Density Functional Theory Study of Formaldehyde Oligomers

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ABSTRACT: Hydrogen-bonded formaldehyde oligomers (dimer to pentamer) are studied using density functional theory (DFT), the B3LYP method, and the 6-311+G* basis set. Many-body interaction energies are obtained to study the contribution of many-body terms to binding energy. The basis set superposition error (BSSE)-corrected total energies are $-229.08170, -343.61410, -458.16660,$ and $-572.70901$ hartrees for dimer, trimer, tetramer, and pentamer, respectively, with corresponding binding energies $-2.55, -4.86, -6.99,$ and $-9.49$ kcal/mol. Two-body energies have been found to contribute significantly to the total binding energy in dimer to pentamer, whereas higher-order interaction energies are negligible. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 101: 67–72, 2005

Key words: DFT; binding energy; many-body interaction

1. Introduction

Formaldehyde (H$_2$CO) is an important industrial chemical used to make other chemicals, building materials, and household products. It is used in glues, wood products, preservatives, permanent press fabrics, paper product coatings, and certain insulation materials. It is also widely used as an industrial fungicide, germicide, and disinfectant. There are several experimental and theoretical studies on formaldehyde [1–11]. Although formaldehyde has long been a subject of theoretical and experimental studies, there is still interest in the structure–property relationship for this molecule.

The literature on formaldehyde allows one to attain a good understanding of the structure and dynamics of formaldehyde, but the details of the hydrogen bonded cluster and interaction can still be considered an open question. Study of such hydrogen-bonded clusters is of paramount importance to understand a variety of important processes in chemistry and biochemistry [12]. Proper description of nonadditivity contribution to the interaction energy is crucial in describing the properties of hydrogen-bonded molecular clusters. The binding energy of intermolecular interactions plays significant roles in a wide range of physical, chemical and biological fields. Clusters containing more
than two molecules behave cooperative effects, which are reflected in changes of some properties with increase in cluster size such as interaction energy and dipole moment. Proper characterization of these phenomena is therefore crucial to understanding the behavior of cluster.

Density functional theory (DFT) offers a promising tool that may be applied to hydrogen-bonded systems. The properties obtained by DFT are found to agree well with those obtained by MP2 calculations for hydrogen-bonded complexes [13–15]. In this article, we present a study of the hydrogen-bonded formaldehyde cluster (from dimer to pentamer), using the DFT method. We therefore report geometry optimization and interaction energies. Many-body interaction energies [16–20] are also calculated, and their contributions to the binding energy are reported. The basis set superposition error (BSSE) are also reported. This article is presented as follows. Section 2 reports the computational detail. Section 3 presents the details of many-body interaction terms. Section 3 briefly summarizes the energy decomposition scheme, including correction for BSSE, using the counterpoise method and generalized counterpoise method [21–23]. The results are discussed in section 4, and the conclusions are given in section 5.

2. Computational Details

The optimized geometries for hydrogen-bonded formaldehyde dimer, trimer, tetramer, and pentamer are obtained using the DFT method. The B3LYP hybrid functional approach [24–27], which consists of the Hartree–Fock, nonlocal exchange and correlation parts is used by implementing the 6-311+G* basis set. All calculations have been carried out with the Gaussian 98 program [28].

3. Many-Body Interaction Energies

The total energy $E_n$ of the $n$-body cluster (“body” referring to a H$_2$CO molecule hereafter) can be written as the sum of the one-, two-, three-, four-, … $n$-body terms according to

$$ E_n = E(1234 \ldots n) = \sum_{i=1}^{n} E(i) \quad \text{One-body} $$

$$ + \sum_{i=1}^{n-1} \sum_{j>i}^{n} \Delta^2 E(ij) \quad \text{Two-body} $$

$$ + \sum_{i=1}^{n-2} \sum_{j>i}^{n-1} \sum_{k>j}^{n} \Delta^3 E(ijk) \quad \text{Three-body} $$

$$ + \Delta^4 E(1234 \ldots n) \quad n\text{-body}, $$

where $E(i)$ are the relaxed H$_2$CO molecule in the cluster and $E(ij)$, $E(ijk)$, … are the energies of the various dimers, trimers, and so on. The pairwise two-body interaction energies and higher three-body and four-body, …, $n$-body interaction energies are defined as the following equations:

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

$$ \Delta^3 E(ijk) = E(ijk) - \{E(i) + E(j) + E(k)\} $$

$$ - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(jk)\} $$

$$ \Delta^4 E(ijkl) = E(ijkl) - \{E(i) + E(j) + E(k) + E(l)\} $$

$$ - \{\Delta^2 E(ij) + \Delta^2 E(ik) + \Delta^2 E(ik) + \Delta^2 E(jk) \} $$

$$ + \Delta^2 E(jl) + \Delta^2 E(kl) \} - \{\Delta^3 E(ijk) + \Delta^3 E(ijl) $$

$$ + \Delta^3 E(ikl) + \Delta^3 E(jkl)\}, $$

and so on. For a cluster of size $n$, there are $n(n-1)/(2!)$ two-body terms, $n(n-1)(n-2)/(3!)$ three-body terms, etc.

The binding energy of the $n$-body cluster is

$$ B_{E_n} = E_n - nE_F, $$

where $E_F$ is the energy of the H$_2$CO monomer in the gas phase. The term involving the one-body term

$$ E_R = \sum_{i=1}^{n} E(i) - nE_F $$

can therefore be represented as the total relaxation energy, $E_R$, of the H$_2$CO molecules in the cluster with respect to the gas phase monomer and is a measure of the degree of the strain that drives the distortion of the H$_2$CO molecules in the cluster. The average relaxation energy per H$_2$CO molecule is then $E_R/n$.

We have used the function counterpoise (fCP) method [21–23] to calculate BSSE in our analysis. The BSSE-corrected energy of a subsystem $ijkl$ at the cluster geometry is evaluated in the full basis of
a larger system \((ijkl \ldots n)\) and denoted by the term 
\(E(ijkl \ldots n)\). Accordingly, the \(n\)-body terms are 
substituted with the BSSE-corrected ones:

\[
\Delta^2 E_C(ij) = E(ijijkl \ldots n) - \{E(ijkl \ldots n)
\]

\[
+ E(jijkl \ldots n)
\]

\[
\Delta^3 E_C(ijk) = E(ijkijkl \ldots n) - \{E(ijkl \ldots n)
\]

\[
+ E(jijkl \ldots n) + E(kijkl \ldots n)
\]

\[
- \{\Delta^2 E(ijijkl \ldots n)
\]

\[
+ \Delta^2 E(ikijkl \ldots n) + \Delta^2 E(ikijkl \ldots n)
\]

and so on. The total BSSE is the difference between 
the corrected and uncorrected interaction energies

\[(BSSE)_n = BE_Cn - BE_n.\]

The geometries of the various subsystems are those 
found in the cluster, and not the relaxed ones. The 
above scheme has been adopted to estimate the 
BSSE corrections to the all-possible dimers (two-
body), trimers (three-body), and tetrathers (four-
body), in the pentamer.

### 4. Results and Discussion

The optimized geometries for the \(H_2CO\) dimer, 
trimer, and tetramer, pentamer are shown in Figure 
1. Geometry optimization for these structures were 
carried out employing DFT/B3LYP method with 
the 6-311+G* basis set. It was observed that at this 
level of theory, all the geometric parameters and 
dipole moment for formaldehyde monomer are in 
good agreement with the experimental measurements [29, 30]. For monomer, the C=O and C—H 
distances in this work are 1.201 Å and 1.108 Å and 
the respective distances obtained experimentally 
are 1.208 and 1.116 Å. \(\angle H—C—H\) and dipole 
moment in this work are 116.21° and 2.47 debye, 
respectively, whereas these parameters measured 
experimentally as 116.18° and 2.32 debye.

In dimer to pentamer, there is an anti-parallel 
arrangement of \(H_2CO\) molecules. There are 1, 2, 3, 
and 4 hydrogen-bonded anti-parallel pairs of \(H_2CO\) 
molecules in dimer, trimer, tetramer, and pentamer, 
respectively. In each structure, two subunits are 
bound through two hydrogen bonds. One bond 
consists of the hydrogen atom of the left formalde-
hyde acting as the proton donor and the oxygen 
atom of the right formaldehyde acting as the accep-
tor, while in the other hydrogen atom of the right 
formaldehyde acts as proton donor and oxygen of 
the left formaldehyde acts as proton acceptor. The 
hydrogen bond distances in dimer to pentamer are 
listed in Table I. The total energies of the optimized 
geometries and BSSE-corrected total energies are
given in Table II along with dipole moment of the structures.

The interaction energies for H\textsubscript{2}CO dimer are listed in Table III. The binding energy for dimer has been found to be \(-2.55\) kcal/mol. It can be seen that two-body energy makes a greater contribution to binding energy than does the relaxation energy. The former has 95\% and the latter has only a 5\% contribution. Both two-body as well as relaxation energies are attractive. The interaction energies for trimer are listed in Table IV. The binding energy for trimer is \(-4.86\) kcal/mol. Similar to dimer, the two-body interaction energy contributes significantly to binding energy here as well, whereas the three-body interaction is almost negligible. Looking toward the values of two-body interaction energies, it can be seen that pair 12 and 23 has almost the same interaction energy (about \(-2.45\) kcal/mol), whereas for pair 13, it is only 0.31 kcal/mol, as there is an indirect interaction between these two molecules. Also, for the former two pairs, the interaction energy is attractive, whereas for the latter it is repulsive. Here as well, the relaxation energy contributes about 5\% to the binding energy and is attractive.

The three-body interaction is repulsive and is negligible (0.009 kcal/mol), as compared with two-body and relaxation energies.

The interaction energies for tetramer are given in Table V. From Table V, it can be seen that similar to dimer and trimer, in tetramer also more contribution to binding energy is of two-body energies. Three-body energies and four-body energies are negligible.

**TABLE II**

<table>
<thead>
<tr>
<th>Species</th>
<th>$E$</th>
<th>$E_C$</th>
<th>$\mu$ (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer</td>
<td>(-229.0819244)</td>
<td>(-229.08170)</td>
<td>0.034</td>
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<tr>
<td>Trimer</td>
<td>(-343.614535)</td>
<td>(-343.61410)</td>
<td>2.414</td>
</tr>
<tr>
<td>Tetramer</td>
<td>(-458.1672197)</td>
<td>(-458.16660)</td>
<td>0.003</td>
</tr>
<tr>
<td>Pentamer</td>
<td>(-572.7098678)</td>
<td>(-572.70901)</td>
<td>2.406</td>
</tr>
</tbody>
</table>

**TABLE III**

<table>
<thead>
<tr>
<th>Terms</th>
<th>BSSE corrected B3LYP/6-311+\textsuperscript{G*}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2</td>
<td>(-2.42)</td>
</tr>
<tr>
<td>Relaxation energy</td>
<td>(-0.13)</td>
</tr>
<tr>
<td>Total two-body energy</td>
<td>(-2.42)</td>
</tr>
<tr>
<td>Additive energy</td>
<td>(-2.42)</td>
</tr>
<tr>
<td>Nonadditive energy</td>
<td>0.00</td>
</tr>
<tr>
<td>Binding energy</td>
<td>(-2.55)</td>
</tr>
</tbody>
</table>

* All energies are in kcal/mol.

**TABLE IV**

<table>
<thead>
<tr>
<th>Terms</th>
<th>BSSE corrected B3LYP/6-311+\textsuperscript{G*}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2</td>
<td>(-2.46)</td>
</tr>
<tr>
<td>1 3</td>
<td>0.31</td>
</tr>
<tr>
<td>2 3</td>
<td>(-2.45)</td>
</tr>
<tr>
<td>1 2 3</td>
<td>0.009</td>
</tr>
<tr>
<td>Relaxation energy</td>
<td>(-0.27)</td>
</tr>
<tr>
<td>Total two-body</td>
<td>(-4.60)</td>
</tr>
<tr>
<td>Total three-body</td>
<td>0.009</td>
</tr>
<tr>
<td>Additive energy</td>
<td>(-4.60)</td>
</tr>
<tr>
<td>Nonadditive energy</td>
<td>0.009</td>
</tr>
<tr>
<td>Binding energy</td>
<td>(-4.85)</td>
</tr>
</tbody>
</table>

* All energies are in kcal/mol.

**TABLE V**

<table>
<thead>
<tr>
<th>Terms</th>
<th>BSSE corrected B3LYP/6-311+\textsuperscript{G*}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2 3</td>
<td>0.024</td>
</tr>
<tr>
<td>1 2 4</td>
<td>0.014</td>
</tr>
<tr>
<td>1 3 4</td>
<td>0.009</td>
</tr>
<tr>
<td>2 3 4</td>
<td>0.024</td>
</tr>
<tr>
<td>1 2 3 4</td>
<td>0.005</td>
</tr>
<tr>
<td>Relaxation energy</td>
<td>(-0.38)</td>
</tr>
<tr>
<td>Total two-body</td>
<td>(-6.69)</td>
</tr>
<tr>
<td>Total three-body</td>
<td>0.071</td>
</tr>
<tr>
<td>Four-body</td>
<td>0.005</td>
</tr>
<tr>
<td>Additive energy</td>
<td>(-6.69)</td>
</tr>
<tr>
<td>Nonadditive energy</td>
<td>0.076</td>
</tr>
<tr>
<td>Binding energy</td>
<td>(-6.99)</td>
</tr>
</tbody>
</table>

* All energies are in kcal/mol.
negligible as compared with two-body energies. When there is direct interaction between two H₂CO molecules (pairs 12, 23, and 34), the interaction energies are attractive and contribute significantly to the binding energies, whereas when there is indirect interaction (pairs 13, 15, 24 and 35) and are repulsive. Some of the three-body energies here have attractive contribution and some have repulsive contribution to the binding energy but the total contribution of the three-body energy is repulsive. All the four-body energies have repulsive contribution result in repulsive contribution from total four-body energy. Relaxation energy and five-body energies are attractive. Three-body, four-body and five-body energies have very little contribution to binding energy as compared with two-body energies.

From the values of additive and nonadditive energies, it can be concluded that all the structures have attractive additive energy whereas the nonadditive energies are repulsive. Also, contribution to binding energies from additive energies is about 95% and that from nonadditive energies is about 1%. The relaxation energies contribute about 5% to the binding energies for all the structures.

Thermochemical analysis has also been carried out to investigate thermal stability of these oligomers. The change of Gibbs free energy (ΔG) from monomer to oligomers

\[ n(H₂CO) \rightarrow (H₂CO)_n \]

is calculated as

\[ \Delta G = G[(H₂CO)_n] - nG[H₂CO] \]

It has been observed that the change of Gibbs free energy from monomer to dimer, trimer, tetramer, pentamer is 5.13, 9.95, 14.98, and 19.95 kcal/mol respectively at 298.15 K and 1 atm. It can be said that the entropy terms for these association reactions are large and unfavorable.

5. Conclusions

Hydrogen-bonded fomaldehyde dimer, trimer, tetramer, and pentamer are studied using the DFT/B3LYP method with 6-311+G* basis set. Many-body interaction energies and their contribution to the binding energies are studied. For all the struc-

### TABLE VI

Interaction energies for the H₂CO pentamer.*

<table>
<thead>
<tr>
<th>Terms</th>
<th>BSSE corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B3LYP/6-311+G*</td>
</tr>
<tr>
<td>1 2</td>
<td>-2.45</td>
</tr>
<tr>
<td>1 3</td>
<td>0.31</td>
</tr>
<tr>
<td>1 4</td>
<td>-0.081</td>
</tr>
<tr>
<td>1 5</td>
<td>0.04</td>
</tr>
<tr>
<td>2 3</td>
<td>-2.48</td>
</tr>
<tr>
<td>2 4</td>
<td>0.31</td>
</tr>
<tr>
<td>2 5</td>
<td>-0.081</td>
</tr>
<tr>
<td>3 4</td>
<td>-2.48</td>
</tr>
<tr>
<td>3 5</td>
<td>0.31</td>
</tr>
<tr>
<td>4 5</td>
<td>-2.46</td>
</tr>
<tr>
<td>1 2 3</td>
<td>0.009</td>
</tr>
<tr>
<td>1 2 4</td>
<td>-0.005</td>
</tr>
<tr>
<td>1 2 5</td>
<td>-0.019</td>
</tr>
<tr>
<td>1 3 4</td>
<td>0.000</td>
</tr>
<tr>
<td>1 3 5</td>
<td>-0.005</td>
</tr>
<tr>
<td>1 4 5</td>
<td>-0.009</td>
</tr>
<tr>
<td>2 3 4</td>
<td>0.005</td>
</tr>
<tr>
<td>2 3 5</td>
<td>0.009</td>
</tr>
<tr>
<td>2 4 5</td>
<td>0.005</td>
</tr>
<tr>
<td>3 4 5</td>
<td>0.019</td>
</tr>
<tr>
<td>1 2 3 4</td>
<td>0.014</td>
</tr>
<tr>
<td>1 2 3 5</td>
<td>0.029</td>
</tr>
<tr>
<td>1 2 4 5</td>
<td>0.029</td>
</tr>
<tr>
<td>1 3 4 5</td>
<td>0.014</td>
</tr>
<tr>
<td>2 3 4 5</td>
<td>0.009</td>
</tr>
<tr>
<td>1 2 3 4 5</td>
<td>-0.024</td>
</tr>
</tbody>
</table>

Relaxation  
-0.50

Total two-body  
-9.07

Total three-body  
0.019

Total four-body  
0.086

Five-body  
-0.024

Additive energy  
-9.07

Nonadditive energy  
0.081

Binding energy  
-9.49

* All energies are in kcal/mol.
tures, it is observed that two-body interaction energies have more contribution whereas higher-body energies are very small as compared with two-body energies. Relaxation energies have about 5% contribution to the binding energies. We are also investigating many-body contribution to the binding energy for other type of H$_2$CO dimer, trimer, tetramer, and pentamer structures as an extension of this work.

References