Ab initio study & Density functional investigational of Adenine & Thymine;
Comparison of primitive Gaussian and NBO calculation

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Abstract
We have performed quantum-chemical ab initio in various basis sets at the Hartree-Fock and B3LYP levels for Adenine and Thymine with the program GAUSSIAN98. The Dipole, Quadrupole, Octapole and Hexadecapole moments and primitive in nine basis sets for these molecules are presented. The most stabilized forms of these molecules are observed in 6-311++G** basis set. We have evaluated coefficient hybridation of bonds and occupancy orbital, donor and acceptors. NBO calculations show that hybridization of coefficient and occupancy in several basis sets is different.

INTRODUCTION
The uracil moiety is one of the important nucleobase residues in nucleotides and nucleic acids1. Nucleotides, are playing a key role in biology e.g., in the information storage via RNA and DNA or in energy-transfer processes. The use structurally altered nucleotides as probes provide one way to study the involved enzymic reactions. Ab initio quantum-chemical calculations with inclusion of electron correlation have recently provided a relatively consistent picture on base pair interaction energies and geometries. We have therefore performed calculations of this type for A and T. This can lead to a more detailed information on structure, charge distribution and energetic of these bases. In addition, the results obtained have been related to geometrical data for the A and T derived from an analysis of a set of experimental high resolution molecule structure. Adenine and Thymine (Fig. 1) is the important nucleobase residue in nucleotides and nucleic acids. Nucleotides are playing a key role in biology e.g. in the information storage via RNA and DNA or energy transfer processes5.

Thymine and uracil are weak acids in which two position namely C2=O and C4=O have approximately equal tendencies for enolization and ionization6. However one of these positions enolization, inhibits that of the other. Thymine has then only one dissociation constant. Electrostatic properties (Dipole, Quadrupole,...) were studied with ab-initio density functional method and so for Adenine and Thymine are discussed and compared to various basis set calculated at the HF & B3LYP levels7,8. NBO analysis is based on a method for optically transforming a given wave function into localized form corresponding to the one center (lone pair) and two-center (bond) elements of the chemist's Lewis structure picture9.

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Fig. 1 Molecular structure of Adenine and Thymine.

The second-order perturbative estimates of donor-acceptor (bond-antibond) interactions in the NBO basis10. This is carried out by examining all possible interactions between filled (donor) Lewis-type NBOs and empty(acceptor) non-Lewis NBOs and estimating their energetic importance by 2nd-order perturbation theory11. Since these interactions...
lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbital (and thus to departures from the idealized Lewis structure description) they are referred to as delocalization corrections to the zeroth-order natural Lewis structure. For each donor NBO(i) and acceptor NBO(j) the stabilization energy $E_2$ associated with delocalization (2e-stabilization) $i \rightarrow j$ is:

$$E_2 = \Delta E_{(ij)} = \frac{q_i}{F_{(ij)}} (\varepsilon_j - \varepsilon_i)$$

Where $q_i$ is the donor orbital occupancy, $\varepsilon_i$ and $\varepsilon_j$ are diagonal elements (orbital energies) and $F_{(ij)}$ is the aff-diagonal NBO fock matrix element. In HF theory the energy has the form:

$$E_{HF} = V + \langle hp \rangle + \frac{1}{2} \langle p_j(p) \rangle - \frac{1}{2} \langle p_k(p) \rangle$$

Where $V$ is the nuclear repulsion energy, $P$ is the density matrix, $\langle hp \rangle$ is the one-electron(kinetic plus potential) energy $\frac{1}{2} \langle p_j(p) \rangle$ is the classical coulomb repulsion of the electrons and $-\frac{1}{2} \langle p_k(p) \rangle$ is the exchange energy resulting from the quantum (fermions) nature of electrons. In density functional theory the exact exchange (HF) for a single determinant is replaced by a more general expression the exchange-correlation functional which can include terms accounting for both exchange energy and the electron correlation which is omitted from Hartree-Fock theory:

$$E_{ks} = V + \langle hp \rangle + \frac{1}{2} \langle p_j(p) \rangle + \varepsilon_x[p] + \varepsilon_c[p]$$

Where $\varepsilon_x[p]$ is the exchange functional and $\varepsilon_c[p]$ is the correlation functional. The correlation functional of Lee, Yang and Parr which includes both local and nonlocal term. BLYP request the Beck exchange functional and LYP correlation functional.

Basis set effects:

A basis set is the mathematical description of the orbital within a system (which is turn combine to approximate the total electronic wave function used to perform the theoretical calculation). Larger basis set more accurately approximate the orbital by imposing fewer restrictions on the location of the electron in space. In the true quantum mechanical picture electrons have a finite probability of existing anywhere in space. This limit corresponds to the infinite basis set expansion in the chart in the previous section. The standard basis sets use linear combination of Gaussian function to form the orbital. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbital. These basis function themselves are composed of Gaussian functions. The former are then referred to as contracted Gaussian (or contracted functions) and the latter referred to as primitives.

**COMPUTATIONAL DETAILS**

Ab initio calculations at the HF/6-31G, HF/6-31G*,HF/6-311G, HF/6-311G**, HF/6-311+G, HF/6-311++G, HF/6-311+G**, HF/6-311++G**, B3LYP/6-31G, B3LYP/6-31G*, B3LYP/6-311G, B3LYP/6-31G*, B3LYP/6-311G**, B3LYP/6-311+G, B3LYP/6-311++G, and B3LYP/6-311++G** for Adenine and Thymine were carried out to determine the molecule structure with the program GAUSSIAN98. Energy minima of the optimized molecule have been verified at the Hartree-Fock and B3LYP levels.

The Natural Bond Orbital (NBO) analysis was performed by using the NBO as implement in Gaussian 98. NBO calculations have been done at HF and B3LYP levels. We have computed hybridation coefficient of four bonds for Adenine and Thymine at HF and B3LYP levels in nine basis sets. We evaluated lowest occupancy orbital, highest energy, donor, acceptor and lowest charge atoms in nine basis sets.

**RESULT AND DISCUSSION**

The calculated amounts of dipole, quadrupole, octapole and hexadecapole moments at the HF and B3LYP levels in various basis sets are given in table 1-4. Figure 2 shows the change in Dipole moments corresponds to primitive for Adenine and also figure 3-5 show variation of quadrupole, octapole and hexadecapole of those molecules versus primitive. These data shows that for Adenine at the HF and B3LYP levels and also for Thymine at the HF level, we have the least energy in 6-311++G** basis set but the least amount of hexadecapole moment at XXXX tensor element obtained in 6-311+G basis set. Whereas the calculated energy for Thymine at the B3LYP level is minimum in 6-311++G** basis set but the amount of hexadecapole moment at XXXX tensor element is the least amount in 6-311++G basis set.

We have computed hybridation coefficient of four bonds in Adenine and Thymine at HF and B3LYP levels (table 5-8). Hybridation coefficient is different in various methods and basis sets. In Adenine at HF and B3LYP levels the lowest occupancy orbital with the highest energy is N7. In Thymine at HF and B3LYP levels the lowest occupancy orbital with the highest energy is N1 (see tables 9-12). N7 in Adenine and N1 in Thymine is site for complexation with cations.
Table 1. Calculated Dipole, Quadropole, Octapole and Hexadecapole Moments in various basis sets at HF level for Adenine.

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Table 2. Calculated Dipole, Quadropole, Octapole and Hexadecapole Moments in various basis sets at B3LYP level for Adenine.

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Table 3. Calculated Dipole, Quadrupole, Octapole and Hexadecapole Moments in various basis set at HF level for Thymine.

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Table 4. Calculated Dipole, Quadrupole, Octapole and Hexadecapole Moments in various basis sets at B3LYP level for Thymine.

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</table>

Hartee-Fock

- F.Assadian et al.
Fig. 2 Dipole, Quadrupole, Octapole, Hexadecapole moments VS. Primitive Gaussian Function for Adenine at the different basis sets.
Fig. 3  Dipole, Quadrupole, Octapole, Hexadecapole moments VS. Primitive Gaussian Function for Adenine at the different basis sets.
For Thymine at HF and B3LYP levels, hybridization coefficient:
in C4 – C5: σ(C4) > π(C4), σ(C5) < π(C5)  
in C6 – O7: σ(C6) > π(C6), π(O7) < σ(O7) and σ(C6) > π(C6)  
These below results are due to polarized basis sets and at HF and B3LYP levels:

<table>
<thead>
<tr>
<th>N1 – C2</th>
<th>sp</th>
<th>n σ(C6-31G) &gt; n σ(C6-31G)</th>
<th>n σ(C6-31G) &gt; n σ(C6-31G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3 – C4</td>
<td>sp</td>
<td>n σ(C6-311G) &gt; n σ(C6-311G)</td>
<td>n σ(C6-311G) &gt; n σ(C6-311G)</td>
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<tr>
<td>C4 – C5</td>
<td>sp</td>
<td>n σ(C6-31G) &gt; n σ(C6-31G)</td>
<td>n σ(C6-31G) &gt; n σ(C6-31G)</td>
</tr>
</tbody>
</table>

These below results are due to diffused basis sets:

<table>
<thead>
<tr>
<th>N1 – C2</th>
<th>sp</th>
<th>n σ(C6-31G) &gt; n σ(C6-31G)</th>
<th>HF, B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3 – C4</td>
<td>sp</td>
<td>n σ(C6-31G) &gt; n σ(C6-31G)</td>
<td>HF, B3LYP</td>
</tr>
<tr>
<td>C4 – C5</td>
<td>sp</td>
<td>n σ(C6-31G) &gt; n σ(C6-31G)</td>
<td>HF, B3LYP</td>
</tr>
<tr>
<td>C6 – O7</td>
<td>sp</td>
<td>n σ(C6-31G) &gt; n σ(C6-31G)</td>
<td>HF, B3LYP</td>
</tr>
</tbody>
</table>

We find that: For Adenine at HF and B3LYP levels, hybridization coefficient:
in N1 – C6 σ(C6) > π(C6), σ(C6) > π(C6)  
in C2 – N3 σ(C2) > π(C2), σ(C2) > π(C2)  
in C4 – C5 σ(C4) > π(C4), σ(C5) < π(C5)  
These below results are due to polarized basis sets at HF level:

<table>
<thead>
<tr>
<th>N1 – C6</th>
<th>sp</th>
<th>n σ(C6-31G) &gt; n σ(C6-31G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2 – N3</td>
<td>sp</td>
<td>n σ(C6-311G) &gt; n σ(C6-311G)</td>
</tr>
</tbody>
</table>

This below result is due to diffused basis sets at HF and B3LYP levels:

| C6 – N10 | sp | n σ(C6-31G) > n σ(C6-31G) |

Table 5. Hybridization coefficient of six bonds calculated by NBO method in HF level at different basis sets for Adenine.

<table>
<thead>
<tr>
<th>N1-C6</th>
<th>C2-N3</th>
<th>C4-C5</th>
<th>C6-N10</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31g</td>
<td>σ</td>
<td>0.7607(Sp)</td>
<td>0.7607(Sp)</td>
</tr>
<tr>
<td></td>
<td>π</td>
<td>0.8015(Sp)</td>
<td>0.8015(Sp)</td>
</tr>
</tbody>
</table>

Table 6. Hybridization coefficient of six bonds calculated by NBO method in B3LYP level at different basis sets for Adenine.

<table>
<thead>
<tr>
<th>N1-C6</th>
<th>C2-N3</th>
<th>C4-C5</th>
<th>C6-N10</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31g</td>
<td>σ</td>
<td>0.7591(Sp)</td>
<td>0.7591(Sp)</td>
</tr>
<tr>
<td></td>
<td>π</td>
<td>0.7924(Sp)</td>
<td>0.7924(Sp)</td>
</tr>
</tbody>
</table>
Table 7. Hybridization coefficient of six bonds calculated by NBO method in HF level at different basis sets for Thymine.

<table>
<thead>
<tr>
<th></th>
<th>N1-C2</th>
<th>N3-C4</th>
<th>C4-C5</th>
<th>C6-O7</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ</td>
<td>0.7913</td>
<td>0.6114</td>
<td>0.7089</td>
<td>0.5960</td>
</tr>
<tr>
<td>π</td>
<td>0.6642</td>
<td>0.7475</td>
<td>0.5301</td>
<td>0.8480</td>
</tr>
<tr>
<td>6-31g*</td>
<td>0.7980</td>
<td>0.6144</td>
<td>0.7088</td>
<td>0.5854</td>
</tr>
<tr>
<td>π</td>
<td>0.6608</td>
<td>0.7505</td>
<td>0.5217</td>
<td>0.8532</td>
</tr>
<tr>
<td>6-31g</td>
<td>0.7892</td>
<td>0.6124</td>
<td>0.7069</td>
<td>0.6003</td>
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<tr>
<td>π</td>
<td>0.6642</td>
<td>0.7476</td>
<td>0.5262</td>
<td>0.8560</td>
</tr>
<tr>
<td>6-31g*</td>
<td>0.7998</td>
<td>0.6131</td>
<td>0.7072</td>
<td>0.5897</td>
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<tr>
<td>π</td>
<td>0.6596</td>
<td>0.7516</td>
<td>0.5207</td>
<td>0.8532</td>
</tr>
<tr>
<td>6-31g*</td>
<td>0.8034</td>
<td>0.6143</td>
<td>0.7088</td>
<td>0.5854</td>
</tr>
<tr>
<td>π</td>
<td>0.6617</td>
<td>0.7498</td>
<td>0.5218</td>
<td>0.8532</td>
</tr>
<tr>
<td>6-31+g</td>
<td>0.7787</td>
<td>0.6131</td>
<td>0.7085</td>
<td>0.6044</td>
</tr>
<tr>
<td>π</td>
<td>0.6565</td>
<td>0.7463</td>
<td>0.5241</td>
<td>0.8532</td>
</tr>
<tr>
<td>6-31+g</td>
<td>0.7787</td>
<td>0.6131</td>
<td>0.7084</td>
<td>0.6044</td>
</tr>
<tr>
<td>π</td>
<td>0.6565</td>
<td>0.7463</td>
<td>0.5241</td>
<td>0.8532</td>
</tr>
<tr>
<td>6-31+g*</td>
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<tr>
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<tr>
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<td>0.6096</td>
<td>0.7085</td>
<td>0.5937</td>
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<td>π</td>
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<td>0.7491</td>
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Table 8. Hybridization coefficient of six bonds calculated by NBO method in B3LYP level at different basis sets for Thymine.

<table>
<thead>
<tr>
<th></th>
<th>N1-C2</th>
<th>N3-C4</th>
<th>C4-C5</th>
<th>C6-O7</th>
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</thead>
<tbody>
<tr>
<td>σ</td>
<td>0.7890</td>
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<td>π</td>
<td>0.6846</td>
<td>0.7289</td>
<td>0.5604</td>
<td>0.8241</td>
</tr>
<tr>
<td>6-31g*</td>
<td>0.7919</td>
<td>0.6107</td>
<td>0.7092</td>
<td>0.5917</td>
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<tr>
<td>π</td>
<td>0.6801</td>
<td>0.7331</td>
<td>0.5580</td>
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<tr>
<td>6-31g</td>
<td>0.7888</td>
<td>0.6115</td>
<td>0.7078</td>
<td>0.6010</td>
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<tr>
<td>π</td>
<td>0.6831</td>
<td>0.7309</td>
<td>0.5611</td>
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Acknowledgment

We are grateful to Dr. M. Monajemi, Department of Chemistry, Science & Research Campus, I.A. University, P.O.Box 14515-755, Tehran, Iran.
Fig. 4 Dipole, Quadrupole, Octapole, Hexadecapole moments VS. Primitive Gaussian Function for Tymine at the different basis sets.
Fig. 5 Dipole, Quadrupole, Octapole, Hexadecapole moments VS. Primitive Gaussian Function for Thymine at the different basis sets.
### Table 9. Occupancy orbital, Energy, Donor, Acceptor, Natural charge and Total Lewis for Adenine at HF level.

<table>
<thead>
<tr>
<th>Lowest Occupancy</th>
<th>Highest Energy (kcal/mol)</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Natural charge</th>
<th>Total Lewis (%)</th>
</tr>
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<tbody>
<tr>
<td>6-31g</td>
<td>1.67243</td>
<td>-0.39338</td>
<td>N7</td>
<td>BD(2) C 4- C 5</td>
<td>N10 -0.87236</td>
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<td>BD(2) C 8- N9</td>
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<td>6-31g*</td>
<td>1.67093</td>
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<td>N7</td>
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</table>

### Table 10. Occupancy orbital, Energy, Donor, Acceptor, Natural charge and Total Lewis for Adenine at B3LYP level.

<table>
<thead>
<tr>
<th>Lowest Occupancy</th>
<th>Highest Energy (kcal/mol)</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Natural charge</th>
<th>Total Lewis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31g</td>
<td>1.60319</td>
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<td>BD(2) C 4- C 5</td>
<td>N10 -0.80443</td>
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<td>N10 -0.74140</td>
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<td>BD(2) C 8- N9</td>
<td>96.9559</td>
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<tr>
<td>6-31g**</td>
<td>1.60120</td>
<td>-0.29546</td>
<td>N7</td>
<td>BD(2) C 4- C 5</td>
<td>N10 -0.80498</td>
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<td>6-31g*</td>
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<td>-0.28996</td>
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<td>BD(2) C 4- C 5</td>
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<td>BD(2) C 8- N9</td>
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### Table 11. Occupancy orbital, Energy, Donor, Acceptor, Natural charge and Total Lewis for Thymine at HF level.

<table>
<thead>
<tr>
<th>Lowest Occupancy</th>
<th>Highest Energy (kcal/mol)</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Natural charge</th>
<th>Total Lewis (%)</th>
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<tbody>
<tr>
<td>6-31g</td>
<td>1.71842</td>
<td>-0.41440</td>
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<td>BD(2) C 2- O 8</td>
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<tr>
<td>6-31g*</td>
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<td>-0.39619</td>
<td>N1</td>
<td>BD(2) C 2- O 8</td>
<td>N1 -0.76252</td>
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<td>BD(2) C 6- O 7</td>
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<tr>
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<td>1.72011</td>
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<td>N1 -0.77623</td>
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<td>BD(2) C 6- O 7</td>
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<tr>
<td>6-31g*</td>
<td>1.72802</td>
<td>-0.40085</td>
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<td>N1 -0.72344</td>
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<td>-0.39601</td>
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<tr>
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<tr>
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<td>N1 -0.72777</td>
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<td>BD(2) C 6- O 7</td>
<td>98.2589</td>
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</tbody>
</table>
Table 12. Occupancy orbital, Energy, Donor, Acceptor, Natural charge and Total Lewis for Thymine at B3LYP level.

<table>
<thead>
<tr>
<th>6-31g</th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>
| Lower Occupancy | Highest Energy (kcal/mol) | Donor | Acceptor | Natural charge | Total Lewis (%)
| 1.63869 | -0.28569 | N | BD*(2) C 2- O 8 | C 9 | -0.70986 | 97.7948 |
| BD*(2) C 6- O 7 |
| 1.64755 | -0.27410 | N | BD*(2) C 2- O 8 | C 9 | -0.68207 | 97.7948 |
| BD*(2) C 6- O 7 |
| 1.64116 | -0.29421 | N | BD*(2) C 2- O 8 | N 1 | -0.62153 | 97.7977 |
| BD*(2) C 6- O 7 |
| 1.65113 | -0.28263 | N | BD*(2) C 2- O 8 | N 1 | -0.64127 | 97.7881 |
| BD*(2) C 6- O 7 |
| 1.63900 | -0.30082 | N | BD*(2) C 2- O 8 | N 1 | -0.61978 | 97.8079 |
| BD*(2) C 6- O 7 |
| 1.63509 | -0.29900 | N | BD*(2) C 2- O 8 | N 1 | -0.68064 | 97.7969 |
| BD*(2) C 6- O 7 |
| 1.64906 | -0.29088 | N | BD*(2) C 2- O 8 | N 1 | -0.63657 | 97.8006 |
| BD*(2) C 6- O 7 |
| 1.65022 | -0.29131 | N | BD*(2) C 2- O 8 | N 1 | -0.64244 | 97.8036 |
| BD*(2) C 6- O 7 |

REFERENCES