Intermolecular interactions in organometallic crystal

Wojciech Jankiewicz, Rafał Podeszwa

Institute of Chemistry, University of Silesia
wojtekjankiewicz@gmail.com

Abstract

CuJN₂ - (5-chloro-7-carboxy-2-methyl-N-O-quinoline)-bis(triphenylophosphine)copper(I) is a recently obtained complex consisting of two phenylphosphines and quinoline derivative. We performed a theoretical study of intermolecular interactions between molecules in this system and of the effects of changes in the intramonomer geometries. Empirically obtained coordinates by X-ray crystallography were used as a starting point to perform computations based on density functional theory (DFT) and second-order Møller-Plesset perturbation theory (MP2).

1. The Investigated System

Empirically obtained coordinates by X-ray crystallography were used as a starting point to perform computations based on density functional theory (DFT) and second-order Møller-Plesset perturbation theory (MP2).

2. The purposes of the research

In our research we are going to:

• Establish the most important configurations of interacting monomers in the examined system,
• Investigate the nature of interaction,
• Estimate the cohesion energy of the crystal.

3. Theory

Our study is mainly based on two computational methods:

3.1 DFT

We use hybrid functional B3LYP to approximate the exchange-correlation energy functional in density functional theory (DFT)

\[ E_{XCD} = \sum_r \left( \frac{f}{k^r} \sum_{i=1}^{N} \sum_{j=1}^{N} E_{ij}^{(r)} \right) + \alpha \left( \frac{f}{k^r} \sum_{i=1}^{N} \sum_{j=1}^{N} E_{ij}^{(r)} \right) \]

where following components of the sum are:

1. exchange-correlation energy from local spin density approximation (LSDA)
2. difference between exchange HF energy and LSDA exchange energy
4. Lee-Yang-Parr’s correlation energy

\[ E_{XCD} = \frac{1}{2} \sum_r \frac{f}{k^r} \sum_{i=1}^{N} \sum_{j=1}^{N} E_{ij}^{(r)} \]

This correction provides accurate interaction energies and has correct asymptotical dispersion component. This is particularly important for molecular crystals, where multiple long-range interactions are present. The dispersion correction is taken into account during geometry optimization of the system. The general expression is given below:

\[ E_{disp} = \frac{3}{8} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{C_{ij}^{6}}{R_{ij}^{6}} \]

4.1 Structure of the Crystal

\[ \text{X-RAY} \quad \text{SAMPLE} \]

4.2 Interaction configurations

\[ \text{Figure 3: The closest environment of the reference molecule} \]

5. Results

Table 2: The most important interactions. Energies in kcal/mol computed using self-consistent field method, density functional theory/+D3 method and Møller-Plesset's perturbation theory. Distances in angstroms.

<table>
<thead>
<tr>
<th>No</th>
<th>R[A]</th>
<th>SCF</th>
<th>DFT</th>
<th>DFT+D</th>
<th>MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.31</td>
<td>4.61</td>
<td>4.31</td>
<td>-15.35</td>
<td>-10.61</td>
</tr>
<tr>
<td>2</td>
<td>9.35</td>
<td>0.75</td>
<td>0.27</td>
<td>-28.41</td>
<td>-19.41</td>
</tr>
<tr>
<td>3</td>
<td>10.28</td>
<td>5.69</td>
<td>6.73</td>
<td>-19.08</td>
<td>-14.03</td>
</tr>
<tr>
<td>4</td>
<td>10.94</td>
<td>4.79</td>
<td>4.82</td>
<td>-13.84</td>
<td>-9.40</td>
</tr>
<tr>
<td>5</td>
<td>11.11</td>
<td>4.07</td>
<td>4.08</td>
<td>-15.12</td>
<td>-9.28</td>
</tr>
<tr>
<td>6</td>
<td>11.61</td>
<td>1.77</td>
<td>1.50</td>
<td>-14.44</td>
<td>-9.51</td>
</tr>
<tr>
<td>7</td>
<td>12.41</td>
<td>2.05</td>
<td>1.92</td>
<td>-3.71</td>
<td>-1.97</td>
</tr>
<tr>
<td>8</td>
<td>12.79</td>
<td>1.37</td>
<td>1.38</td>
<td>-4.26</td>
<td>-2.73</td>
</tr>
<tr>
<td>9</td>
<td>13.00</td>
<td>1.77</td>
<td>1.70</td>
<td>-3.95</td>
<td>-2.12</td>
</tr>
<tr>
<td>10</td>
<td>14.12</td>
<td>4.38</td>
<td>4.29</td>
<td>-6.78</td>
<td>-5.04</td>
</tr>
</tbody>
</table>

6. Conclusions

• The most important intermolecular interaction configurations have been established.
• The dominant contribution of dispersion interactions to stabilize the crystal has been shown.
• The estimated cohesion energy has been established as 477.06 kcal/mol and after hydrogen optimization 20.34 kcal/mol.

Figure 1: X-ray structure of the monomer

Figure 2: Getting crystal structure process

Table 1: Short characteristic of investigated system.

| Number of atoms in monomer: | 92 |
| Number of monomers in unit cell: | 2 |

Figure 5: Example of intermolecular configurations

Table 2: The most important interactions. Energies in kcal/mol computed using self-consistent field method, density functional theory/+D3 method and Møller-Plesset’s perturbation theory. Distances in angstroms.

References

[1] J.G. Małecki, to be published... (CCDC 972976)