∠HCH	∠HCO		
Monomer								
BLYP	6-31+G(d,p)	1.221	1.118	—	116.03	121.98	2.4	-114.48493826
B3LYP	6-31+G(d,p)	1.209	1.108	—	116.19	121.90	2.516	-114.51152421
Expt		1.203 <sup>a</sup>	1.100	—	116.7	—	2.323 <sup>c</sup>	
		1.203 <sup>b</sup>	1.100	—	116.18	—	2.33168 <sup>d</sup>	
Linear dimer								
BLYP	6-31+G(d,p)	1.223	1.116	2.919	116.29	121.85	—	-228.97211
		1.224	1.116	—	115.65	122.16	—	
B3LYP	6-31+G(d,p)	1.210	1.107	2.794	116.43	121.78	5.4485	-229.02600
		1.211	1.106	—	115.64	122.17	—	

<sup>a</sup>Ref. [41], <sup>b</sup>Ref. [42], <sup>c</sup>Ref. [43],  
<sup>d</sup>Ref. [44]

relaxation energy also has significant contribution to the binding energy of a respective complex. The contribution from relaxation energy decreases from 7% in dimer to 5.8% in heptamer. The total four-body energy is almost negligible for tetramer and pentamer. However, it becomes repulsive as we go from tetramer to heptamer. The case is similar for total six-body energy in hexamer and heptamer. It has about 13.6% and 46.8% repulsive contribution to the binding energy of hexamer and heptamer, respectively. The attractive % contribution from total five-body energy increases from 0.3% in pentamer to 6.8% in heptamer. The only one seven-body energy in heptamer is also not negligible. It is attractive and contributes about 10% to the binding energy of heptamer.

#### Hydrogen bond co-operativity effects

We now highlight the co-operativity effects using several indicators such as the strength of hydrogen bond, energy per hydrogen bond, inter- and intramolecular distances, excess energy, dipole co-operativity etc. Energy per hydrogen bond is defined as the binding energy divided by number of

hydrogen bonds in a cluster. Excess energy is the difference between the binding energy and the summation of all the interaction energies for the hydrogen bonded pairs. The dipole co-operativity is defined as  $\{[\mu_n - n\mu_m]/(n-1)\}$  where  $\mu_n$  is the dipole moment of an oligomer,  $n$  represents the number of monomers in oligomer and  $\mu_m$  is the dipole moment of a monomer [40]. The additive energy is the sum of all two-body interaction energies whereas the sum of all higher-body energies represents the non additive energy. Table 5 gives the hydrogen bond distances in linear formaldehyde oligomers. Table 6 shows the O—C intermolecular distances, angles  $\angle C=O-H$  and intramolecular angles  $\angle H-C=O$  for these oligomers. In Table 7, total binding energies, energy per hydrogen bond, excess energies, additive energies and non-additive energies for the linear oligomers are collected.

As can be seen from Tables 5 and 6, the co-operative nature of the hydrogen bonds affects the intermolecular geometries. From Table 5, the two hydrogen bonds are of equal strength for the dimer. When a third molecule is added to the dimer, the hydrogen bonds between first and second molecules get shortened. In trimer, the two hydrogen bonds

**Table 2** Vibrational frequency (cm<sup>-1</sup>) for the C=O stretching vibration and dipole moment (debye) of formaldehyde monomer and linear dimer

Method	Basis set	Vibrational frequency		Dipole moment (debye)
		Monomer	Dimer	Moomer
BLYP	6-31+G(d,p)	1729.94	1731.96	2.4
B3LYP	6-31+G(d,p)	1748.16	1812.01	2.516
Expt		1764 <sup>a</sup>		2.333 <sup>c</sup>
		1777.8 <sup>b</sup>		2.33168 <sup>d</sup>

<sup>a</sup>Ref. [45], <sup>b</sup>Ref. [46], <sup>c</sup>Ref. [43], <sup>d</sup>Ref. [44]

**Table 3** Dipole moment, total energy and C=O stretching vibrational frequency for linear formaldehyde oligomers at B3LYP/ 6-31+G(d,p) level

	Dipole moment (debye)	Energy(a.u.)	Vib freq for C=O stretch (cm <sup>-1</sup> )
HCHO	2.51	-114.5115243	1819.59
(HCHO) <sub>2</sub>	5.44	-229.0260042	1812.01
(HCHO) <sub>3</sub>	8.47	-343.5412618	1807.71
(HCHO) <sub>4</sub>	11.57	-458.0567887	1805.10
(HCHO) <sub>5</sub>	14.68	-572.5724350	1803.43
(HCHO) <sub>6</sub>	17.80	-687.0881387	1802.39
(HCHO) <sub>7</sub>	20.92	-801.6038863	1801.61

**Table 4** Many-body energies (kcal mol<sup>-1</sup>) for linear formaldehyde oligomers obtained at B3LYP/6-31+g(d,p) level

Many-body term	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer
Total two body energy	-1.72	-3.69	-5.76	-7.81	-9.91	-12.02
Total three body energy	————	-0.23	-0.49	-0.88	-1.23	-3.00
Total four body energy	————	————	-0.04	-0.02	1.58	6.03
Total five body energy	————	————	————	-0.03	-3.27	-9.68
Total six body energy	————	————	————	————	1.62	6.67
Total seven body energy	————	————	————	————	————	-1.42
Relaxation energy (kcal/mol)	-0.13	-0.29	-0.42	-0.58	-0.71	-0.83
Binding energy (kcal/mol)	-1.85	-4.21	-6.71	-9.32	-11.92	-14.25
BSSE corrected energy (Hartree)	-229.0257874	-343.5407715	-458.0561218	-572.5715942	-687.0869751	-801.6020508

formed by the third molecule with second molecule are a little longer than those between the first and second molecule. As the number of molecules increases in oligomer, the two hydrogen bonds between first and second molecules become shorter and stronger. The change of about 0.038 Å is found for these two hydrogen bonds going from dimer to heptamer. The change in hydrogen bond lengths is more prominent for the interior molecules thereby showing the strong hydrogen bond co-operativity effects. The hydrogen bonds for the interior molecules are stronger than those for the end molecules.

In Table 6, the C–O intermolecular distances are shown for the linear formaldehyde oligomers. It is 3.222 Å for the dimer. As the number of molecules in oligomer increases, this distance between the first and second molecule decreases showing the positive co-operativity effect. This change is about 0.044 Å from dimer to heptamer. Different C–O distances for the same oligomer are also not equal. Those at the ends are longer than the interior molecules. This again indicates the positive co-operativity of hydrogen

bonds. The change in average C–O distance is about 0.074 Å from dimer to heptamer. A change in intermolecular  $\angle C=O-H$  and intramolecular angle  $\angle H-C=O$  can also be seen from Table 6. Different  $\angle C=O-H$  angles for the same oligomer are not equal. Two intramolecular angles  $\angle H-C=O$  for the same molecule for all the oligomers are found to be almost equal.

An increase in dissociation energy per hydrogen bond is another indication of the hydrogen bond co-operativity. It is found that an increase in dissociation energy per hydrogen bond is about 29% for the heptamer. There is an enhancement of co-operativity, which is defined as the  $[D_n - (n-1)D_2]/(n-2)$ , by about 24% from monomer to dimer. Here,  $D_n$  and  $D_2$  denotes the dissociation energy for the cluster of size  $n$  and dimer respectively and  $n$  is the number of molecules in oligomers.

Enhancement of the dipole moment of a cluster also results from the co-operativity effect. From Table 3, it can be seen that  $\mu_n > n\mu_1$ , for all  $n$ , where  $\mu_n$  is the dipole moment of oligomer of size  $n$  and  $\mu_1$  is that of the isolated monomer. This indicates the hydrogen bond co-operativity effect. The dipole moment per molecule in a cluster has increased from 2.51 to 2.99 from monomer to heptamer. Thus there is an enhancement of about 8.4% in dimer to 19.1% in the heptamer. The enhancement of dipole co-operativity is from 11.9% for the dimer to 33% for the heptamer. Table 7 gives the binding energy, energy per hydrogen bond, excess energy, additive energy and non-additive energy. The energy per hydrogen bond increases from dimer to heptamer. An increase in energy per hydrogen bond, calculated as binding energy/( $n-1$ ), is from 1.85 to 2.38 from dimer to heptamer. It corresponds to an increase of about 14% to 29%. The significant increase in the magnitude of the energy per hydrogen bond for the large clusters than the dimer is again due to the positive co-operativity effect.

The excess energy, which is a measure of indirect interaction energy among the molecules not hydrogen bonded to each

**Table 5** Hydrogen bond lengths (Å) in formaldehyde oligomers

Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer
2.793	2.779	2.773	2.770	2.768	2.755
2.795	2.780	2.750	2.750	2.748	2.756
————	2.787	2.737	2.725	2.713	2.720
————	2.786	2.734	2.721	2.724	2.714
————	————	2.761	2.721	2.718	2.707
————	————	2.761	2.721	2.703	2.705
————	————	————	2.775	2.723	2.711
————	————	————	2.746	2.718	2.702
————	————	————	————	2.748	2.717
————	————	————	————	2.762	2.715
————	————	————	————	————	2.773
————	————	————	————	————	2.745



**Table 6** O—C intermolecular distance, angles  $\angle C=O\cdots H$  and  $\angle H-C=O$  for the formaldehyde oligomers at B3LYP/6-31+g(d,p) level

Cluster size(n)	Distance (Å), angle (degree)	Average
	O—C	
2	3.222	3.222
3	3.203 3.213	3.208
4	3.185 3.158 3.187	3.176
5	3.182 3.144 3.143 3.187	3.164
6	3.181 3.140 3.131 3.142 3.181	3.155
7	3.178 3.137 3.126 3.127 3.137 3.184	3.148
	Angles ( $\angle C=O\cdots H$ )	
2	158.73 162.11	160.42
3	158.77 160.33 162.06 158.65	159.95
4	159.42 160.92 160.25 159.46 159.80 159.75	159.93
5	159.47 160.85 160.17 159.37 159.54 159.45 157.98 161.60	159.80
6	158.80 161.49 159.90 159.77 159.22 160.07 160.43 159.29 158.27 161.48	159.97
7	159.58 160.67 160.08 159.57 159.58 159.74 160.11 159.40 159.64 159.71 158.40 161.80	159.86
	Angles ( $\angle H-C=O$ )	
1	121.90 121.90	121.9
2	121.78 121.78 122.18 122.18	121.98
3	121.75 121.76 122.02 122.03 122.14 122.15	121.97
4	121.75 121.75 122.04 122.06 122.06 122.11 122.21 122.20	122.02
5	121.75 121.74 122.03 122.06 122.10 122.10 122.13 122.12 122.21 122.24	122.04
6	121.75 121.74 122.04 122.06 122.11 122.09 122.10 122.13 122.13 122.23 122.21	122.06
7	121.74 121.74 122.05 122.05 122.09 122.10 122.10 122.11 122.12 122.11 122.05 122.20 122.17 122.20	122.06

other, is another indication of hydrogen bond co-operativity. As can be seen, the excess energy increases from 0.13 to 4.1 kcal mol<sup>-1</sup> from dimer to heptamer. It indicates that the interactions between molecules in linear formaldehyde oligomers are long-ranged. It also indicates that the molecules which are not involved in the formation of new hydrogen bonds also contribute to the hydrogen bond co-operativity effect. The hydrogen bond co-operativity can also be seen from the non-additive energies. Those are attractive from trimer to heptamer and become more attractive with an increase of the cluster size. This is an indication of hydrogen bond co-operativity for these oligomers.

## Conclusions

We have studied hydrogen bonded linear formaldehyde oligomers using DFT method. The calculated dipole moment and geometrical parameters from this work are in agreement with the experimental determinations. The hydrogen bond co-operativity effects are studied using several indicators which confirm the positive co-operativity effects in linear formaldehyde oligomers. The hydrogen bonds in the middle part of linear oligomers are slightly stronger than the hydrogen bonds at both ends of oligomers. Strong hydrogen bond co-operativity effects are observed for the linear oligomers.

**Table 7** Total binding energy, energy per hydrogen bond, excess energy, additive energy and non-additive energy for formaldehyde oligomer. All energies are in kcal mol<sup>-1</sup>

Cluster size (n)	Total B. E.	Energy per H-bond	Excess energy	Additive energy	Non-additive energy
2	-1.85	-0.95	0.13	-1.72	0.00
3	-4.21	-1.05	0.8	-3.68	-0.22
4	-6.71	-1.11	1.6	-5.75	-0.53
5	-9.32	-1.16	2.56	-7.81	-0.92
6	-11.91	-1.19	3.47	-9.90	-1.30
7	-14.24	-1.18	4.1	-12.01	1.39

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