

Scientific paper

# Electronic Structures and Spectroscopic Properties of the Self-assembly Complexes for Dipyridone

Chao Yan and Shi Wu\*

Department of Chemistry, Zhejiang University, Hangzhou 310 027, China

\* Corresponding author: E-mail: wushi@zju.edu.cn; tel: 8657188206529; fax: 8657188206529

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## Abstract

The DFT and semiempirical methods were utilized to study the structures and spectra of the self-assembly complexes formed by dipyridone derivatives. The complexes with the negative binding energies could be formed via hydrogen bonding between two monomers. Due to the presence of the electron-donating substituents on the monomers, the binding affinities of the complexes were generally increased. Simultaneously, the LUMO-HOMO energy gaps of the complexes were widened, and the first absorptions in the electronic spectra were blue-shifted relative to that of the monomer. As the hydrogen bonds were formed, the IR stretching vibrations of the N–H bonds in the complexes were weakened. The chemical shifts of the carbon atoms on the C=O bonds were changed downfield under the effect of the electron-donating groups.

**Keywords:** Dipyridone, hydrogen bonds, energy gap, B3LYP/3-21G.

## 1. Introduction

The simple subunits of molecules are often used to self-assembly to form two- or three-dimensional ordered functional supramolecular aggregates via hydrogen bonds owing to the stability, orientation and saturation. The modification on the subunits can realize the conductivity, fluorescence and intelligence of the aggregates. Thus hydrogen bonding plays an important role both in the formation of the functional materials for the polymers<sup>1,2</sup> and the interaction of the biological macromolecules in the human being.<sup>3–6</sup> Then the interests in the other fields were also stimulated.<sup>7,8</sup> Wen et al. revealed that the change of the etching pattern could indicate the existence of the hydrogen-bonding interaction between the adsorbed polymers and acetaminophen crystal surface.<sup>1</sup> Park et al. found that the volume fraction of the hydrogen-bonding functional group was an important factor in determining the miscibility.<sup>2</sup> Buck et al. believed both the competing interaction and atomic thermal motion broadened the distribution of the donor-acceptor contacts in the human lysozyme.<sup>3</sup> Mukherjee et al. suggested that the pyramidal rather than planar amino groups improved the hydrogen bonds in the protein-DNA complex.<sup>4</sup> Cavallari et al. recommended that

the different activity of the repressor and mutant could be ascribed to a varied dynamical behavior in view of the hydrogen bonding interaction with DNA.<sup>5</sup> Yokomizo et al. proved that the time-averaged hydrogen bonding patterns in the human lysozyme were significant only near the protein surface.<sup>6</sup> Ahn et al. found that the various polymorphs of oxalyl dihydrazide displayed a range of different hydrogen-bonding arrangements.<sup>7</sup> The protic solvents could accelerate the rate of the decarboxylation for benzisoxazole-3-carboxylic acids in the presence of the hydrogen bonds.<sup>8</sup> In addition, the hydrogen bonds will affect the electroreduction waves of the imidazole derivatives,<sup>9</sup> and the improved semiempirical method based on the hydrogen bonding systems has been established theoretically.<sup>10</sup>

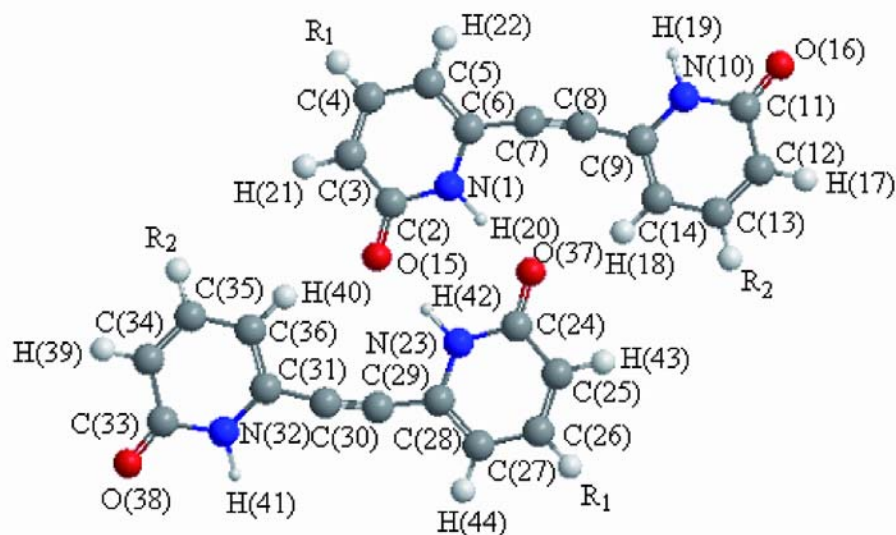
2-pyridone is an important precursor of antibiotics which are used as inhibitors of the DNA gyrase. Thus 2-pyridone<sup>11</sup> and its derivatives<sup>12,13</sup> are widely investigated and exploited. J. D. Wuest and coworkers have proved that dipyridone can be formed by linking the two 2-pyridone using the functional groups like the acetylene or amine.<sup>14,15</sup> Asymmetric dipyridones are ready to form a dimer, whereas symmetric dipyridones are easy to self-assembly to form the linear and planar polymers in aprotic solvent.<sup>14</sup> The formation of the polymers via hydrogen bonding is an important approach of preparing liquid-cry-

stal and other functional polymers. There have been only a few reports on the hydrogen-bonding complexes formed by dipyrindones. In this passage, we want to investigate the structures and properties of the self-assembly complexes based on dipyrindones. First we optimized the geometries of the monomer and complexes to achieve the binding energies of the complexes. Then we could determine whether the complexes would be formed or not. After this we changed the substituents and explored their effects on the stabilities of the complexes. At last, we predicted the spectroscopic characters of the complexes so that the theoretical data can be helpful to the experimental research.

## 2. Computational Methods

The hydrogen bonded complexes can be considered as the supramolecular systems, where electrons delocalize and move in the whole system. Then the minimum of total energy on the potential curve can be found. The host-guest interactions<sup>16</sup> were measured with the help of the binding constants,<sup>17,18</sup> stability constants,<sup>19</sup> and equilibrium constants<sup>20</sup> experimentally and theoretically. The binding energy of a complex was defined as the total energy of the complex minus the energies of the two monomers. Although dipyrindones linked by the acetylenic or amino groups have been synthesized in the experiment, other derivatives have not been prepared yet under the re-

striction of the experimental conditions. Theoretical studies have the advantage in predicting their possible structures and relative stabilities of the unknown complexes, as well as exploring the regularities of stabilities for the complexes when the substituents exist. The AM1 and DFT methods in GAUSSIAN 03<sup>21</sup> package were used to study the structures and spectra of super-molecular complexes and organic compounds.<sup>22–27</sup> Complex I was formed via the hydrogen bonding by the two dipyrindone linked with the acetylenic group. The lengths of the hydrogen bonds in complex I were designed within 0.20–0.22 nm. Complexes II–XI were designed by changing the substituents on the monomers as shown in Figure 1. Geometry optimization for the monomer and complexes was performed using the AM1 and DFT methods at B3LYP/STO-3G and B3LYP/3-21G levels, respectively, to achieve the binding energies of the complexes. On the basis of the B3LYP/3-21G optimized geometries, the electronic spectra of the complexes were computed with the INDO/CIS method<sup>28</sup> as in the ZINDO program without any adjustment of the parameters.<sup>29–31</sup> 197 configurations including the ground state were states generated by exciting electrons from 14 highest occupied molecular orbitals (HOMO) into 14 lowest unoccupied molecular orbitals (LUMO). Then the IR frequencies and intensities of the complexes were calculated utilizing the AM1 method. At last, the NMR spectra for the monomer and complexes were investigated employing the GIAO method at B3LYP/3-21G level.

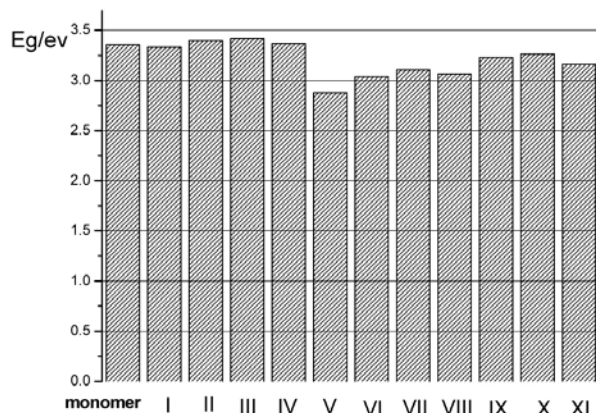


**Figure 1.** The optimized geometries of the hydrogen bonding complexes at the B3LYP/3-21G level.

Complex I:  $R_1 = R_2 = \text{H}$ ; Complex II:  $R_1 = \text{CH}_3$ ,  $R_2 = \text{H}$ ; Complex III:  $R_1 = \text{CH}_2\text{CH}_3$ ,  $R_2 = \text{H}$ ;  
 Complex IV:  $R_1 = \text{CH}(\text{CH}_3)_2$ ,  $R_2 = \text{H}$ ; Complex V:  $R_1 = \text{CHO}$ ,  $R_2 = \text{H}$ ;  
 Complex VI:  $R_1 = \text{COCH}_3$ ,  $R_2 = \text{H}$ ; Complex VII:  $R_1 = \text{COOCH}_3$ ,  $R_2 = \text{H}$ ;  
 Complex VIII:  $R_1 = \text{COOH}$ ,  $R_2 = \text{H}$ ; Complex IX:  $R_1 = R_2 = \text{COOH}$ ;  
 Complex X:  $R_1 = -\text{CH}=\text{CH}_2$ ,  $R_2 = \text{H}$ ; Complex XI:  $R_1 = -\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ ,  $R_2 = \text{H}$ .

### 3. Results and Discussion

**Configurations and stabilities:** The stabilities of the complexes are characterized using the binding energies. The larger absolute values of the binding energies lead to the higher stabilities of the complexes. The negative sign means the decrease of the total energy when a complex is formed. The absolute values of the binding energies for complexes I–XI with the AM1 method were within the range of 0.41–0.44 eV (Table 1), larger than the experimental results 0.28 eV in the hydrogen bonded complex of Cl<sub>2</sub>O with the hydroxyl radical.<sup>32</sup> It would be found that the larger binding energies of these complexes are arisen from the extra weaker hydrogen bonds between O(15) and H(40) as well as O(37) and H(18) besides the normal ones between O(15) and H(42), O(37) and H(20). These more hydrogen bonds made the complexes deformed and hydrogen bonds departed from the normal straight line spontaneously, shown in Figure 1. The X-ray experiment also showed that the acetylenic dipyrindone is non-planar and the hydrogen bonds in the dimer were bent about 13° from the linear form.<sup>14</sup>



**Figure 1.** LUMO-HOMO energy gaps (Eg) of the monomer and complexes.

The binding energy of complex II of the two methods was larger than that of complex I, illustrating that the electron-donating groups are favorable to the formation of hydrogen bonding. The binding energies of complexes III and IV of the two methods were lower than that of complex II, and thus the steric effect of the bulky substituents weakened the hydrogen bonds. The presence of the electron-withdrawing groups is disadvantageous to the hydrogen bonds since the binding energies of complexes V–VIII

of the two methods were less than that of complex I. In complex IX, the extra hydrogen bonds, between the oxygen atoms in the carboxyl groups located at the R<sub>2</sub> position and H (21) as well as H (43), lead to higher binding energy of complex IX at B3LYP/3-21G level. The binding energy of complex XI optimized with the B3LYP/3-21G method was greater than that of complex X owing to the stronger electron-donating capacity of the substituent.

The lengths of the hydrogen bonds in complexes II, VI and XI were 0.1664, 0.1659 and 0.1660 nm. These values were consistent with 0.1716 nm of the O...H bond determined by the X-ray diffraction.<sup>15</sup> These short hydrogen bonds are arisen from the partial proton transfer from nitrogen to oxygen atoms, similar to the situation in the linear polymeric array of the dipyrindone with an amine linkage.<sup>15</sup> Minor differences in the subunit structure of the complexes could change the behavior of the aggregation.<sup>33</sup> The binding energy of complex I optimized at the B3LYP/3-21G level, after the rectification of the basis set superposition errors (BSSE), was –1.7587 eV. Then the error of complex I was 0.0020 eV, which is less than 0.1037 eV of the hydrogen-bonded complex formed by Cl<sub>2</sub>O with OH.<sup>32</sup>

**Electronic structure:** A small molecule behaves as an insulator because of its large energy gap. Supramolecular complexes formed by the two small molecules often possess the decreased energy gaps, thus their properties such as conductivities and fluorescence can be improved. The energy gaps are affected by the substituents, and then many attempts have been made to reduce the energy gaps. The energy gaps can be determined experimentally using the electrochemical method, and can also be computed theoretically. The LUMO-HOMO energy gaps of complexes II–IV calculated at the B3LYP/3-21G level were 3.3979, 3.4178 and 3.3683 eV, wider than that of complex I (3.3332 eV). The presence of the electron-donating substituents enhances the stabilities of the complexes. This is because the density of electron cloud on the monomer is enlarged and the conjugated effect is improved. In contrast, the electron-withdrawing substituents reduced the energy gaps of complexes V–XI to 2.8793, 3.0385, 3.1076, 3.0654, 3.2287, 3.2643 and 3.1604 eV, respectively. The decrease in the energy gaps degrades the stabilities of the complexes. Additionally, the energy gaps of complexes V–VII were amplified gradually, which had a relationship with the increasing electron-donating capacities of the substituents.

There is little charge transfer between the two monomers according to the Mulliken charges of the monomers,

**Table 1.** The binding energies  $\Delta E$  (eV) of complexes I–XI optimized with AM1 and B3LYP/3-21G methods.

Complexes	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
$\Delta E$ (AM1)	–0.4314	–0.4320	–0.4303	–0.4300	–0.4197	–0.4083	–0.4199	–0.4206	–0.4147	–0.4444	–0.4277
$\Delta E$ (B3LYP/3-21G)	–1.7607	–1.7685	–1.7628	–1.7630	–1.6238	–1.6488	–1.7313	–1.6635	–2.0709	–1.7208	–1.7718

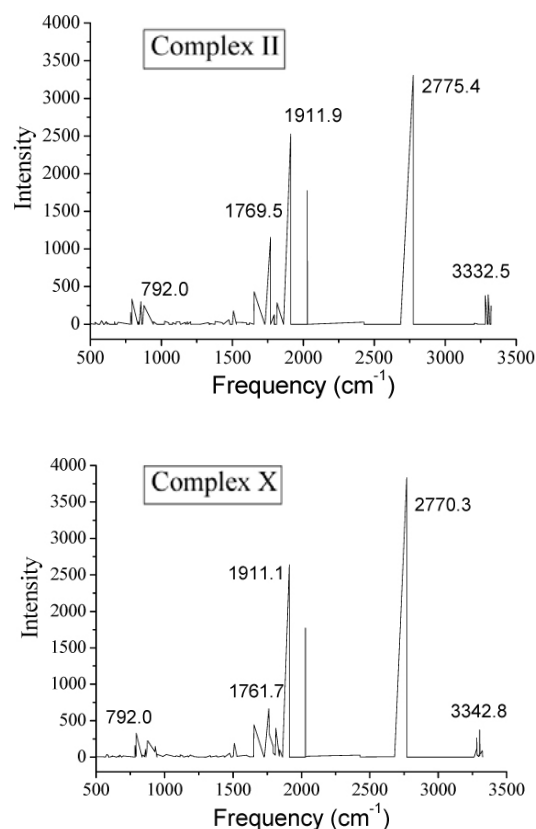
and substituents have almost no effect on the charge transfer. The Mulliken charges of O(15) and O(37) were  $-0.5604$ , and those of H(20) and H(42) were  $0.3764$  in complex II. There exists a strong hydrogen bonding interaction between O(15) and H(42) as well as O(37) and H(20).

**Electronic absorption spectra:** It is well-known that the absorption of the electromagnetic radiation especially in the UV and Near-IR region of the spectra provides important information about the energy gaps of the supramolecular complexes. The first absorption at  $371.3$  nm in the electronic spectrum of the monomer is strong absorption, which should be corresponded to the experimental UV absorption  $332$  nm of analogous dipyrindone linked by an amine.<sup>15</sup> The multiplier of the calculated values is  $0.90$ . Then the absorptions in the electronic spectra predicted theoretically of the other complexes can be reliable. The first absorption peak of complex II was computed to be at  $354.0$  nm, generated by the  $\pi \rightarrow \pi^*$  electronic transition from HOMO  $a_g(84)$  to LUMO  $a_g(85)$  (Table 2). HOMO and LUMO of complex II were composed of the  $P_z$  orbitals of the carbon atoms C(12) and C(28), respectively, and the contribution coefficients were  $-0.3574$  and  $0.2645$ . C(28) is connected with N(23), and close to the hydrogen bond. The formation of the hydrogen bonds has a great influence on the strong and first absorption in the electronic spectrum of the complex.

The main absorptions of complex II were slightly blue-shifted relative to those of complex I. The absorptions of complexes II, III and IV looked alike, indicating the alkyl groups had little effect on the electronic spectra. The first absorption peaks of complexes III and IV ( $353.3$  and  $355.3$  nm) were blue-shifted compared with that of complex I ( $356.7$  nm) thanks to their bigger energy gaps. On the contrary, the first absorption peaks of complexes V–IX located at  $364.7$ ,  $360.1$ ,  $365.0$ ,  $366.2$ , and  $371.1$  nm, respectively, were red-shifted compared with that of complex I. This is mainly related to the less energy gaps. The appearances of the electronic spectra for complexes V, VI and VII were resembled, indicating that the substituents

with the similar functional groups could not change the spectroscopic characteristics greatly.

**IR spectra:** The thermal stabilities of supramolecular complexes are related to the delocalization of electrons and strength of the bonds in the chain, which can be reflected in the IR spectra. In the monomer, the stretching vibration of the C=O bonds was located at  $1767.9$   $\text{cm}^{-1}$ , which was consistent with the experimental value  $1672$



**Figure 2.** The IR spectra of complexes II and X with the AM1 method.

**Table 2.** The electronic spectra of complexes II, V, VI and X.

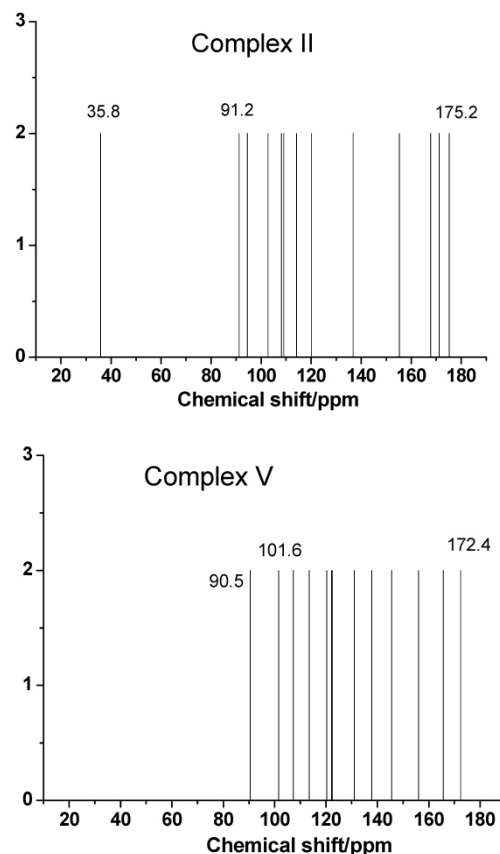
$\lambda/\text{nm}$	$f$	Transition nature	Coefficient	$\lambda/\text{nm}$	$f$	Transition nature	Coefficient
Complex II				Complex V			
354.0	1.9605	$a_g(84) \rightarrow a_g(85)$	$-0.6226$	364.7	1.8906	$b_u(88) \rightarrow a_g(89)$	$0.6051$
293.9	0.0014	$a_g(77) \rightarrow a_g(85)$	$0.2932$	312.5	0.0013	$b_u(84) \rightarrow b_u(90)$	$0.6950$
291.3	0.0987	$a_g(82) \rightarrow b_u(86)$	$0.4640$	307.0	0.4853	$b_u(88) \rightarrow a_g(91)$	$0.5357$
289.5	0.0014	$b_u(80) \rightarrow a_g(90)$	$0.4241$	292.8	0.0019	$a_g(83) \rightarrow a_g(91)$	$0.3834$
266.9	0.0010	$a_g(84) \rightarrow b_u(93)$	$0.5896$	285.5	0.0018	$b_u(80) \rightarrow b_u(90)$	$0.4257$
Complex VI				Complex X			
360.1	1.9593	$a_g(94) \rightarrow b_u(95)$	$-0.6058$	355.4	2.0021	$a_g(88) \rightarrow b_u(90)$	$0.6391$
309.6	0.0012	$b_u(90) \rightarrow b_u(96)$	$0.6789$	297.7	0.0017	$b_u(84) \rightarrow b_u(90)$	$0.5452$
302.6	0.4358	$a_g(94) \rightarrow a_g(97)$	$-0.5198$	296.4	0.2629	$a_g(88) \rightarrow b_u(92)$	$-0.5098$
292.1	0.0014	$a_g(89) \rightarrow a_g(97)$	$-0.2983$	291.4	0.0017	$a_g(81) \rightarrow b_u(92)$	$0.3519$
284.6	0.0011	$a_g(87) \rightarrow b_u(95)$	$-0.2966$	290.9	0.0010	$b_u(80) \rightarrow b_u(89)$	$-0.3999$

$\text{cm}^{-1}$  of 2-pyridone.<sup>14</sup> The experiment also showed that the IR spectrum of analogous dipyrindone containing an amine linkage exhibits an absorption at  $1647\text{ cm}^{-1}$ ,<sup>15</sup> due to the stretching vibration of the C=O bonds. This supports the above calculation though there still exists a small deviation between  $1767.9$  and  $1647\text{ cm}^{-1}$  with the multiplier  $0.93$ . In complex I, the stretching vibration of the C=O bonds was located at  $1763.6\text{ cm}^{-1}$ , red-shifted compared with that of the monomer. This is arisen from the formation of the hydrogen bonding. The experiment also showed that the IR frequency of 2-pyridone is changed from  $1672$  to  $1654\text{ cm}^{-1}$  when the dimer is formed via the hydrogen bonding.<sup>14</sup>

The strongest absorption peaks of complexes I, II, III, IV, V, VI, X and XI were located at  $2776.7$ ,  $2775.4$ ,  $2776.4$ ,  $2760.1$ ,  $2771.1$ ,  $2765.9$ ,  $2770.3$  and  $2759.1\text{ cm}^{-1}$ , respectively, where the monomer has no absorptions. These absorptions were related to the formation of the hydrogen bonds. The N(23)-H(42) and N(1)-H(20) bonds were weakened in the presence of the hydrogen bonds, and the stretching vibrations of these N–H bonds were distinctly red-shifted in contrast to the normal N–H bonds in the monomer. On the other hand, the vibration frequencies of the N(10)-H(19) and N(32)-H(41) bonds were changed less because they were located far away from the hydrogen bonding sites. These results were supported by the experiment that the N–H bond length is longer ( $0.1061\text{ nm}$ ) than the usual owing to the formation of the hydrogen bonds in the dipyrindone.<sup>15</sup>

The IR spectrum of complex X looked analogous to that of complex II though there is a small change in the frequencies of the absorptions (Figure 2). The N–H stretching vibration of complex XI was greatly red-shifted relative to that of complex X. This was aroused by the intensification of the hydrogen bonding and relaxation of the N–H bonds in complex XI in the presence of the  $-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$  group.

**NMR spectra:** The change in electron density of carbon atoms can be reflected by chemical shifts in the  $^{13}\text{C}$  NMR spectrum, which is helpful to explore the effect of substituents. The chemical shifts of H(20) and H(42) in complex I were  $18.1\text{ ppm}$ , basically identical to the experimental result  $14.1\text{ ppm}$ .<sup>14</sup> The calculation results are adjusted by a multiplier of  $0.79$ . This large deviation is caused by the less estimation and systematic error on the shielding effect on the GIAO method using B3LYP method.<sup>34</sup> In the  $^{13}\text{C}$  NMR spectrum of complex II (Figure 3), the carbon atom with the chemical shift at  $35.8\text{ ppm}$  and above  $160\text{ ppm}$  were assigned as  $sp^3\text{-C}$  on the methyl group and  $sp^2\text{-C}$  on the C=O bonds, respectively. Those with the chemical shifts in the range  $90\text{--}110$  and  $110\text{--}160\text{ ppm}$  were ascribed to the  $sp\text{-C}$  atoms and  $sp^2\text{-C}$  atoms on the C=C bonds in the aromatic rings. Compared with that of complex I ( $173.6\text{ ppm}$ ), the chemical shift at  $175.2\text{ ppm}$  of complex II was turned into the low field. The reason was that the density of the electron cloud of the  $sp^2\text{-C}$  atoms on the C=O



**Figure 3.** The  $^{13}\text{C}$  NMR spectra of some complexes at B3LYP/3-21G level.

bonds was decreased and the shielding effect was lessened thanks to the strengthened hydrogen bonding.

The carbon atoms with the chemical shift of  $13\text{--}30\text{ ppm}$  in complexes III and IV were classified as  $sp^3\text{-C}$  on the substituents. The chemical shifts above  $160\text{ ppm}$  of complexes III and IV were transferred downfield in comparison with those of complex I. This was caused by the decreased electron density of the  $sp^2\text{-C}$  atoms on the C=O bonds under the simultaneous influence of the oxygen atom and electron-donating group. In the  $^{13}\text{C}$  NMR spectra of complexes V to IX, the absorption peaks in the range  $90\text{--}110$  and  $110\text{--}160\text{ ppm}$  of the carbon atoms on the C $\equiv$ C and C=C bonds were changed upfield obviously. This indicated that the electron density of the carbon atoms on the C $\equiv$ C and C=C bonds was augmented and the shield effect was also intensified. The chemical shifts above  $160\text{ ppm}$  of the carbon atoms on the C=O bonds were transferred downfield except complex V, compared with those of complex I.

## 4. Conclusion

The complexes could be formed by dipyrindones via the hydrogen bonding. The hydrogen bonding would be

normally strengthened in the presence of the electron-donating groups, and the energy gaps of the complexes increased. In the electronic spectra of the complexes with electron-donating substituents, the first absorption peaks were blue-shifted, compared with that of the parent complex. The IR stretching vibrations of the N–H bonds in the complexes were red-shifted to 2700–2800 cm<sup>-1</sup> due to the formation of the hydrogen bonding. The <sup>13</sup>C chemical shifts of the carbon atoms on the C=O bonds were transferred downfield.

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## Povzetek

S semiempiričnimi metodami in metodo DFT smo predpostavili strukturo in spektralne lastnosti kompleksov, ki jih tvorijo derivati dipiridona. Kompleksi se tvorijo z vodikovo vezjo med dvema monomeroma. Jakost vodikove vezi in s tem afiniteto za tvorbo kompleksov povečajo elektron donorske substituenti. Pri tvorbi kompleksov se povečajo energijske razlike med LUMO in HOMO orbitalami, kar v elektronskih spektrih povzroči modri premik glede na spektre monomerov. S tvorbo vodikovih vezi postanejo vzdolžna nihanja N–H vezi šibkejša, prav tako pa se zaradi elektron donorskih skupin poveča značilni kemijski premik jeder <sup>13</sup>C na karbonilni skupini.