



DFT Study on the Substituent Effect of Anticancer Picoline-Diazido-Pt(IV) Compounds

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The geometric structure of azido Pt(IV) compounds containing picoline was calculated by using density functional theory(DFT) at the LSDA/SDD level. The ESP distribution shows the possible reaction sites of the compounds. In addition, the frequency calculation results assigned the infrared spectra of these compounds, and specified important stretching and bending vibrations. The HOMO-LUMO energy gaps of these compounds are also calculated to explain the charge transfer of the molecules. The distribution of Mulliken charges and natural atomic charges of these atoms is also calculated. Natural bond orbital (NBO) analysis explains the intramolecular interactions and their electron density.

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1 INTRODUCTION

Metal platinum therapy is usually a cancer treatment plan including cisplatin (1), carboplatin (2, 3) and oxaliplatin (4). Especially the successful medical treatment of cisplatin can be called a milestone in cancer chemotherapy. But the incidental properties of these three platinum drugs include poor drug resistance, side effects and targeting (5, 6). In order to solve the problems of these drugs, new drug designs have been implemented to obtain better therapeutic effects. One of the solutions involves introducing new groups into the system to become Pt(IV) to give the compound new stability and new functional groups (7, 8). Drug improvement based on cisplatin (9, 10) and carboplatin (11) are also promising directions to improve the properties of the parent compounds. In addition, a class of compounds can obtain active reactants through light-induced activation, which may be a new direction for targeted therapy. Photodynamic therapy(PDT) is a kind of light therapy that achieves therapeutic effects by producing highly reactive singlet oxygen ${}^{1}O_{2}$ (12). However, the tumor affected by hypoxia is a barrier that is not easy to recover for oxygen-dependent PDT (13). Photoactivated chemotherapy (PACT), a light therapy that is not limited to oxygen, is considered a promising therapy. Some members of transition metals often become prodrugs of PACT (14, 15). The compounds suitable for this method are not limited by the oxygen concentration, and can form a reactive active substance after being irradiated (16).

As a new type of anti-tumor platinum drug, Pt(IV) compounds containing azido have excellent stability in the dark, and they involve the release of azido groups and the production of reactive Pt(II) reactants after being irradiated (17, 18). In addition after these compounds have been developed, they can obviously overcome the easy-to-reducible properties of diiodide Pt(IV) compounds (19). The introduction of new groups has become an effective way to improve the performance of azido-containing compounds. One of the transformation methods for cisplatin, namely the introduction of

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heterocyclic imines(especially pyridine), has been found to have significant damaging capabilities for cancer tissue (20, 21). In addition, the way *cis*-diammine-(pyridine)-chloroplatinum(II) (or cDPCP) binds to DNA and the way it inhibits transcription are different from drugs such as cisplatin (22). Such monofunctional compound provides an excellent idea for appropriately improving the pharmacological activity of drug such as cisplatin.

In previous studies, we have introduced and classified the mechanism of action and toxicity of azido-containing Pt(IV) complexes in detail (23). The addition of the aromatic group(py) can significantly increase the phototoxicity of the compound trans, trans, trans-[Pt(N₃)₂(OH)₂(NH₃)(py)] compared with the amine-based compound *trans,trans,trans*-[Pt(N₃)₂(OH)₂(NH₃)₂] (24, 25). The single pyridine compound *trans, trans, trans*- $[Pt(N_3)_2]$ $(OH)_2(NH_3)(py)$] is non-selective to a variety of cisplatin cells. Moreover, the photoactivation process of trans, trans, trans-[Pt (N₃)₂(OH)₂(NH₃)(py)] and DFT/TDDFT calculations prove that its reaction involves the drop of azide ligand (26). Trans, trans, trans- $[Pt(N_3)_2(OH)_2(py)_2](1)$ is a promising candidate, which can bind to DNA firmly after being activated, and can show much higher photocytotoxicity than cisplatin (27). Furthermore, compound 1 tends to have higher intracellular accumulation and photocytotoxicity compared with its monopyridine azido compound (28). The picoline analog trans, trans, trans- $[Pt(N_3)_2(OH)_2(R_1)(R_2)]$ of compound 1 also have excellent phototoxicity to cisplatin-resistant cells and other specific cell lines. They are the compounds $2(R_1 = 2$ picoline, R_2 =pyridine), $3(R_1 = 3$ -picoline, R_2 =pyridine), $4(R_1 = 4$ picoline, R_2 =pyridine), 5(R_1 = 3-picoline, R_2 = 3-picoline) and 6 $(R_1 = 4$ -picoline, $R_2 = 4$ -picoline) (29).

Generally speaking, we hope that Pt(IV) diazonium compounds are stable in the dark and have cytotoxic effects after being reduced to Pt(II) compounds. For Pt(IV) compounds, their stability is a very important criterion for evaluating whether a compound is excellent when it is not reduced to Pt(II). Therefore, our manuscript focuses more on the stability of tetravalent complexes. Although there have been many experimental studies on such compounds, there are few theoretical studies on these compounds (30). Previous studies have shown that long-range corrected functional, LC-ωPBE, exhibits good characteristics in DFT calculation of cisplatin geometry optimization and Pt ligand vibration. In addition, PBE0 and mPW1PW functional combined with the LanL2TZ(f) basis set of Pt can be used to calculate the IR and Raman spectra of cisplatin (31). Compared with the experimental data, the B3LYP/(aug-ccpVDZ + GD3BJ) method can predict the vibrational spectra of carboplatin, oxaliplatin, nedaplatin and heptaplatin well (32). We have optimized the geometric structure of compound 1 and analyzed the vibration spectrum before (33). In addition, the HOMO-LUMO orbital, natural bond orbital (NBO) and charge distribution of the compounds are also analyzed.

2 COMPUTATIONAL DETAILS

In density functional theory, Local Spin Density Approximation (LSDA) will underestimate the band gap value, and it is not

suitable for systems with rapidly changing electron densities. The Generalized Gradient Approximation (GGA) often includes the gradient correction as the LSDA correction (34, 35). Hybrid functionals can better describe systems with more serious electronic self-interactions. Hybrid functionals can adjust the ratio of HF exchange functionals and DFT exchange functionals by changing the linear combination coefficients, so that the calculated results are closer to the real results of the experiment.

In previous research, We screened some functional methods and basis sets in Gaussian 16 that are suitable for pyridinecontaining azido Pt(IV) complexes (33). When calculating the geometric optimization data, the functionals with smaller deviations from the experimental data are CAM-B3LYP, PBE1PBE, LSDA, etc. But we found that the LSDA functional method has small errors with the experimental values on the key bond length data of Pt-N(N₃), Pt-O(OH) and N(N₃)-N(N₃). In the same way, although LANL2DZ (36) also has a small deviation, the calculation results of the SDD basis set show that bond lengths [Pt-N(N₃), Pt-O(OH) and N(N₃)-N(N₃)] fit well. Therefore, we choose LSDA functional and SDD basis set as our calculation method. All calculation results are obtained at the local spin-density approximation(LSDA) (37, 38) & Stuttgart/ Dresden and D95 ECPs(SDD) (39, 40) level of the density functional theory (DFT) method in Gaussian 16 (41) software. Firstly, the molecular structure of the compounds was optimized to analyze the structural characteristics of the compounds. The optimized structure is used for frequency calculation, and their characteristic absorption peaks are assigned. Electrostatic potential (ESP) is considered to be a possible method to predict the location of the interaction reaction. The ESP distribution of the compounds is drawn by Multiwfn program (42) and Visual Molecular Dynamics 1.9.3 (VMD 1.9.3) program (43). In addition, electronic properties such as HOMO-LUMO energy, Mulliken charge distribution and natural bond orbital (NBO) and natural atomic charge are calculated and analyzed.

3 RESULTS AND DISCUSSION

3.1 Cytotoxic Activity

For the structure of the selected compounds 1, 2, 3, 4, 5 and 6, the main difference lies in the different positions and different amounts of picoline. In this article, we will discuss the effect of substituents on the properties of the compounds. Previous studies have completed the toxicity testing of these compounds through experiments, and their toxicity data is shown in Table 1 (29). Except for compound 2 which exhibits moderate toxicity in the dark, other compounds have good stability in the dark. In addition, compound 2 also has poor phototoxicity (14.5µM in human ovarian cells), and other compounds have good phototoxicity IC₅₀ values (3.1-7.2 μ M in human ovarian cells). In addition, compared with compound 5 (10.4 μM), compounds 3 and 4 showed better phototoxicity(3.3 and 4.6 μ M) for the cisplatin-resistant cell line (A2780cis). Compared with its analogs 4 and 5, compound 6 has good cytotoxicity among the selected compounds (44).

DFT Study	of	Pt(IV)	Compounds
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TABLE 1 Cytotoxicity of compounds 1, 2, 3, 4, 5 and 6 in A2780 an	d
cisplatin-resistant cells(A2780cis) (29).	

compound	IC ₅₀ [μΝ	/l] (420 nm)
	A2780	A2780cis
1	6.7	^a DN
2	14.5	15.5
3	4.0	3.3
4	5.4	4.6
5	7.2	10.4
6	2.1	4.1

^aDN, not determined.

3.2 Molecular Geometry and ESP Analysis

The chemical structures and optimized molecular structures of the selected compounds 1, 2, 3, 4, 5 and 6 are shown in Figures 1 and **2**. For the compounds, the leaving group N_3 is usually the primary research object due to its importance in the first reaction stage, and the release rate of the N₃ group is the reference feature for the rate of photoactivation (18, 45). The OH group is the key group when the compounds and nucleosides are combined, and the non-leaving group containing pyridine will significantly affect the photocytotoxicity of the compounds (24, 46). We have optimized their structure on the LSDA/SDD level, and the optimized structure data of the bond length and bond angle are summarized in Table 2. The date is used to evaluate the possible influence of the substituent effect on the stability and cytotoxicity of the compounds. We compared the calculated dates of complexes 1, 3, 4, 5 and 6 with the experimental values. The results show that their calculated bond length data is relatively close to the experimental data. In this part only, we have uniformly numbered the structures of the compounds for the convenience of research and discussion (Figure S1).

The poorer cytotoxicity of compounds 2 and 4 than other compounds may be related to the bond length of the Pt-N bond. Previous studies have shown that after the introduction of 2-picoline, compound 2 has the fastest reduction rate among our selected compounds (29). The steric clash between the methyl group of 2-picoline and the axial hydroxyl ligand makes the compound 2 is easier to be



FIGURE 2 | The optimized structure of compounds 1, 2, 3, 4, 5 and 6.

restored (47). The data in Table 2 shows that the Pt-N₃ bond lengths (Pt1-N1 and Pt1-N4) of compound 2 are 2.036 and 2.036 Å, respectively. The Pt-N₃ bond lengths of compounds 1, 3, 4, 5 and 6 are 2.032-2.033 Å. Therefore, the results show that the binding ability between the Pt-N bonds between the Pt and the azido group in the compound 2 is weaker than that of the compounds 3, 4, and 6, which indicates that the azido group is easily released from the compound 2 after being irradiated by light. Because the photoreaction of the azido compound involves the reduction of Pt(IV) to Pt(II) and the drop of N₃ after being irradiated. In addition, the Pt1-N1 and Pt1-N4 bond lengths of the compound 5 are 2.037 and 2.030 Å, which are the longest and shortest bond lengths respectively compared with other compounds. That is to say, the binding ability of the Pt atom and the N1 atom of the compound 5 is very weak, and the binding ability to the N4 atom is very strong compared with other compounds. Therefore, according to the previous report, the two azido groups of the compound 5 may be released one by one to participate in the photolysis pathway, and the second N₃ group may be released after binding to the nucleotide (46).





Geometry	Exp.	1	2	3	4	5	6
R(Pt1-O1)	2.027	2.017	2.013	2.016	2.017	2.017	2.018
R(Pt1-O2)	1.990	2.017	2.027	2.017	2.017	2.019	2.018
R(Pt1-N1)	2.046	2.033	2.036	2.033	2.033	2.037	2.033
R(Pt1-N4)	2.043	2.033	2.036	2.032	2.033	2.030	2.033
R(Pt1-N7)	2.047	2.004	2.025	2.005	2.004	2.006	2.004
R(Pt1-N8)	2.046	2.004	2.016	2.005	2.005	2.006	2.004
R(N5-N6)	1.146	1.187	1.187	1.187	1.187	1.187	1.187
R(N4-N5)	1.128	1.243	1.244	1.243	1.243	1.243	1.243
R(N1-N2)	1.215	1.243	1.243	1.243	1.243	1.242	1.243
R(N2-N3)	1.140	1.187	1.188	1.187	1.187	1.188	1.187
R(N8-C3)		1.353	1.354	1.353	1.353	1.350	1.353
A(N1-Pt1-N4)		180.0	176.7	179.9	179.9	179.4	180.0
D(Pt1-N1-N2-N3)	175.7	179.8	-178.2	179.6	179.6	177.5	179.5
D(Pt1-N4-N5-N6)	177.9	-179.7	-178.4	-179.1	-179.5	-180.0	-179.5
D(N2-N1-N4-N5)	176.8	-180.0	-77.6	-179.9	177.6	-170.9	180.0
D(C1-N8-N7-C2)	119.5	-1.4	22.1	-0.9	-2.1	0.2	-1.5

TABLE 2 | Optimized bond length(in Å) and bond angle(in deg) of compounds 1, 2, 3, 4, 5 and 6.

It has been confirmed that the production of O_2 in the photoproduct is likely to come from the hydroxyl groups of such compounds, and the decomposition of these hydroxyl groups after recombination is the key to the release of oxygen (46, 48). The results of the bond length between Pt atom and O atom show that the bond lengths of Pt-O1 and Pt-O2 of compound 2 are 2.013 and 2.027 Å, while the Pt-O bond lengths of the other compounds are relatively equal (2.017-2.019 Å). Therefore, the binding ability of the Pt-O2 bond of the compound 2 is weaker than other compounds, and the binding ability of the Pt-O1 of the compound 2 is less than other compounds.

An important event for the inactivation of cisplatin in cells is the replacement of amines, which affects the activity of the drug directly (49). The azido Pt(IV) compounds, trans, trans, trans-[Pt $(N_3)_2(OH)_2(NH_3)_2$ & trans, trans, trans- $[Pt(N_3)_2(OH)_2(NH_3)]$ (py)], both have the dissociation of NH₃ after being illuminated (24, 50). The pyridine group of the new compound 1 has not been observed to be released and has high cytotoxicity, so the addition of the pyridyl group can compensate for the loss of phototoxicity after the amino group is replaced (51). The bond lengths of Pt1-N7 and Pt1-N8 of the selected compound 2 are 2.025 and 2.016 Å, respectively, which are longer than the bond lengths of Pt-N(pyridine) bonds in other compounds (2.004-2.006 Å). In other words, the binding capacity of the compound 2 with Pt atoms is much smaller than that of other compounds. Therefore, according to previous studies, the stability of the Pt-N bond between the Pt atom and the pyridine group is directly related to the phototoxicity of the compounds. As shown in the data in Table 1, compound 2 has poor phototoxicity compared with other compounds, which is consistent with our calculation results.

We have compared compounds 2, 3 and 4 with different substitution positions, and the results show that meta-picoline compound 3 and para-picoline compound 4 are basically the same. For Ortho-picoline compound 2, although the bond length of Pt-O1 is smaller than that of compounds 3 and 4, the bond lengths of Pt-O2, Pt1-N1, Pt1-N4, Pt1-N7, and Pt1-N8 are all longer than compounds 3 and 4. Therefore, for single pyridine

compounds with different substitution positions, the substituent effect is more significant on compound 2. And the bond length of compound 2 is mostly longer, which may be related to its poor phototoxicity and dark stability. For the effect of different numbers of picoline substituents, we have analyzed the bond lengths of compounds 1, 4 and 6, and the results show that their bond length data are not much different. The bond length analysis results of compounds 1 and 3 are basically the same. The bond lengths of Pt1-N4 and N8-C3 of compound 5 are slightly smaller than that of compounds 1 and 3, and the bond lengths of Pt-O2, Pt1-N1, Pt1-N7 and Pt1-N8 are all longer. Moreover, the cytotoxicity of compound 5 is relatively small, so the number of substituents may also have a significant impact on cytotoxicity.

In addition, the two pyridine/picoline ligands of compound 2 have a large angular deflection (dihedral angle of 22.1°), which may be caused by the steric hindrance of compound **2**. Among the six types of compounds, the bond lengths of Pt-N(N₃), Pt-OH and Pt-N(pyridine) mentioned above are in the order of Pt-N(N₃)>Pt-OH>Pt-N(pyridine). Therefore, the order of the binding ability between Pt and adjacent groups is the pyridine (non-leaving group)>OH>N₃(leaving group) for the compounds we selected. The above analysis is consistent with the results shown by the mechanism of action of these compounds.

The surface electrostatic potential (ESP) can provide a reference for the interaction mode between molecules, and the interaction between molecules depends on the ESP extreme point of the binding site (52–57). The extreme values of the positive and negative potentials drawn with Multiwfn and VMD are shown in **Figure 3**. In the figure, the ESP value of the blue area is negative, and the red area is positive. The para-position of the N atom in pyridine/picoline in all compounds is the most vulnerable site to nucleophilic attack, and the maximum ESP value comes from compound 1 (32.80 kcal/mol). Compound 6 has a methyl substituent at the para position, which causes its extreme point to shift to the meta H position. The N₃ and OH⁻ regions of all compounds have one or more ESP minimums, which are the most vulnerable to proton attack. The lower ESP values are -39.89 and 39.90 kcal/mol for compounds 5 and 6.





For the mono-substituted compounds 2, 3 and 4 with different substitution positions, the minimum points of ESP are -36.04, -38.37 and -38.55 kcal/mol, respectively. So the para-compound 4 has the smallest extreme point for different substituent positions. For 3-picoline compounds 1, 3 and 5, their minimum ESP values are -37.06, -38.37, and -39.89 kcal/mol, respectively. For 4-picoline compounds 1, 4 and 6, their minimum ESP values are -37.06, -38.55 and -39.90 kcal/mol, respectively. Therefore, the ESP value results of the compounds with different numbers of substituents show that the minimum value of ESP decreases due to the increase of the number of substituents.

3.1 Vibrational Assignments

The optimized structure of the selected compounds has been shown in **Figure 2**. The infrared characteristic peaks of different compounds have been assigned, and **Figure 4** has shown their infrared vibration spectra. The infrared vibration frequencies and corresponding vibration intensities of some important groups are summarized in **Table 3**. All vibrations are obtained by optimized calculations at the LSDA/SDD level. It is worth mentioning that in addition to the strong azido group's stretching vibration intensity, the vibration modes of other groups also have high peak intensity. Among the selected vibration modes, stretching vibration and bending vibration are the most active vibration modes.

3.3.1 Hydroxido Vibrations

In all the compounds, the asymmetric stretching vibration v_{asym} (OH) of the hydroxyl group was observed at 3525-3527 cm⁻¹, which is basically consistent with the previously measured OH stretching vibration (58, 59). In addition, OH in-plane deformation vibration δ (OH) was observed at 468-480 cm⁻¹. After the pyridine group of compound 1 was replaced by picoline, the positions of the other complexes only shifted slightly (compounds 2 and 3 shifted around 10 cm⁻¹, the compounds 4, 5 and 6 shifted around 5 cm⁻¹). For the

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TABLE 3 | Frequencies(cm-1) and infrared intensitiesa(km/mol) calculated for compounds 1, 2, 3, 4, 5 and 6.
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Assignment ^b	1	2	3	4	5	6					
v _{asym} (N ₃ -Pt-N ₃)	424 (40.1)	420 (23.6)	425 (38.5)	424 (39.3)	425 (38.3)	425 (37.2)					
δ (OH)	480 (168.9)	468 (80.2)	471 (112.0)	477 (168.9)	475 (113.3)	475 (172.3)					
υ _{sym} (HO-Pt-OH)	566 (0.0)	558 (5.5)	564 (0.6)	565 (0.0)	563 (0.5)	564 (0.0)					
υ _{asym} (HO-Pt-OH)	587 (50.5)	584 (50.6)	587 (49.6)	587 (35.6)	587 (48.6)	588 (45.5)					
γ (py)	785 (86.5)	782 (71.1)	781 (35.9)	781 (37.3)	820 (64.8)	843 (86.2)					
v _{sym} (N ₃)	1267 (92.5)	1265 (69.5)	1268 (89.4)	1267 (91.8)	1268 (69.2)	1268 (91.1)					
δ (py)	1471 (76.0)	1470 (35.3)	1469 (35.8)	1470 (62.0)	1497 (83.3)	1466 (76.4)					
δ (py)	1646 (3.9)	1649 (19.9)	1648 (8.3)	1662 (50.5)	1648 (9.0)	1662 (97.6)					
v _{asym} (N ₃)	2056 (982.1)	2052 (684.6)	2057 (969.4)	2056 (987.7)	2056 (952.2)	2056 (998.3)					
υ _{sym} (CH ₃)	-	2880 (123.1)	2990 (10.7)	2987 (6.1)	2990 (11.1)	2987 (3.6)					
vasym (CH3)	_	3026 (3.0)	3078 (5.7)	3077 (8.6)	3078 (6.1)	3077 (12.5)					
υ _{sym} (CH _{py})	3111 (97.5)	3092 (61.7)	3110 (53.9)	3110 (92.0)	3113 (65.6)	3109 (96.1)					
υ _{asym} (OH)	3527 (39.5)	3527 (41.0)	3527 (36.5)	3526 (37.7)	3526 (28.0)	3525 (36.8)					

^aIR intensity: the value in parentheses. ^bVibrational modes: v = stretch; scr = scissoring; $\gamma =$ out-of-plane angle bending, $\delta =$ in-plane deformation, sym = symmetric and asym = asymmetric. Out-of-phase and in-phase notations refer to the phase between dissimilar vibrations or analogous vibrations when more than one of the same moieties exists. asymmetric stretching vibration v_{asym} (HO-Pt-OH) between the metal Pt atom and the hydroxyl ligand, compound 2 was observed to appear at 584 cm⁻¹, and the compounds 1, 3, 4, 5, 6 were observed at 587-588 cm⁻¹. Therefore, in this vibration mode, the differently substituted picoline has little effect on the infrared absorption position. The symmetric stretching vibration v_{sym} (HO-Pt-OH) between the metal Pt atom and the hydroxyl ligand is observed at 263-566 cm⁻¹ (except for compound 2 at 558 cm⁻¹). However, it is worth noting that the infrared absorption intensity of compounds 1, 2, 3, 4, 5, 6 in the v_{sym} (HO-Pt-OH) vibration mode is not strong.

3.3.1 Azido Vibrations

The azido asymmetric stretching vibration $v_{asym}(N_3)$ has the strongest absorption intensity peak in all vibration modes. Except for the slight shift of the wavenumber of compound 2 (2052 cm⁻¹), the calculated wavenumbers of other compounds are all around 2056 cm⁻¹. Another vibration mode of the azido group is symmetric stretching $v_{sym}(N_3)$, and their absorption peaks are observed at 1265-1268 cm⁻¹. In addition, the $v_{asym}(N_3$ -Pt-N₃) absorption peaks of compounds 1, 3, 4, 5, 6 were observed at 420-425 cm⁻¹.

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3.3.3 Pyridine Vibrations

There have been previous studies on the vibrational spectroscopy of pyridine compounds bound to different metals (60, 61). There are many types of in-plane deformation vibration of pyridine groups $\delta(py)$, one of which is that the wavenumbers of compounds 1, 2, 3 and 5 are 1646-1649 cm⁻¹. However, the corresponding vibration peaks of the two 4-picoline compounds 4 and 6 have a similar shift, and their peaks are observed at 1662 cm⁻¹ and 1662 cm⁻¹. Therefore, for compounds 1, 4 and 6 with different amounts of 4-picoline, the absorption wavenumber of these compounds increased after adding 4-picoline. For another $\delta(py)$ vibration, the wavenumbers of the other compounds are concentrated at 1466-1471 cm⁻¹ except for the deviation of compound 5(1497 cm⁻¹). The reason for the shift is that the methyl of the compound 5 is working, and the similar wavenumber is observed in the $\delta(3\text{-pic})$ of the compound 3. For the out-of-plane angle bending vibration $\gamma(py)$ of the pyridine group, the vibrations of compounds 1, 2, 3, 4, 5 are observed to be distributed at 781-785 cm⁻¹, and the vibrations wavenumber of compounds 5 and 6 are respectively observed at 820 cm⁻¹ and 843 cm⁻¹. Therefore, for the influence of picoline substitution on the wavenumber of $\gamma(py)$, the unsubstituted and monosubstituted compounds only have a small deviation, but the disubstituted compounds 5 and 6 have a larger deviation. For the wavenumber of $\gamma(py)$ vibration, unsubstituted compound=mono-substituted compounds<di-substituted compounds, the wavenumber of double-substituted compounds has increased a lot. That is because the methyl group is added to the unsubstituted pyridine,

which increases the wavenumber of the out-of-plane bending vibration of the compounds 5 and 6.

3.3.4 Methyl Vibrations and C-H Vibrations

For the compounds 2, 3, 4, 5 and 6, the introduction of picoline allowed the methyl characteristic absorption $v_{sym}(CH_3)$ and $v_{asym}(CH_3)$ to be observed. The wavenumber of the $v_{sym}(CH_3)$ of compound 2 was observed at 2880 cm⁻¹, and the wavenumbers of the other compounds (2987-2990 cm⁻¹) shifted by about 100 cm⁻¹. In addition, the infrared absorption intensity of the compound 2 is higher than other compounds for this vibration mode. For the methyl asymmetric stretching vibration v_{asym} (CH₃) on the pyridine group, the wavenumbers of compounds 2, 3, 4, 5, and 6 are observed at 3026, 3078,3077, 3078, and 3077 cm⁻¹, respectively. The two C-H bonds connected to the N atom on the pyridine have a strong infrared absorption intensity in their symmetric stretching vibration $v_{sym}(CH_{py})$. The absorption wavenumber of compound 2 is 3092 cm⁻¹, while the compounds 1, 3, 4, 5, 6 have no significant shift (3109-3113 cm⁻¹). The v(CH₃) vibration wavenumbers of compounds 2, 3, 4, 5, and 6 have been increased after the CH₃ group forms a bond with pyridine. However, due to the steric hindrance of the compound 2, the vibration wavenumber of $v(CH_3)$ of the compound 2 is smaller than that of compounds 1, 3, 4, 5, 6. Therefore, the vibrational spectral distribution of the ortho-picoline compound 2 is most affected by the substituent effect.

3.4 HOMO-LUMO Analysis

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) respectively represent the ability to provide electrons and the ability to obtain electrons (62). The energy gap between HOMO and LUMO determines the charge transfer effect in the molecule (63, 64). The energy gap of the compounds selected in this article is calculated using the LSDA/ SDD level (Table 4, Figure 5). The energy gaps of compounds 1 and 3 are 2.13121 eV and 2.14264 eV, which are the two smaller energy gaps of all the compounds. The compound 2 has the largest energy gap value(2.23788 eV). The HOMO-LUMO transition means that the electron density of compound 2 is transferred from OH to N₃, and compounds 1, 3, 4, 5 and 6 all have electron density transfer from N₃ to py. It is only worth noting that the electron density transfer caused by the HOMO-LUMO transition of compounds 5 and 6 is not obvious, and their energy gap is second only to compound 2(2.16985 and 2.18618 eV).

The analysis of the mono-substituted compounds 2, 3 and 4 shows that the energy gap is 2>4>3. Therefore, the reactivity of these analogs is meta-compound>pair-compound>ortho-compound. The analysis of different numbers of substituents shows that the order of the energy gap of the compounds is 1>3>5. Di-3-picoline compound 5 has the highest reactivity, followed by mono-3-picoline compound 3, and non-picoline compound 1 is the smallest. Similarly, the order of reactivity of different numbers of 4-picoline compounds is also 1>4>6. Therefore, as the number of substituents in the compounds increases, the energy gap value of the compounds decreases.

DFT is not enough to satisfy Koopmans Theorem due to the difference between functionals, which results in the calculated vertical

TABLE 4 HOMO-LUMO energy gaps and related molecular properties of the compounds 1, 2, 3, 4,	5 and 6.
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Molecular properties	1	2	3	4	5	6
Energies (a µ)	-1090 81013	-1129 99212	-1129 99031	-1129 99151	-1169 08848	-1169 09029
E _{HOMO} (eV)	-5.64586	-5.77212	-5.58436	-5.57484	-5.55470	-5.50600
E _{LOMO} (eV)	-3.51465	-3.53424	-3.44172	-3.40989	-3.38485	-3.31982
Energy gap (eV)	2.13121	2.23788	2.14264	2.16495	2.16985	2.18618
Ionization Potential(IP)	7.76631	8.04239	7.83384	7.82211	7.78902	7.73630
Electron Affinity(EA)	1.82360	1.59132	1.57894	1.53401	1.43707	1.32066

ionization potential (VIP) value not approximately equal to -E (HOMO) and vertical electron affinity (VEA) not approximately equal to -E(LUMO) (65). The electron affinity and ionization potential data in Table 4 are calculated using the LSDA functional method and the SDD basis set. The electron affinities corresponding to compounds 1, 2, 3, 4, 5 and 6 are 1.82360, 1.59132, 1.57894, 1.53401, 1.43707 and 1.32066 eV, and their ionization potentials are 7.76631, 8.04239, 7.83384, 7.82211, 7.778902 and 7.73630 eV respectively. For all the compounds, the electron affinity values of compounds 2, 3 and 4 are almost the same, which may be due to the fact that they are isomers. The value of the electron affinity of the compound 1 is the largest, which means that it has the greatest ability to gain an electron compared with other compounds. The electron affinity of compounds 5 and 6 indicates that they have poor electronacquiring ability compared with other compounds. Therefore, the order of the ability to obtain electrons is unsubstituted compound>monosubstituted compounds>disubstituted compounds. The order of the ionization potential is 2>3>4>5>1>6. So compound 2 is the least easily ionized among all compounds. The compound 2 is easily reduced by obtaining an electron, which may be the reason for its large dark toxicity. It is worth noting that compound 6 has the largest phototoxic index (PI, PI is the ratio of cytotoxicity after irradiation to cytotoxicity in the dark) (29). The small IP and EA of compound 6 show that it neither loses nor gains electrons easily, and shows good stability in all compounds.

In different mono-substituent compounds 2, 3 and 4, the order of IP and EA values is the 2>3>4. Therefore, the ability of mono-substituted compounds to obtain electrons is ortho-



compound>meta-compound>para-compound. The IP values of compounds with different numbers of 3-picoline substituents is 3>5>1, and the IP values of compounds with different numbers of 4-picoline substituents is 4>1>6. The EA values of different numbers of picoline substituents are 1>3>5 and 1>4>6, which indicates that the electron-acquiring ability of the compounds decreases after the number of their picoline substituents increases. The ability to be reduced after obtaining electrons is unsubstituted compounds.

3.5 Mulliken and Natural Population Analysis

Mulliken charges and natural atomic charges analysis is a good way to view the charge distribution between the atoms of a molecule. They can also indicate the positive and negative charges (electron donor and electron acceptor), dipole moment and polarizability of the selected compounds (66, 67). The distributions of Mulliken charges and natural atomic charges calculated using LSDA/SDD levels are shown in **Table 5**. The comparison of the charge distributions of the two methods is shown in **Figure 6**.

The calculated natural charge shows that the Pt atoms of the selected compounds have positive charge, and the positive charge is the largest among all the atoms (0.6045-0.6140 e). Among all the compounds, the smallest Pt positive charge, the largest $N(Pt-N_3)$ negative charge and the larger $R(Pt - N_{N3})$ show that compound 30 is easier to be reduced to Pt(IV) than other compounds (68) All H atoms are also positively charged (0.2514-0.5200 e). The O atoms of the hydroxyl groups of all compounds have negative charge (between -0.8648 e and -0.8783 e). Except for the N(N₃) atoms in the middle of the azido group have positive charge, all other N atoms(the N(N₃) atoms at both ends of the azido group, and the N(py) atom of pyridyl group connected to the Pt atom) have negative charge.

The C11, C26 and C28 (corresponding atoms of other compounds) of compound 1 all have negative charge, and its C9, C10, C24 and C25 (corresponding atoms of other compounds) all have positive charges. And the methyl C atoms of compounds 2, 3, 4, 5, and 6 are all negatively charged. And the C_{CH3} atoms of compounds 2, 3, 4, 5 and 6 all have negative charge. The C13 of the compound 1 has positive charge, while the other compounds have negative charge. The charge distribution of the *para*-C atoms of the py group is different between different compounds. The C15 of compound 1 (the corresponding *para*-C atoms of compounds 2, 3 and 5) have negative charge, while the corresponding atoms of compounds 4 and 6 have positive charge, while the compound 1, 2, 3, 4 and 5 all have negative charge, while the compound 6 has positive charge.

TABLE 5 | The calculated Mulliken charges and natural atomic charges of compounds 1, 2, 3, 4, 5 and 6.

PI J.03300 O.6112 PTI -0.0188 (PL) -0.018 (PL) NP 0.0334 0.1483 NV 0.0764 0.1505 NP 0.0764 0.1612 NP 0.03573 0.04738 0.0408 N3 0.0468 0.0357 0.0575 0.0771 HR 0.3580 0.6166 HT 0.3397 0.6163 0.0774 0.0307 0.3397 0.6163 NB -0.1666 0.3014 NB 0.2162 0.3066 0.777 0.3057 0.3397 0.6163 NB -0.1666 0.3014 NB 0.2162 0.2026 0.10 0.1285 0.0173 0.0265 0.0177 0.3007 0.0143 0.0143 112 0.0265 C3 0.0277 0.3007 0.0142 0.0148 0.0148 0.0144 0.0148 0.0141 0.0148 0.0141 0.0148 0.0149 0.0141 0.0149 0.0141 0.0149 0.0141 0.0149 0.0141	Atoms	Mulliken charges	Natural charges	Atoms	Mulliken charges	Natural charges	Atoms	Mulliken charges	Natural charges
Pri -0.0200 0.6102 Pri -0.0788 0.0646 Pri -0.0134 0.0121 NS -0.1418 NS -0.1483 NS -0.1483 NS -0.1471 NS -0.1418 NS -0.1473 -0.0573 -0.0573 -0.0573 -0.0573 -0.0573 -0.0573 -0.0573 -0.0574 -0.0573 -0.0574 -0.0573 C6 -0.0573 -0.0573 -0.0578 -0.0579 -0.0577 -0.0377 -0.0377 -0.0377 -0.0377 -0.0579 -0.0779 C1 -0.9181 -0.0580 C10 -0.03871 -0.0898 -0.0728 -0.0789 C1 -0.9181 -0.0580 C10 -0.0181 -0.0181 -0.0286	1				2			3	
N2 0.0384 0.1493 N2 0.0790 0.1590 N2 0.0438 0.01493 0.01495 0.01388 N3 0.01495 0.01498 N4 0.01495 0.01498 N4 0.01495 0.01498 N4 0.01498 0.01498 0.01498 0.01498 0.01498 0.01498 0.01498 0.01498 0.01498 0.01498 0.01498 0.014978 0.0588 0.014978 0.05880 0.05876 0.03977 0.5182 H8 0.01587 0.03977 0.5188 N8 -0.1880 -0.01680 C1 -0.0998 N8 -0.1887 -0.02976 1 -0.29817 0.05976 C11 -0.02985 C11 -0.09985 C11 -0.09986	Pt1	-0.0300	0.6102	Pt1	-0.0768	0.6045	Pt1	-0.0418	0.6121
NB 0.1433 0.4468 NB 0.1435 0.1328 NB 0.1436 0.1412 C6 0.0573 1.04739 05 0.0774 0.0783 0.0575 0.0575 H6 0.3890 0.5165 H7 0.3890 0.5165 H7 0.3890 0.5165 H7 0.3890 0.5177 0.6163 N8 0.0655 1.0314 0.0650 C10 0.0680 C10 0.1384 0.0677 C10 0.0655 1.0950 C11 0.0389 1.0980 C11 0.1384 0.0677 C11 0.0261 1.0950 C11 0.0389 1.0980 1.0980 0.0286 C14 0.0262 1.11 0.0289 1.13 0.0289 1.13 0.0289 1.13 0.0289 1.13 0.0289 1.13 0.0289 1.14 0.0289 0.0289 1.038 0.0289 1.038 0.0289 1.038 0.0289 1.038 0.0289 1.038 0.0289 <td< td=""><td>N2</td><td>0.0354</td><td>0.1493</td><td>N2</td><td>0.0640</td><td>0.1500</td><td>N2</td><td>0.0334</td><td>0.1501</td></td<>	N2	0.0354	0.1493	N2	0.0640	0.1500	N2	0.0334	0.1501
CAL -0.557/3 -0.94790 CAL -0.5499 -0.94848 CAL -0.557/6 -0.94741 H6 0.3670 0.5176 H6 0.3577 0.5176 H6 0.3577 0.5176 H6 0.3690 0.5176 H7 0.5000 H7 0.3077 0.5178 N8 -0.1165 H7 0.5000 0.02074 -0.30996 N8 -0.11474 -0.31945 C9 -0.0561 0.0665 0.3777 0.30906 N8 -0.114747 -0.02861 C11 -0.2568 C112 -0.2685 0.12871 H1 -0.23817 -0.02861 C13 -0.2684 0.28641 C14 -0.1882 -0.1645 C14 -0.3280 -0.31952 H17 0.2684 0.2865 H16 0.2686 0.2614 H16 0.26260 0.26241 -0.1665 0.2671 H16 0.2666 0.2671 H16 0.2666 0.2671 H16 0.2666 0.2671 H17	N3	-0 1433	-0 1406	N3	-0 1485	-0 1358	N3	-0 1436	-0 1412
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	04	-0.5573	-0.8739	04	-0.5469	-0.8648	04	-0.5576	-0.8741
HT 0.3380 0.5185 H3 0.2379 0.5182 H4 0.3377 0.5183 NS 0.1685 0.3914 NS 0.2192 0.3905 0.3377 0.5183 NS 0.1685 0.3914 NS 0.2102 0.3905 NS 0.0377 0.5183 C10 -0.1301 0.0569 0.2102 0.2906 C10 0.3143 0.0461 C11 -0.2268 C12 -0.2852 C11 0.3377 -0.2286 C13 -0.2564 -0.2863 C12 -0.2865 C14 -0.3874 C15 -0.1966 -0.1911 116 0.2261 C271 H15 0.2286 0.2286 H16 0.2284 0.2862 H16 0.2286 0.2381 0.1622 -0.2286 H17 0.2882 0.3800 NR2 -0.1843 -0.1843 -0.1493 -0.1494 N22 -0.1843 -0.2890 C284 -0.1843 -0.1494 -0.1494	05	-0.5573	-0.8739	05	-0.5748	-0.8783	05	-0.5576	-0.8751
mp 0.3880 0.0103 mp 0.3880 0.2880 mp 0.2980 0.0530 0.0530 0.0530 0.0530 0.0280 0.2980 0.11 0.2980 0.11 0.2980 0.11 0.2980 0.1181 0.2880	<u>Ц</u> е	-0.0070	-0.0733	UG	-0.3740	-0.0700	UG	-0.3370	0.5162
Prin Control Control <thcontrol< th=""> <thcontrol< th=""> <thcont< td=""><td></td><td>0.3960</td><td>0.5105</td><td></td><td>0.3979</td><td>0.5162</td><td></td><td>0.3977</td><td>0.5105</td></thcont<></thcontrol<></thcontrol<>		0.3960	0.5105		0.3979	0.5162		0.3977	0.5105
NB 0.10821 0.0865 0.9147 0.3005 0.3005 0.30147 0.3005 C10 0.1301 0.0585 C10 0.0058 0.0005 C10 0.01343 0.0779 C11 0.22019 0.22085 C12 0.2285 0.2561 0.3571 H15 0.2285 0.3581 H17 0.2285 0.3581 H19 0.2595 0.3581 H19 0.4286 0.2291 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4391 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591 0.4591		0.3960	0.0014		0.3990	0.5200		0.3977	0.0103
Cal -0.0821 0.0674 0.2003 Cal -0.2283 0.00491 C10 -0.1311 0.0530 C10 -0.0563 -0.0863 -0.0860 C10 -0.1381 0.0641 C11 -0.2849 -0.2861 C11 -0.0265 -0.2365 -0.2862 -0.2866 -0.2365 -0.2266 -0.2365 -0.2266 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2660 -0.2670 -0.2681 -0.2681 -0.2681 -0.2681 -0.2681	IN8	-0.1655	-0.3914	IN8	-0.2102	-0.3995	IN8	-0.1547	-0.3845
C10 -0.1340 0.0850 C10 -0.0853 0.0890 C10 -0.1343 0.0481 H12 0.3409 0.22865 C11 -0.2555 -0.22892 -0.2006 C11 0.23877 -0.02285 H14 0.3574 0.22861 C14 -0.1852 -0.22852 -0.2006 C12 -0.2265 -0.22865 H14 0.3574 0.22861 C14 -0.1842 -0.1845 C14 0.2986 0.22861 H15 0.25664 0.1911 H15 0.2566 0.2571 H15 0.2595 0.22643 H16 0.2884 0.2629 H16 0.2566 0.26714 H16 0.2620 0.2563 H17 0.22821 0.2652 H17 0.2685 0.26914 H16 0.2620 0.2563 H18 0.2623 0.22671 N18 -0.1186 -0.3622 N18 -0.1622 -0.3669 H18 0.2623 0.22671 N18 -0.1285 -0.3682 N19 -0.1622 -0.3669 N19 -0.1664 -0.3600 N20 -0.1484 -0.1388 N20 0.0330 0.1493 N21 -0.1654 -0.3660 N22 -0.1484 -0.1655 -0.3913 N22 -0.1655 -0.3914 N22 -0.1714 -0.4638 C22 -0.1231 0.0554 C24 -0.1651 -0.3913 N22 -0.1714 -0.4638 C23 -0.0165 -0.3913 N22 -0.1655 -0.3914 N22 -0.1714 -0.4638 C23 -0.0165 -0.3913 N22 -0.1655 -0.3914 N22 -0.1714 -0.4638 C23 -0.0163 -0.0666 C24 -0.1301 0.0630 C24 -0.1321 0.0558 C24 -0.2572 -0.2450 C25 -0.2664 -0.2674 +126 -0.3627 -0.2627 -0.2657 C25 -0.2674 -0.2444 H26 -0.3627 -0.2637 -0.2657 C25 -0.2674 -0.2644 H26 -0.3627 -0.2657 -0.2657 C25 -0.2674 -0.2644 H26 -0.3627 -0.2657 -0.2657 C25 -0.2674 -0.2644 H26 -0.3657 -0.2627 -0.2657 C25 -0.2674 -0.2645 -0.2677 -0.2657 -0.2627 C266 -0.2654 -0.2645 -0.2657 -0.2627 C267 -0.2674 -0.2647 -0.3657 -0.2627 -0.2657 C268 -0.2654 -0.2645 -0.2657 -0.2657 C268 -0.2654 -0.2645 -0.2657 -0.2657 C268 -0.2654 -0.2645 -0.2657 -0.2657 C268 -0.2654 -0.2645 -0.2657 -0.2657 C268 -0.2654 -0.2645 -0.2656 -0.2658 -0.2656 C264 -0.2645 -0.2656 -0.2658 -0.2657 -0.2627 C265 -0.2657 -0.2646 -0.2656 -0.2658 -0.2657 C265 -0.2657 -0.2647 -0.3656 -0.466 -0.2658 -0.2656 C264 -0.2645 -0.2658 -0.2656 -0.2658 -0.2656 C264 -0.2657 -0.6745 -0.5658 -0.4764 -0.464 -0.2668 C264 -0.2674 -0.2684 -0.2674 -0.2686 -0.2658 -0.6764 C266 -0.5577 -0.6745 -0.5588 -0.6769 -0.5588 -0.6769 C10 -0.1680 -0.4768 N8 -0.1763 -0.3696 -0.5154 N8 -0.1770 -0.3668 +0.2676 -0.5584 -0.4764 -0.3696 C11 -0.3676 -0.4684 -0.2686 -0.6769 C12 -0.3676 -0.4584 -0.2686	C9	-0.0921	0.0665	C9	0.3787	0.3005	C9	-0.2693	0.0579
C11 -0.2619 -0.2698 C11 -0.2682 C11 0.3817 -0.0226 C13 -0.2664 -0.2444 H13 0.3371 0.2899 H14 0.3555 0.2896 C14 -0.2444 H13 0.2871 H16 0.22861 0.2271 H15 0.2289 0.2671 H16 0.2289 0.2673 H16 0.2289 1.992 0.2613 H17 0.1862 H17 0.2663 0.271 H16 0.2289 H17 0.2671 H16 0.2281 H17 0.1285 H17 0.1285 H17 0.1283 0.2573 H16 0.2691 H17 0.3600 H18 0.1282 H18 0.1651 -0.3913 N22 N18 N162 -0.1363 N22 0.1493 N22 0.1493 N22 0.1493 N22 0.1493 N22 0.1493 N22 0.0656 C2 0.2414 0.1321 0.2626 0.22857 0.2241 0.2181 N24 0.2626 0.2567	C10	-0.1301	0.0530	C10	-0.0583	0.0690	C10	-0.1343	0.0461
H12 0.3409 0.2885 C12 -0.2852 -0.2060 C12 -0.22656 -0.22865 -0.22865 H14 0.3574 0.2861 C14 -0.1845 C14 -0.2866 -0.1915 H16 0.2561 -0.1866 -0.1911 H15 0.2563 N17 -0.1051 -0.2397 H17 0.2621 0.2623 H17 0.2683 0.2563 N17 -0.1051 -0.3997 H18 0.2623 0.2671 N18 -0.1128 -0.3882 N18 -0.1062 -0.3997 N21 -0.1064 -0.3600 N21 0.04463 -0.1398 N22 -0.1741 -0.4038 -0.1398 N21 -0.1655 -0.3913 N28 N22 0.0366 0.1493 N22 -0.1714 -0.4038 C23 -0.01291 0.0656 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 -0.2430 <td>C11</td> <td>-0.2619</td> <td>-0.2508</td> <td>C11</td> <td>-0.3535</td> <td>-0.2592</td> <td>C11</td> <td>0.3817</td> <td>-0.0226</td>	C11	-0.2619	-0.2508	C11	-0.3535	-0.2592	C11	0.3817	-0.0226
C13 -0.2864 0.2444 H13 0.3371 0.2869 H13 0.3855 0.2865 C14 -0.1862 -0.1862 -0.1862 -0.1862 -0.1862 -0.1862 -0.1952 C15 -0.1868 -0.1911 H15 0.2861 0.2571 H16 0.2880 0.2833 H17 0.2623 0.2623 N17 -0.1051 -0.3308 N19 -0.1064 -0.3800 N19 -0.1188 -0.3822 N18 -0.1062 -0.3308 N20 -0.1063 -0.3800 N19 -0.1188 -0.3822 N19 -0.1444 -0.1444 -0.1444 -0.1444 -0.1444 -0.1433 N22 -0.0354 -0.2450 -0.2450 N21 -0.1458 -0.3434 C143 -0.1317 0.0503 C22 -0.0131 0.0665 C26 -0.2561 -0.2444 H26 0.2857 -0.2426 -0.2561 -0.2561 -0.2561 -0.2561 -0.2561 -0.2561 -0.2561	H12	0.3409	0.2885	C12	-0.2832	-0.2606	C12	-0.2565	-0.2385
H14 0.3574 0.2891 C14 -0.1842 -0.1845 C14 -0.2890 -0.1852 C15 -0.1896 0.2911 H15 0.2283 N17 -0.1051 0.2383 H17 0.2623 0.2571 N18 -0.1025 -0.3892 N18 -0.1084 0.2393 H18 0.2623 0.2571 N18 -0.1285 -0.3882 N18 -0.1044 -0.1434 N21 -0.1434 -0.3800 N20 -0.1483 -0.1398 N20 0.0483 0.2813 N22 0.0458 0.1434 -0.1463 -0.1483 -0.1493 0.0654 N22 0.0458 0.2411 -0.4638 0.22 -0.1493 0.0564 N22 0.0458 0.2241 1.00526 C24 -0.2574 0.0263 N22 0.04574 0.2644 H26 0.3667 0.2830 C28 -0.2679 0.2651 0.2646 0.2651 0.2646 0.2651 0.2651 0.2646	C13	-0.2564	-0.2444	H13	0.3371	0.2869	H13	0.3555	0.2865
C15 -0.1896 -0.1911 H15 0.2861 0.2871 H16 0.2880 0.2823 H17 0.2621 0.2682 H17 0.2693 0.2853 N17 -0.1061 -0.39697 H18 0.2623 0.2871 N18 -0.1295 -0.3862 N18 -0.1062 -0.3806 N20 -0.1063 -0.3900 N19 -0.1186 -0.3829 N19 -0.1434 -0.1444 N21 -0.4466 0.1482 PC1 -0.4666 -0.1482 N21 -0.1655 -0.3313 N22 -0.0356 -0.3914 C28 -0.1347 -0.0630 C23 -0.0297 -0.2480 N22 -0.0351 0.0685 C25 -0.0234 -0.2430 H26 -0.2487 -0.2480 C24 -0.2554 -0.2417 H27 0.3574 0.2880 -0.2611 H30 0.2881 C28 -0.1681 C28 -0.2611 H30 0.2881 C28 -0.1861 -0.2842	H14	0.3574	0.2881	C14	-0.1842	-0.1845	C14	-0.2960	-0.1952
H16 0.2681 0.2682 H16 0.2686 0.2614 H16 0.26823 0.2583 H17 0.2621 0.2682 H17 0.2693 0.0389 N17 -0.1051 -0.3697 H18 0.2623 0.0571 N18 -0.1138 0.0382 N18 -0.1064 -0.1443 N20 -0.1033 -0.3890 N20 -0.1383 H0133 N21 -0.1453 -0.1483 N21 -0.1483 N21 -0.1483 N21 -0.1483 N21 -0.1483 N23 -0.0530 C23 -0.3913 0.0666 N23 -0.0351 C23 -0.1714 -0.4038 C22 -0.1251 0.02534 N23 -0.0564 -0.2504 -0.2430 H25 0.2667 -0.2581 C26 -0.2664 -0.2644 H26 0.3667 0.2687 -0.2699 -0.2690 -0.2690 -0.2690 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691 -0.2691	C15	-0.1866	-0.1911	H15	0.2561	0.2571	H15	0.2586	0.2643
H17 0.2621 0.2622 H17 0.2563 0.2563 N18 -0.1061 -0.3697 N19 -0.1064 -0.3600 N19 -0.1138 -0.3682 N18 -0.1062 -0.3608 N20 -0.1063 -0.3600 N19 -0.1138 -0.3680 N20 -0.1434 N21 -0.1464 -0.1695 -0.3618 N20 0.0630 -0.1391 0.0530 N22 0.0356 -0.3814 C23 -0.1377 0.0630 C24 -0.2572 -0.2480 N24 -0.1655 -0.3814 C23 -0.1377 0.0630 C24 -0.2572 -0.2480 C24 -0.1521 0.0580 C24 -0.2572 -0.2480 -0.2480 C24 -0.2574 -0.2444 H26 0.3257 -0.2477 H27 0.3409 0.2880 -0.2611 H20 0.2681 -0.1686 -0.1916 H29 0.2616 -0.2617 H27 -0.2657 H23 0.2641 0.2681 0.2681 0.2681 0.2681 0.2681	H16	0.2584	0.2629	H16	0.2566	0.2614	H16	0.2620	0.2523
H18 0.2683 0.2571 N18 0.1225 0.3682 N18 0.1062 0.3608 N19 -0.1084 0.03600 N20 0.1483 -0.3682 N18 0.11655 -0.3618 N21 -0.1133 -0.03600 N20 -0.1483 -0.1398 N20 0.0330 0.1433 N21 -0.1134 -0.1406 N21 0.0486 0.1483 N22 -0.1714 -0.4038 C22 -0.1291 0.0684 N22 -0.1655 -0.3914 C23 -0.1347 0.0630 C24 -0.1301 0.0665 C25 -0.2524 -0.2430 H25 0.3067 0.2861 C26 -0.02614 -0.2644 H26 0.3667 0.2861 <	H17	0.2621	0.2652	H17	0.2593	0.2553	N17	-0.1051	-0.3597
N19 -0.1064 -0.3600 N19 -0.1198 -0.3629 N19 -0.1449 -0.1433 N20 -0.1083 -0.3600 N20 -0.1433 -0.1398 N20 -0.1655 -0.3913 N21 -0.1434 -0.1406 N21 -0.4036 0.22 -0.1291 0.0536 N23 -0.1655 -0.3914 C23 -0.1321 0.0526 C24 -0.2277 -0.2450 C25 -0.0921 0.0665 C25 -0.2284 -0.2430 H25 -0.3669 -0.2885 C26 -0.02814 -0.2606 H28 0.3677 0.2889 -0.2816 C276 -0.2854 -0.2444 H26 0.3269 -0.2815 -0.2824 C38 -0.2618 -0.2608 H28 0.2407 0.2615 H28 0.2415 0.2484 C38 -0.2819 H23 0.2607 0.2615 H28 0.2815 0.2484 C30 -0.1866 -0.1910 H30 0.2607 0.2615 H30 0.2875 H30 0.2623 0	H18	0.2623	0.2571	N18	-0.1235	-0.3682	N18	-0.1062	-0.3608
N20 -0.1083 -0.3860 N20 -0.1483 -0.1398 N20 0.0330 0.1493 N21 -0.1434 -0.1406 N21 -0.0408 C22 -0.1695 -0.3913 N22 -0.0356 0.1493 N22 -0.1741 -0.4038 C22 -0.1291 0.0654 N23 -0.1655 -0.3914 C23 -0.1347 0.0530 C23 -0.0281 0.0286 C26 -0.02544 -0.2644 H26 0.3867 0.2430 H26 0.3867 0.2480 -0.2649 -0.2280 -0.2430 H26 0.3866 -0.1916 H27 0.3574 0.2881 C27 -0.2825 -0.2427 H27 0.3866 -0.1916 -0.1916 -0.1916 -0.2618 -0.2618 -0.2618 -0.2618 0.22615 0.2861 0.2261 0.2661 H20 0.2611 0.2661 0.2617 0.2667 H28 0.2629 H32 0.2621 0.2575 H32 0.3445	N19	-0.1064	-0.3600	N19	-0.1198	-0.3629	N19	-0.1449	-0.1434
N21 -0.1434 -0.1406 N21 .0.0466 0.1482 N21 -0.1655 -0.3913 N22 0.0356 0.1493 N22 -0.1347 0.0630 C23 -0.0191 0.0666 C24 -0.1321 0.0526 C24 -0.2567 -0.2890 C25 -0.0621 0.0666 C25 -0.2440 H2E 0.3574 0.2893 -0.2564 C26 -0.2564 -0.2444 H26 0.3269 0.2930 C28 -0.2693 -0.2815 C28 -0.2618 -0.2508 H28 0.3617 0.2915 C28 -0.1866 -0.1916 C30 0.2686 C29 -0.1860 -0.1875 H29 0.2615 0.2448 C30 0.2681 0.22671 0.2667 0.2861 0.22671 C30 0.2682 H31 0.2624 0.2841 0.2662 H31 0.2666 0.2241 H33 0.2623 0.2571 C33 0.83376 0.30611<	N20	-0.1063	-0.3600	N20	-0.1483	-0.1398	N20	0.0330	0.1493
N2 0.0356 0.1432 N2 -0.1714 -0.4058 C2 -0.1211 0.0554 N23 -0.1655 -0.3914 C23 -0.1247 0.0530 C23 -0.0913 0.0665 C24 -0.1291 0.0665 C25 -0.2524 -0.2430 L25 0.2569 -0.2440 C25 -0.2564 H2 0.2367 0.2889 -0.2811 L27 0.3574 0.2881 C27 -0.2625 -0.2427 E28 -0.1866 -0.1916 H28 0.3400 0.2885 C28 -0.2615 H28 0.2615 0.2861 C30 -0.1860 -0.1875 H29 0.2615 0.2867 H31 0.2621 0.2622 H31 0.2623 -0.27764 0.2842 H33 0.2621 0.2621 0.2617 0.2575 H32 0.2735 -0.7354 H34 0.3576 0.3091 H34 0.2626 0.2246 0.22616 0.2844	N21	-0 1434	-0 1406	N21	0.0456	0 1482	N21	-0 1655	-0.3913
N23 0.01655 0.01814 0.22 0.0117 0.0006 C24 -0.1301 0.0630 C24 -0.1321 0.0626 C24 -0.2572 -0.2450 C25 -0.0921 0.0665 C25 -0.2450 H25 0.02839 -0.2574 C26 -0.2564 -0.2444 H26 0.3629 0.2930 C26 -0.2639 -0.2816 C28 -0.2618 -0.2608 H28 0.3617 0.2915 H29 0.2815 0.2885 C30 -0.1866 -0.1910 H30 0.2607 0.2651 H30 0.2681 0.2628 C30 -0.2814 0.2627 H25 0.2445 0.2842 H31 0.2621 0.2675 H32 0.2445 0.2842 H33 0.2623 0.2571 H33 0.0873 -0.7354 H33 0.2624 0.2337 0.2431 H35 0.2266 0.2267 H34 0.0433 0.3237 0.4388	N22	0.0356	0.1400	N22	-0 1714	-0.4038	C22	-0.1201	0.0534
Actional Caling Caling <thcaling< th=""> <thcaling< th=""> <thcaling< <="" td=""><td>N23</td><td>-0.1655</td><td>-0.3917</td><td>C23</td><td>-0 13/7</td><td>0.4000</td><td>C23</td><td>-0.0013</td><td>0.0666</td></thcaling<></thcaling<></thcaling<>	N23	-0.1655	-0.3917	C23	-0 13/7	0.4000	C23	-0.0013	0.0666
C24 -0.1321 0.0320 C24 -0.2372 -0.2470 C25 -0.0321 0.0685 C25 -0.2430 H25 0.3657 0.2860 C26 -0.2564 -0.2444 H26 0.3629 0.2930 C26 -0.2637 0.2857 C28 -0.2618 -0.2508 H28 0.3617 0.2917 H29 0.2615 0.2646 C30 -0.1866 -0.1910 H30 0.2607 0.2651 H30 0.2581 0.26417 0.2561 H31 0.2621 0.2652 H31 0.2663 0.2657 H32 0.3445 0.2663 H32 0.2652 H31 0.2657 H32 0.3445 0.2663 H32 0.2629 H32 0.2621 0.2575 H32 0.3445 0.2663 H33 0.2623 0.2571 C33 -0.8377 0.2737 H36 0.2666 0.2754 H32 0.2377 0.2641 0.2657 H32 0.	C04	-0.1000	-0.0514	020	0.1047	0.0500	020	-0.0310	0.0000
C20 -0.0221 0.0000 C20 -0.2224 -0.2420 F22 0.0300 0.2800 C26 -0.22564 -0.2244 H26 0.3629 0.2980 C26 -0.2639 -0.2811 H27 0.3374 0.2881 C27 -0.2525 -0.2415 C28 -0.1866 -0.1916 H28 0.3409 0.2885 C29 -0.1860 -0.1875 H29 0.2617 0.2261 C30 -0.1866 -0.1910 H30 0.2603 0.2652 H31 0.22617 0.2267 H31 0.2662 H31 0.2663 0.2651 H32 0.2841 H35 0.2806 0.2841 H33 0.2823 0.2571 C33 -0.8735 -0.7554 0.2666 0.2646 0.2619 Atms Mullken charges Natural charges Mullken charges Natural charges Atoms Mullken charges 0.2646 0.2646 0.2641 N2 0.0373 0.4199 N2 0.0294 <td>024</td> <td>-0.1301</td> <td>0.0000</td> <td>024</td> <td>-0.1321</td> <td>0.0020</td> <td>U24</td> <td>-0.2372</td> <td>-0.2430</td>	024	-0.1301	0.0000	024	-0.1321	0.0020	U24	-0.2372	-0.2430
Czeb -0.2594 -0.2494 Pi26 0.3529 0.2503 -0.2503 -0.2513 P27 -0.2574 0.2525 -0.2427 H27 0.3409 0.2886 C28 -0.2618 -0.2508 H28 0.3617 0.2951 H29 0.2486 -0.1875 H29 0.2815 0.22684 C30 -0.1866 -0.1910 H30 0.2607 0.2651 H30 0.2581 0.22684 H31 0.2623 0.2571 C33 -0.8387 -0.7574 H22 0.2445 0.2684 H33 0.2623 0.2571 C33 -0.8387 -0.7641 H34 0.2606 0.2644 H35 0.3024 0.2841 H34 0.2606 0.2646 0.2619 Mailken charges Natural charges Matural charges Natural charges Atoms Muliken charges 0.2841 H34 0.2646 0.2619 N2 0.0373 0.6107 Pt1 -0.0452 0.6112 0.2614 0.	020	-0.0921	0.0005	025	-0.2324	-0.2430	H25	0.0007	0.2000
H2/2 0.3674 0.2281 C2/2 -0.22525 -0.2242 H2/2 0.3409 0.2885 0.2281 C22 -0.2618 -0.2508 H22 0.3617 0.2915 C22 0.1666 -0.1916 H29 0.3409 0.2865 C29 -0.1660 -0.1875 H29 0.2615 0.2626 K31 0.2621 0.2662 H31 0.2626 H31 0.2667 H32 0.3445 0.2842 H33 0.2623 0.2671 C33 -0.0837 -0.7641 C33 -0.7354 H35 0.3024 0.2837 H36 0.2663 0.2649 H35 0.3024 0.2837 H36 0.2649 0.2619 Atoms Muliken charges Atoms Muliken charges Natural charges 0.2842 0.6112 N2 0.0370 0.6107 Pt1 -0.0582 0.6140 Pt1 -0.0452 0.6112 N2 0.0376 0.5174 N2 0.03969	020	-0.2564	-0.2444	H20	0.3629	0.2930	026	-0.2639	-0.2511
C28 -0.2518 -0.2508 FL28 0.3617 0.2515 C28 -0.1866 -0.1916 F29 0.3409 0.2855 C29 -0.1860 -0.1875 H29 0.2615 0.2684 C30 -0.1866 -0.1910 H30 0.2607 0.2651 H30 0.2621 C32584 0.2629 H31 0.2603 0.2675 H32 0.3445 0.2842 H33 0.2623 0.2571 C33 -0.8387 -0.7641 C33 -0.7354 H34 0.3576 0.3024 0.2841 H35 0.2666 0.2642 H35 0.3024 0.2841 H35 0.2666 0.2641 H36 0.3237 0.2337 0.2646 0.2619 Atoms Muliken charges Atoms Muliken charges Natural charges Atoms Muliken charges 0.2644 0.2619 N2 0.0373 0.1499 N2 0.0237 0.2537 H36 0.2648 0.2619 <	H27	0.3574	0.2881	C27	-0.2525	-0.2427	H27	0.3409	0.2885
H29 0.3409 0.2855 C29 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.1866 -0.2671 -0.2651 -0.2675 H32 0.2681 0.2681 0.2681 0.2681 0.2681 0.2681 0.2681 0.2683 -0.2785 -0.7384 H33 0.2623 0.2571 H34 0.3376 0.0801 H34 0.2683 0.2684 0.2619 Atoms Mulliken charges Natural charges Atoms Mulliken charges Natural charges 0.2637 0.2637 H36 0.2646 0.2619 Atoms Mulliken charges Natural charges Mulliken charges Natural charges Natural charges 0.2637 0.2637 H36 0.2644 0.26562 0.6112 N2 0.0373 0.16107 Pt1 -0.0582 0.6140 Pt1 -0.0452 <td< td=""><td>C28</td><td>-0.2618</td><td>-0.2508</td><td>H28</td><td>0.3617</td><td>0.2915</td><td>C28</td><td>-0.1866</td><td>-0.1916</td></td<>	C28	-0.2618	-0.2508	H28	0.3617	0.2915	C28	-0.1866	-0.1916
C30 -0.1866 -0.1910 H30 0.2607 0.2651 H30 0.2581 0.2262 H31 0.2612 0.2662 H31 0.2617 0.2267 H32 0.2462 H31 0.2617 0.2267 H32 0.2461 0.2663 0.2675 H32 0.3445 0.2842 H33 0.2623 0.2671 C33 -0.8387 -0.7641 C33 -0.8735 -0.73544 H34 0.3676 0.3081 H34 0.2663 0.2676 0.2676 H35 0.3024 0.2837 D.2637 H36 0.2646 0.2619 Atoms Muliken charges Natural charges Matural charges Natural charges Atoms Muliken charges Natural charges <	H29	0.3409	0.2885	C29	-0.1860	-0.1875	H29	0.2615	0.2648
H31 0.2621 0.2652 H31 0.2667 H31 0.2617 0.2567 H32 0.2584 0.2629 H32 0.2621 0.2375 H32 0.2457 C33 -0.8387 -0.7641 C33 -0.8735 -0.7354 H33 0.2623 0.2571 C33 -0.8387 -0.7641 C33 -0.8735 -0.7354 H36 0.3024 0.2841 H35 0.2606 0.2646 0.2619 Atoms Muliken charges Natural charges Atoms Muliken charges Natural charges 4 5 6 - 6 - N2 0.0373 0.6107 Pti -0.0582 0.6140 Pti -0.0452 0.6112 N2 0.0373 0.1499 N2 0.0294 0.1501 N2 0.0350 0.1499 N3 -0.1468 -0.1428 N3 -0.1416 -0.1403 N3 -0.1416 -0.1403 N3 -0.1461 -0.1403	C30	-0.1866	-0.1910	H30	0.2607	0.2651	H30	0.2581	0.2626
H32 0.2584 0.2629 H32 0.2621 0.2575 H32 0.3445 0.2842 H33 0.2623 0.2571 C33 -0.8387 -0.7641 C33 -0.8735 -0.7354 H35 0.3024 0.22637 H35 0.2606 0.2644 H36 0.2337 0.2537 H36 0.2646 0.2619 Atoms Mulliken charges Natural charges Atoms Mulliken charges Natural charges 4 5 6 5 6 5 6 5 6 P1 -0.0370 0.6107 Pt1 -0.0582 0.6140 Pt1 -0.0452 0.6112 N2 0.0373 0.1499 N2 0.0294 0.1501 N2 0.0356 0.1499 N3 -0.1468 -0.1428 N3 -0.1416 -0.1403 N3 -0.1461 -0.1451 O4 -0.5577 -0.8745 O5 -0.5582 -0.8774 0.5159 H3 <td< td=""><td>H31</td><td>0.2621</td><td>0.2652</td><td>H31</td><td>0.2603</td><td>0.2652</td><td>H31</td><td>0.2617</td><td>0.2567</td></td<>	H31	0.2621	0.2652	H31	0.2603	0.2652	H31	0.2617	0.2567
H33 0.2623 0.2571 C33 -0.8387 -0.7641 C33 -0.8735 -0.7354 H34 0.3576 0.3081 H34 0.2606 0.2646 0.2616 H36 0.2337 0.2537 H36 0.2606 0.2644 H36 0.2337 0.2537 H36 0.2646 0.2619 Atoms Muliken charges Natural charges Matural charges Natural charges Natural charges 4 -0.0370 0.6107 Pt1 -0.0582 0.6140 Pt1 -0.0452 0.6112 N2 0.0373 0.1499 N2 0.0294 0.1501 N2 0.0350 0.1499 N3 -0.1481 -0.1428 N3 -0.1416 -0.1403 N3 -0.1481 -0.1451 O4 -0.5579 -0.8741 O4 -0.5563 -0.8739 O4 -0.5582 -0.8746 H6 0.3976 0.5160 H6 0.3986 0.5154 H7 0.39869 0.	H32	0.2584	0.2629	H32	0.2621	0.2575	H32	0.3445	0.2842
H34 0.3876 0.3081 H34 0.2663 0.2676 H35 0.2024 0.2837 H35 0.2606 0.2644 Atoms Muliken charges Natural charges Atoms Muliken charges Atoms Muliken charges Natural charges 4 5 6 Pt1 -0.0370 0.6107 Pt1 -0.0582 0.6140 Pt1 -0.0452 0.6112 N2 0.0373 0.1499 N2 0.0294 0.1501 N2 0.0350 0.1499 N3 -0.1488 N3 -0.1416 -0.1403 N3 -0.1451 -0.1451 O4 -0.5579 -0.8741 O4 -0.5583 -0.8739 O4 -0.5582 -0.8747 O5 -0.577 -0.8745 O5 -0.5888 -0.8759 O5 -0.5582 -0.8747 O5 -0.3976 0.5161 H7 0.3996 0.5154 H7 0.3976 0.5161 H7 0.3999 <th< td=""><td>H33</td><td>0.2623</td><td>0.2571</td><td>C33</td><td>-0.8387</td><td>-0.7641</td><td>C33</td><td>-0.8735</td><td>-0.7354</td></th<>	H33	0.2623	0.2571	C33	-0.8387	-0.7641	C33	-0.8735	-0.7354
H35 0.3024 0.2811 H35 0.2606 0.2844 H36 0.2337 0.2537 H36 0.2646 0.2619 Atoms Muliken charges Natural charges Atoms Muliken charges Atoms Muliken charges Atoms Muliken charges Atoms Muliken charges Natural charges Atoms Muliken charges Natural charges 4 5 6 Pt1 -0.0370 0.6107 Pt1 -0.0582 0.6140 Pt1 -0.0452 0.6112 N2 0.0373 0.1499 N2 0.0244 0.1403 N3 -0.1481 -0.1451 Q4 -0.5579 -0.8741 Q4 -0.5563 -0.8739 Q4 -0.5582 -0.8746 H6 0.3976 0.5160 H6 0.3969 0.5154 H7 0.3976 0.5161 H7 0.3969 0.5154 N8 -0.1701 -0.3966 N8 -0.1550 -0.3846 N8 -0.1703 -0.3966 <td></td> <td></td> <td></td> <td>H34</td> <td>0.3576</td> <td>0.3081</td> <td>H34</td> <td>0.2663</td> <td>0.2676</td>				H34	0.3576	0.3081	H34	0.2663	0.2676
H36 0.2337 0.2537 H36 0.2646 0.2619 Atoms Mulliken charges Natural charges 4 5 6 Pt1 -0.0370 0.6107 Pt1 -0.0582 0.6140 Pt1 -0.0452 0.6112 N2 0.0373 0.1499 N2 0.0294 0.1501 N2 0.0350 0.1499 N3 -0.1468 -0.1428 N3 -0.1416 -0.1403 N3 -0.1481 -0.1451 O4 -0.5577 -0.8745 O5 -0.5588 -0.8739 O4 -0.5582 -0.8746 H7 0.3976 0.5160 H6 0.3969 0.5154 H7 0.3969 0.5154 H7 0.3974 0.5159 H7 0.3976 0.5161 H7 0.3969 0.5154 H8 0.1701 </td <td></td> <td></td> <td></td> <td>H35</td> <td>0.3024</td> <td>0.2841</td> <td>H35</td> <td>0.2606</td> <td>0.2644</td>				H35	0.3024	0.2841	H35	0.2606	0.2644
Atoms Mulliken charges Natural charges Atoms Mulliken charges Natural charges				H36	0.2337	0.2537	H36	0.2646	0.2619
4 5 6 Pt1 -0.0370 0.6107 Pt1 -0.0582 0.6140 Pt1 -0.0452 0.6112 N2 0.0373 0.1499 N2 0.0294 0.1501 N2 0.0350 0.1499 N3 -0.1468 -0.1428 N3 -0.1416 -0.1403 N3 -0.1481 -0.1451 O4 -0.5579 -0.8741 O4 -0.5583 -0.8739 O5 -0.5582 -0.8746 H6 0.3976 0.5160 H6 0.3969 0.5155 H6 0.3969 0.5154 N8 -0.1701 -0.3966 N8 -0.1550 -0.8846 N8 -0.1703 -0.3966 V10 -0.1270 0.0594 C10 -0.1325 0.0465 C 10 -0.1280 0.0585 C11 -0.3962 -0.2587 C 11 0.3813 -0.0231 C 11 -0.4084 -0.2598 C12 -0.3973 -0.2528 C 12 -0.2574 -0.2	Atoms	Mulliken charges	Natural charges	Atoms	Mulliken charges	Natural charges	Atoms	Mulliken charges	Natural charges
P11-0.03700.6107P11-0.05820.6140P11-0.04520.6112N20.03730.1499N20.02940.1501N20.03500.1499N3-0.1468-0.1428N3-0.1403N3-0.1481-0.1451O4-0.5579-0.8741O4-0.5563-0.8739O4-0.5582-0.8746O5-0.5577-0.8745O5-0.5588-0.8759O5-0.5582-0.8746H60.39760.5160H60.39690.5155H60.39690.5154H70.39740.5159H70.39760.5161H70.39690.5154N8-0.1701-0.3966N8-0.1550-0.3846N8-0.1703-0.3966C9-0.09010.0721C9-0.26870.0584C9-0.08940.0731C10-0.12700.0594C10-0.13250.0465C10-0.12800.0585C11-0.3962-0.2587C110.3813-0.0231C11-0.4084-0.2598C12-0.3973-0.2528C12-0.2862H130.35520.2876C140.45240.0360C14-0.2962-0.1959C140.45240.0352C140.45240.3698H160.2500N16-0.1063-0.3595N16-0.1063-0.3598H160.2561N18-0.1481-0.1451N17-0.1065-0.3601<		4			5			6	
N2 0.0373 0.1499 N2 0.0294 0.1501 N2 0.0350 0.1499 N3 -0.1468 -0.1428 N3 -0.1416 -0.1403 N3 -0.1481 -0.1451 O4 -0.5579 -0.8741 O4 -0.5563 -0.8739 O4 -0.5682 -0.8747 O5 -0.5577 -0.8745 O5 -0.5588 -0.8759 O5 -0.5682 -0.8746 H6 0.3976 0.5160 H6 0.3969 0.5155 H6 0.3969 0.5154 H7 0.3974 0.5159 H7 0.3976 0.5161 H7 0.3969 0.5154 N8 -0.1701 -0.3966 N8 -0.1550 -0.3846 N8 -0.1703 -0.3966 C10 -0.1270 0.0594 C10 -0.1382 0.0685 C10 -0.1880 0.0585 C11 -0.3962 -0.2587 C11 0.3813 -0.2392 C12 -0.3862 -0.2526	Pt1	-0.0370	0.6107	Pt1	-0.0582	0.6140	Pt1	-0.0452	0.6112
N3-0.1468-0.1428N3-0.1416-0.1403N3-0.1481-0.1451O4-0.5579-0.8741O4-0.5563-0.8739O4-0.5582-0.8747O5-0.5577-0.8745O5-0.5588-0.8759O5-0.5582-0.8746H60.39760.5160H60.39690.5155H60.39690.5154H70.39740.5159H70.39760.5161H70.39690.5154N8-0.1701-0.3966N8-0.1550-0.3846N8-0.1703-0.3966C9-0.09010.0721C9-0.26870.0584C9-0.08940.0731C10-0.12700.0594C10-0.13250.0465C10-0.12800.0585C12-0.3973-0.2528C12-0.2392C12-0.3862-0.2598C140.45240.0360C14-0.2962-0.1959C140.45240.0352C140.45240.0360C14-0.2962-0.1599C140.45240.0352L130.35540.2605H150.26160.2520N16-0.1063-0.3595N16-0.1063-0.3598H160.26160.2520N16-0.1063-0.3595N17-0.1065-0.3601N17-0.0968-0.3549N17-0.1063-0.3595N18-0.1426N18-0.1055-0.3585N18-0.1481-0.1451	N2	0.0373	0.1499	N2	0.0294	0.1501	N2	0.0350	0.1499
04-0.579-0.874104-0.5563-0.873904-0.5582-0.874705-0.5577-0.874505-0.5588-0.875905-0.5582-0.8746H60.39760.5160H60.39690.5155H60.39690.5154H70.39740.5159H70.39760.5161H70.39690.5154N8-0.1701-0.3966N8-0.1550-0.3846N8-0.1703-0.3966C9-0.09010.0721C9-0.26870.0465C10-0.12800.0585C11-0.3962-0.2587C110.3813-0.0231C11-0.4084-0.2598C12-0.3973-0.2528C12-0.2574-0.2392C12-0.3862-0.2526C140.45240.0360C14-0.2962-0.1959C140.45240.0355C140.45240.0360C14-0.2962-0.1959C140.45240.0355N16-0.1063-0.3598H160.26160.2520N16-0.1063-0.3595N17-0.1065-0.3601N17-0.0968-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.3585N18-0.148	N3	-0.1468	-0.1428	N3	-0.1416	-0.1403	N3	-0.1481	-0.1451
O5 -0.5577 -0.8745 O5 -0.5588 -0.8759 O5 -0.5582 -0.8746 H6 0.3976 0.5160 H6 0.3969 0.5155 H6 0.3969 0.5154 H7 0.3974 0.5159 H7 0.3976 0.5161 H7 0.3969 0.5154 N8 -0.1701 -0.3966 N8 -0.1550 -0.3846 N8 -0.1703 -0.3966 C9 -0.0901 0.0721 C9 -0.2687 0.0584 C9 -0.0894 0.0731 C10 -0.1270 0.0594 C10 -0.1325 0.0465 C10 -0.1280 0.0585 C11 -0.3962 -0.2587 C11 0.3813 -0.0231 C11 -0.4084 -0.2598 C12 -0.3973 -0.2528 C12 -0.2574 -0.2392 C12 -0.3682 -0.2567 C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0352	04	-0.5579	-0.8741	04	-0.5563	-0.8739	04	-0.5582	-0.8747
H6 0.3976 0.5160 H6 0.3969 0.5155 H6 0.3969 0.5154 H7 0.3974 0.5159 H7 0.3976 0.5161 H7 0.3969 0.5154 N8 -0.1701 -0.3966 N8 -0.1550 -0.3846 N8 -0.1703 -0.3966 C9 -0.0901 0.0721 C9 -0.2687 0.0584 C9 -0.0894 0.0731 C10 -0.1270 0.0594 C10 -0.1325 0.0465 C10 -0.1280 0.0585 C11 -0.3962 -0.2587 C11 0.3813 -0.0231 C11 -0.4084 -0.2598 C12 -0.3973 -0.2528 C12 -0.2574 -0.2392 C12 -0.3862 -0.22876 C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0352 H15 0.2605 H15 0.2583 0.2640 H15 0.2605 0.2501 <td< td=""><td>05</td><td>-0.5577</td><td>-0 8745</td><td>05</td><td>-0.5588</td><td>-0.8759</td><td>05</td><td>-0.5582</td><td>-0.8746</td></td<>	05	-0.5577	-0 8745	05	-0.5588	-0.8759	05	-0.5582	-0.8746
H7 0.3974 0.5159 H7 0.3976 0.5161 H7 0.3969 0.5154 N8 -0.1701 -0.3966 N8 -0.1550 -0.3846 N8 -0.1703 -0.3966 C9 -0.0901 0.0721 C9 -0.2687 0.0584 C9 -0.0894 0.0731 C10 -0.1270 0.0594 C10 -0.1325 0.0465 C10 -0.1280 0.0585 C11 -0.3962 -0.2587 C11 0.3813 -0.0231 C11 -0.4084 -0.2598 C12 -0.3973 -0.2528 C12 -0.2574 -0.2392 C12 -0.3862 -0.2526 H13 0.3554 0.2605 H13 0.3552 0.2876 C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0352 H15 0.2615 0.2605 H15 0.2583 0.2640 H15 0.2605 0.2601 N16 -0.1063 -0.3598 H16 0.2616 0.2520 N16 -0.1063 -0.3595 <td>H6</td> <td>0.3976</td> <td>0.5160</td> <td>H6</td> <td>0.3969</td> <td>0.5155</td> <td>H6</td> <td>0.3969</td> <td>0.5154</td>	H6	0.3976	0.5160	H6	0.3969	0.5155	H6	0.3969	0.5154
In 0.0014 0.0100 In 0.0101 In 0.0000 0.0101 N8 -0.1701 -0.3966 N8 -0.1550 -0.3846 N8 -0.1703 -0.3966 C9 -0.0901 0.0721 C9 -0.2687 0.0584 C9 -0.0894 0.0731 C10 -0.1270 0.0594 C10 -0.1325 0.0465 C10 -0.1280 0.0585 C11 -0.3962 -0.2587 C11 0.3813 -0.0231 C11 -0.4084 -0.2598 C12 -0.3973 -0.2528 C12 -0.2574 -0.2392 C12 -0.3862 -0.2526 H13 0.3554 0.2878 H13 0.3542 0.2862 H13 0.3552 0.2876 C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0352 H15 0.2605 H15 0.2583 0.2640 H15 0.2605 0.2601 N16 -0.1063 -0.3598 H16 0.2520 N16 -0.1063 -0.3595	H7	0.3974	0.5159	H7	0.3976	0.5161	H7	0.3969	0.5154
No-0.1761-0.0360No-0.1360-0.0360No-0.1360-0.0540No-0.1760-0.0380C9-0.09010.0721C9-0.26870.0584C9-0.08940.0731C10-0.12700.0594C10-0.13250.0465C10-0.12800.0585C11-0.3962-0.2587C110.3813-0.0231C11-0.4084-0.2598C12-0.3973-0.2528C12-0.2574-0.2392C12-0.3862-0.2526H130.35540.2878H130.35420.2862H130.35520.2876C140.45240.0360C14-0.2962-0.1959C140.45240.0352H150.26150.2605H150.25830.2640H150.26050.2601N16-0.1063-0.3598H160.26160.2520N16-0.1063-0.3595N17-0.1065-0.3601N17-0.0968-0.3549N17-0.1063-0.3595N18-0.1426N18-0.1055-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.1548N190.03500.1499N20-0.1655-0.3914N200.04030.1511N20-0.1704-0.3966C21-0.12960.0531N21-0.1546-0.3865C21-0.12800.0585C22-0.09270.0664C22-0.2722<	NB	-0.1701	-0.3966	NI8	-0.1550	-0.3846	NB	-0 1703	-0.3966
Cos Closerie Closerie Cos Closerie Cos Closerie Cos Closerie	CQ	-0.0901	0.0000	CQ	-0.2687	0.0584	C9	-0.0894	0.0300
C10 -0.1270 0.0394 C10 -0.1223 0.0403 C10 -0.1280 0.0383 C11 -0.3962 -0.2587 C11 0.3813 -0.0231 C11 -0.4084 -0.2598 C12 -0.3973 -0.2578 C12 -0.2574 -0.2392 C12 -0.3862 -0.2576 H13 0.3554 0.2878 H13 0.3542 0.2862 H13 0.3552 0.2876 C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0352 N16 -0.1063 -0.3598 H16 0.2616 0.2520 N16 -0.1063 -0.3595 N17 -0.1065 -0.3601 N17 -0.0968 -0.3549 N17 -0.1063 -0.3595 N18 -0.1426 N18 -0.1055 -0.3585 N18 -0.1481 -0.1451 N19 0.0324 0.1493 N19 -0.1569 -0.1548 N19 0.0350 0.1499	C10	-0.0901	0.0721	C10	-0.2007	0.0304	C10	-0.0094	0.0731
C11-0.3862-0.2587C110.3813-0.0231C11-0.4084-0.2598C12-0.3973-0.2528C12-0.2574-0.2392C12-0.3862-0.2526H130.35540.2878H130.35420.2862H130.35520.2876C140.45240.0360C14-0.2962-0.1959C140.45240.0352H150.26150.2605H150.25830.2640H150.26050.2601N16-0.1063-0.3598H160.26160.2520N16-0.1063-0.3595N17-0.1065-0.3601N17-0.0968-0.3549N17-0.1063-0.3595N18-0.1442-0.1426N18-0.1055-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.1548N190.03500.1499N20-0.1655-0.3914N200.04030.1511N20-0.1704-0.3966C21-0.12960.0531N21-0.1546-0.3865C21-0.12800.0585C22-0.09270.0664C22-0.27220.0488C22-0.08950.0730	010	-0.1270	0.0094	010	-0.1323	0.0403	010	-0.1280	0.0000
C12 -0.3973 -0.2528 C12 -0.2574 -0.2392 C12 -0.3862 -0.2526 H13 0.3554 0.2878 H13 0.3542 0.2862 H13 0.3552 0.2876 C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0362 H15 0.2615 0.2605 H15 0.2583 0.2640 H15 0.2605 0.2601 N16 -0.1063 -0.3598 H16 0.2616 0.2520 N16 -0.1063 -0.3595 N17 -0.1065 -0.3601 N17 -0.0968 -0.3549 N17 -0.1063 -0.3595 N18 -0.1426 N18 -0.1055 -0.3585 N18 -0.1481 -0.1451 N19 0.0324 0.1493 N19 -0.1569 -0.1548 N19 0.0350 0.1499 N20 -0.1655 -0.3914 N20 0.0403 0.1511 N20 -0.1704 -0.3966 C21 -0.1296 0.0531 N21 -0.1546 -0.3865 C21 <td></td> <td>-0.3962</td> <td>-0.2587</td> <td></td> <td>0.3813</td> <td>-0.0231</td> <td></td> <td>-0.4084</td> <td>-0.2598</td>		-0.3962	-0.2587		0.3813	-0.0231		-0.4084	-0.2598
H13 0.3554 0.2878 H13 0.3542 0.2862 H13 0.3552 0.2876 C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0352 H15 0.2615 0.2605 H15 0.2583 0.2640 H15 0.2605 0.2601 N16 -0.1063 -0.3598 H16 0.2616 0.2520 N16 -0.1063 -0.3595 N17 -0.1065 -0.3601 N17 -0.0968 -0.3549 N17 -0.1063 -0.3595 N18 -0.1422 -0.1426 N18 -0.1055 -0.3585 N18 -0.1481 -0.1451 N19 0.0324 0.1493 N19 -0.1569 -0.1548 N19 0.0350 0.1499 N20 -0.1655 -0.3914 N20 0.0403 0.1511 N20 -0.1704 -0.3966 C21 -0.1296 0.0531 N21 -0.1546 -0.3865 C21 -0.1280 0.0585 C22 -0.0927 0.0664 C22 -0.2722 0.0488 <td>C12</td> <td>-0.3973</td> <td>-0.2528</td> <td>C12</td> <td>-0.2574</td> <td>-0.2392</td> <td>C12</td> <td>-0.3862</td> <td>-0.2526</td>	C12	-0.3973	-0.2528	C12	-0.2574	-0.2392	C12	-0.3862	-0.2526
C14 0.4524 0.0360 C14 -0.2962 -0.1959 C14 0.4524 0.0352 H15 0.2615 0.2605 H15 0.2583 0.2640 H15 0.2605 0.2601 N16 -0.1063 -0.3598 H16 0.2616 0.2520 N16 -0.1063 -0.3595 N17 -0.1065 -0.3601 N17 -0.0968 -0.3549 N17 -0.1063 -0.3595 N18 -0.1442 -0.1426 N18 -0.1550 -0.3585 N18 -0.1481 -0.1451 N19 0.0324 0.1493 N19 -0.1569 -0.1548 N19 0.0350 0.1499 N20 -0.1655 -0.3914 N20 0.0403 0.1511 N20 -0.1704 -0.3966 C21 -0.1296 0.0531 N21 -0.1546 -0.3865 C21 -0.1280 0.0585 C22 -0.0927 0.0664 C22 -0.2722 0.0488 C22 -0.0895 0	H13	0.3554	0.2878	H13	0.3542	0.2862	H13	0.3552	0.2876
H150.26150.2605H150.25830.2640H150.26050.2601N16-0.1063-0.3598H160.26160.2520N16-0.1063-0.3595N17-0.1065-0.3601N17-0.0968-0.3549N17-0.1063-0.3595N18-0.1422-0.1426N18-0.1055-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.1548N190.03500.1499N20-0.1655-0.3914N200.04030.1511N20-0.1704-0.3966C21-0.12960.0531N21-0.1546-0.3865C21-0.12800.0585C22-0.09270.0664C22-0.27220.0488C22-0.08950.0730	C14	0.4524	0.0360	C14	-0.2962	-0.1959	C14	0.4524	0.0352
N16 -0.1063 -0.3598 H16 0.2616 0.2520 N16 -0.1063 -0.3595 N17 -0.1065 -0.3601 N17 -0.0968 -0.3549 N17 -0.1063 -0.3595 N18 -0.1426 N18 -0.1055 -0.3585 N18 -0.1481 -0.1451 N19 0.0324 0.1493 N19 -0.1569 -0.1548 N19 0.0350 0.1499 N20 -0.1655 -0.3914 N20 0.0403 0.1511 N20 -0.1704 -0.3966 C21 -0.1296 0.0531 N21 -0.1546 -0.3865 C21 -0.1280 0.0585 C22 -0.0927 0.0664 C22 -0.2722 0.0488 C22 -0.0895 0.0730	H15	0.2615	0.2605	H15	0.2583	0.2640	H15	0.2605	0.2601
N17-0.1065-0.3601N17-0.0968-0.3549N17-0.1063-0.3595N18-0.1426N18-0.1055-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.1548N190.03500.1499N20-0.1655-0.3914N200.04030.1511N20-0.1704-0.3966C21-0.12960.0531N21-0.1546-0.3865C21-0.12800.0585C22-0.09270.0664C22-0.27220.0488C22-0.08950.0730	N16	-0.1063	-0.3598	H16	0.2616	0.2520	N16	-0.1063	-0.3595
N18-0.1422-0.1426N18-0.1055-0.3585N18-0.1481-0.1451N190.03240.1493N19-0.1569-0.1548N190.03500.1499N20-0.1655-0.3914N200.04030.1511N20-0.1704-0.3966C21-0.12960.0531N21-0.1546-0.3865C21-0.12800.0585C22-0.09270.0664C22-0.27220.0488C22-0.08950.0730	N17	-0.1065	-0.3601	N17	-0.0968	-0.3549	N17	-0.1063	-0.3595
N19 0.0324 0.1493 N19 -0.1569 -0.1548 N19 0.0350 0.1499 N20 -0.1655 -0.3914 N20 0.0403 0.1511 N20 -0.1704 -0.3966 C21 -0.1296 0.0531 N21 -0.1546 -0.3865 C21 -0.1280 0.0585 C22 -0.0927 0.0664 C22 -0.2722 0.0488 C22 -0.0895 0.0730	N18	-0.1442	-0.1426	N18	-0.1055	-0.3585	N18	-0.1481	-0.1451
N20 -0.1655 -0.3914 N20 0.0403 0.1511 N20 -0.1704 -0.3966 C21 -0.1296 0.0531 N21 -0.1546 -0.3865 C21 -0.1280 0.0585 C22 -0.0927 0.0664 C22 -0.2722 0.0488 C22 -0.0895 0.0730	N19	0.0324	0.1493	N19	-0.1569	-0.1548	N19	0.0350	0.1499
C21 -0.1296 0.0531 N21 -0.1546 -0.3865 C21 -0.1280 0.0585 C22 -0.0927 0.0664 C22 -0.2722 0.0488 C22 -0.0895 0.0730	N20	-0.1655	-0.3914	N20	0.0403	0.1511	N20	-0.1704	-0.3966
C22 -0.0927 0.0664 C22 -0.2722 0.0488 C22 -0.0895 0.0730	C21	-0.1296	0.0531	N21	-0.1546	-0.3865	C21	-0.1280	0.0585
	C22	-0.0927	0.0664	C22	-0.2722	0.0488	C22	-0.0895	0.0730

(Continued)

TABLE 5 | Continued

Atoms	Mulliken charges	Natural charges	Atoms	Mulliken charges	Natural charges	Atoms	Mulliken charges	Natural charges
C23	-0.2571	-0.2450	C23	-0.1029	0.0549	C23	-0.3867	-0.2527
H24	0.3568	0.2880	C24	0.3830	-0.0155	H24	0.3552	0.2876
C25	-0.2624	-0.2512	H25	0.3694	0.2855	C25	-0.4078	-0.2598
H26	0.3409	0.2885	C26	-0.2557	-0.2443	H26	0.3376	0.2877
C27	-0.1871	-0.1919	H27	0.3380	0.2862	C27	0.4524	0.0352
H28	0.2616	0.2648	C28	-0.3485	-0.1995	H28	0.2606	0.2601
H29	0.2578	0.2624	H29	0.2545	0.2617	H29	0.2576	0.2577
H30	0.3376	0.2877	H30	0.2610	0.2514	H30	0.3376	0.2877
H31	0.2577	0.2582	H31	0.3441	0.2843	H31	0.2576	0.2577
C32	-0.8645	-0.7396	C32	-0.8738	-0.7353	C32	-0.8649	-0.7395
H33	0.2565	0.2606	H33	0.2660	0.2672	H33	0.2585	0.2630
H34	0.2747	0.2758	H34	0.2604	0.2642	H34	0.2743	0.2754
H35	0.2568	0.2615	H35	0.2643	0.2616	H35	0.2542	0.2587
H36	0.2617	0.2566	C36	-0.8631	-0.7362	C36	-0.8649	-0.7395
			H37	0.2410	0.2519	H37	0.2543	0.2588
			H38	0.2869	0.2787	H38	0.2743	0.2754
			H39	0.2663	0.2682	H39	0.2584	0.2628

the addition of a methyl group, which often results in the decrease of the negative charge of the C atom or the conversion of the C atom from negative to positive.

3.6 Natural Bond Orbital Analysis

Natural bond orbital(NBO) analysis explains the Lewis structure, bond type, hybridization type, and the strength of the orbital interaction between the electron donor(i) and the electron acceptor(j) (69). In this article, NBO analysis of selected compounds is performed at the LSDA/SDD level. The strength of the i-j interaction is estimated by the magnitude of the secondorder perturbation interaction energy $E^{(2)}$, which is derived from the second-order perturbation method:

$$\mathbf{E}^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_i - \epsilon_i}$$

Where q_i is the donor orbital occupancy, ε_i and are the diagonal elements orbital energies, and F(i,j) is the off-diagonal NBO Fock matrix element. The larger E⁽²⁾ indicates the stronger the interaction, the greater the donation tendency between the electron donor and the electron donor, and the greater the degree of conjugation of the entire system. The delocalization of the electron density between the bonded/lone paired NBO orbital and the antibonded NBO orbital corresponds to a stable donoracceptor interaction (70). The second-order perturbation stability energy E⁽²⁾ (kcal/mol) of the compound 1 discussed in this article is listed in Table 6. The NBO information of other compounds is basically the same as that of the compound 1 (Table S1, Figure S2). The N(N₃) bonding donor of compound 11 σ (Pt1-N19) to the anti-bonding acceptor σ^* (Pt1-O4), σ^* (Pt1-N8) and σ^* (Pt1-N19) lead to large σ - σ * stability energy. Their stability energies are 114.62, 105.57 and 43.66 kcal/mol, respectively. The stability energy of the bond donor σ (Pt1-N19) to the anti-bond acceptor π^*



Donor (i)	Types	ED/e	Acceptor(j)	Types	ED/e	^a E ⁽²⁾ (kcal/mol)	^b E(i)–E(j)(a.u)	^с F(i,j)(a.u)
BD(1)Pt1-N8	σ	1.92667	BD*(1)Pt1-O4	σ*	0.42369	42.76	0.93	0.196
BD(1)Pt1-N8	σ	1.92667	BD*(1)Pt1-N8	σ^*	0.42866	16.27	0.74	0.108
BD(1)Pt1-N8	σ	1.92667	BD*(1)Pt1-N19	σ^{*}	0.4628	36.74	0.73	0.163
BD(1)Pt1-N19	σ	1.76366	BD*(1)Pt1-O4	σ^*	0.42369	114.62	0.75	0.275
BD(1)Pt1-N19	σ	1.76366	BD*(1)Pt1-N8	σ^{*}	0.42866	105.57	0.56	0.229
BD(1)Pt1-N19	σ	1.76366	BD*(1)Pt1-N19	σ^{\star}	0.4628	43.66	0.55	0.147
BD(1)Pt1-N19	σ	1.76366	BD*(3)N21-N22	π^{*}	0.34724	39.22	0.28	0.096
BD(2)N23-C24	π	1.77504	BD*(2)C25-C28	π^{\star}	0.26323	17.11	0.3	0.065
BD(2)C26-C30	π	1.61949	BD*(2)N23-C24	π^{\star}	0.47008	28.24	0.19	0.066
BD(2)C26-C30	π	1.61949	BD*(2)C25-C28	π^{*}	0.26323	13.44	0.23	0.052
LP(2)N19		1.42835	BD*(2)N21-N22	π^{\star}	0.55482	125.92	0.13	0.115

 ${}^{a}E^{(2)}$ = means energy of hyper conjugative interaction (stabilization energy).

^bE(j) – E(i) - Energy difference between donor and acceptor i and j NBO orbitals.

 $^{c}\textit{F(i,j)}$ is the fock matrix element between i and j NBO orbitals.

BD stands for bond, BD* stands for antibonding.

The bond corresponding to the σ -bonding orbital is called the σ bond; the bond corresponding to the σ -antibonding orbital is called the σ ^{*} bond. The bond corresponding to the π -bonding orbital is called the π ^{*} bond.

 σ^* represents the σ bond formed by the electron on the antibonding orbital.

(N21-N22) is 39.22 kcal/mol. In addition, there is also a strong interaction between the bond donor σ (Pt1-N8) of N(py) and the anti-bond acceptor σ^* (Pt1-O4), σ^* (Pt1-N8) and σ^* (Pt1-N19). The E⁽²⁾ are respectively 42.76, 16.27 and 36.74 kcal/mol. Another larger π - π^* interaction stability energy related to the degree of conjugation occurs in pyridine. The bond donor π (C26-C30) to the anti-bonding acceptor π^* (N23-C24) and π^* (C25-C28), their interaction stability energies E⁽²⁾ are 28.24 and 13.44 kcal/mol. The interaction energy between the bond donor π (N23-C24) and the anti-bond acceptor π^* (C25-C28) is 17.11 kcal/mol. In addition, the magnitude of the interaction energy from the lone pair of electrons LP(N19) to π^* (N21-N22) is 125.92 kcal/mol, and the large E⁽²⁾ value shows the electron donation in the N₃ group.

4 CONCLUSION

The azido picoline compound is a promising anti-tumor compound. In this work, for the first time, we have shown the structural information and infrared spectrum information of the azido picoline compounds. The predicted structural characteristics can be used as a theoretical basis for screening candidates in the future, and the infrared spectrum information accurately identifies the characteristic absorption peaks of the compounds. HOMO-LUMO, NBO analysis and the distribution of natural atomic charges are calculated to study the electronic properties of these compounds. In the later work, we will explore the interaction between these compounds and small biological molecules.

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DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**. Further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

MM performed the statistical analysis, organized the database and wrote the manuscript. HG contributed to conception and design of the study. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fonc.2021.749178/full#supplementary-material

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