Electronic Supplementary Information #3
Theoretical Studies

Title: Metal Complexes of π-Expanded Ligands (7): Syntheses, Structures and Properties of Pt(II) Complexes Containing Isomeric 1- and 2-alkyliminomethyl Pyrene Ligands

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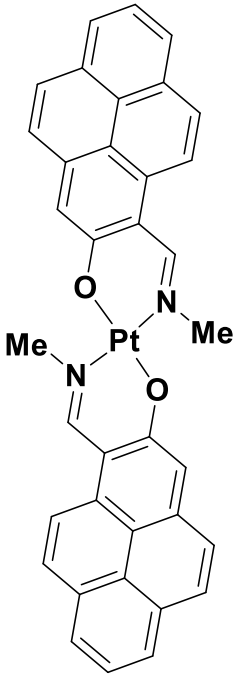
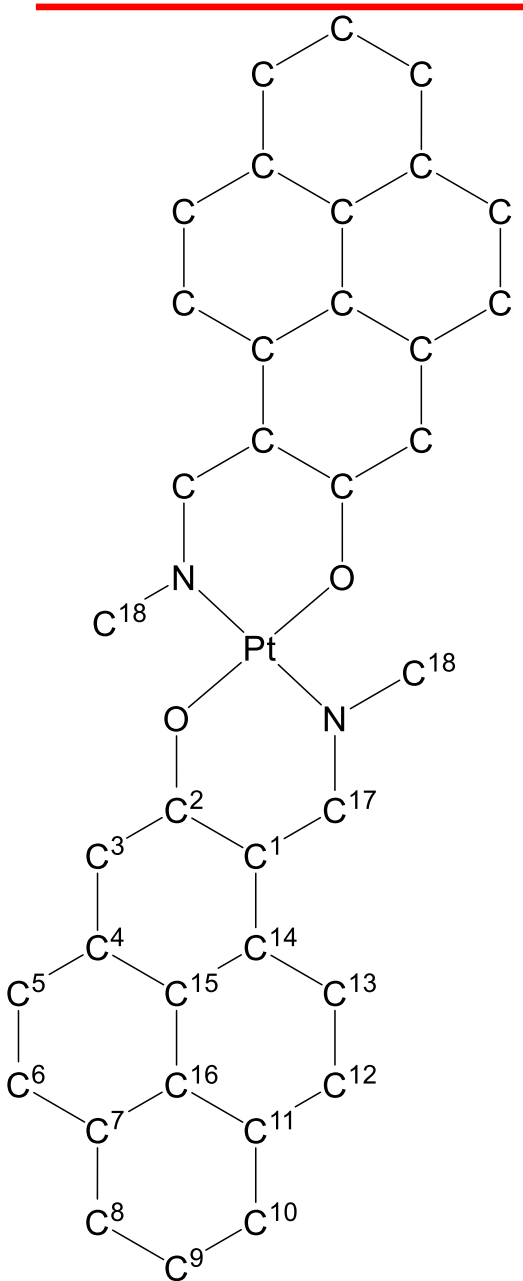
Part-1
Theoretical Studies of *anti*-**2** (New Pt complex)



Program:	Gaussian R-09W Ver.7 + Gauss View Ver.5
Method:	B3LYP
Basis Set:	Hay-Wadt's ECP for Pt, 6-31G(d) for C, H, N, and O
Optimized Structure:	C_i
Comment#1:	Considering the cost of the calculation, alkyl groups on the nitrogens, *n*-C_8H_{17} of **2(Pt)**, are replaced by methyl groups.
Comment #2:	The results of TDDFT are shown in *Supporting Information* #***2*(Pt)** along with experimental data.

Comparison of the Bond Distances (Å)

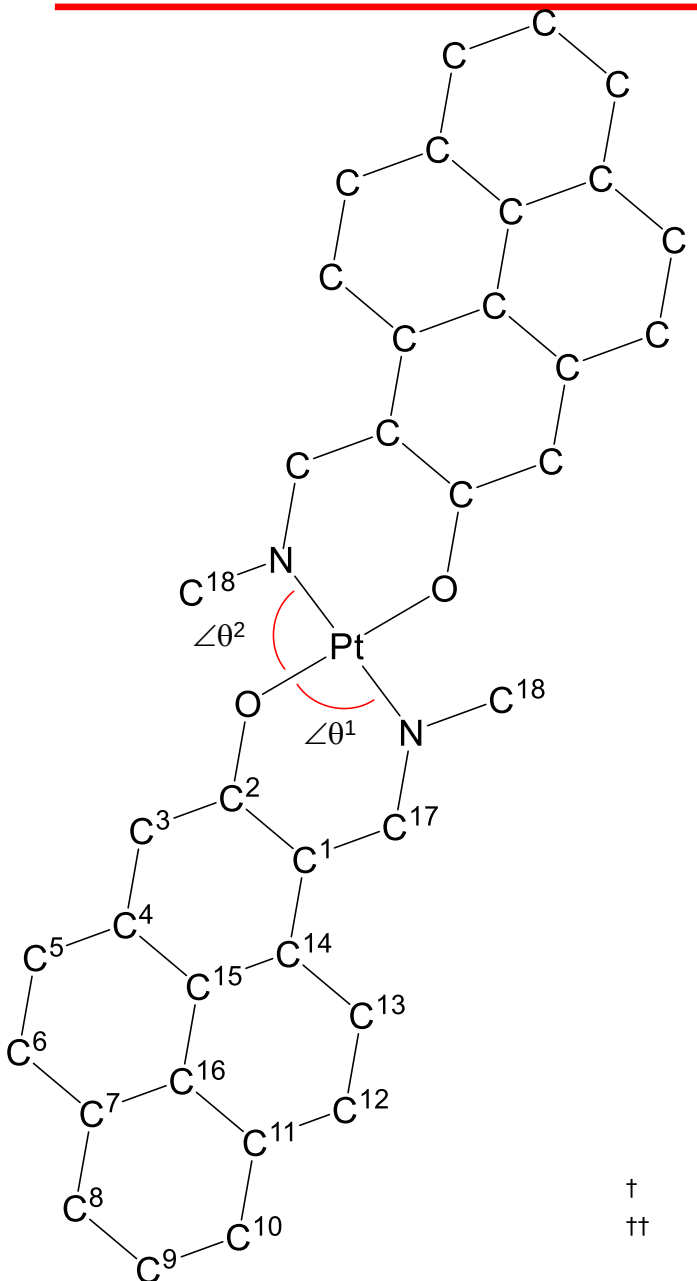


Bond	Theoretical Study†	Diffraction Study for **2**†† Molecule #1	Bond	Theoretical Study	Diffraction Study for **2**†† Molecule #1
Pt-N	2.029	2.000(7)	C^6-C^7	1.440	1.429(14)
Pt-O	2.011	1.953(6)	C^7-C^8	1.400	1.388(14)
O-C^2	1.308	1.307(13)	C^7-C^{16}	1.430	1.419(13)
N-C^{17}	1.303	1.294(12)	C^8-C^9	1.399	1.398(14)
N-C^{18}	1.466	1.482(11)	C^9-C^{10}	1.389	1.389(15)
C^1-C^2	1.434	1.418(11)	C^{10}-C^{11}	1.409	1.400(14)
C^1-C^{14}	1.446	1.453(12)	C^{11}-C^{12}	1.427	1.452(15)
C^1-C^{17}	1.433	1.425(12)	C^{11}-C^{16}	1.425	1.391(13)
C^2-C^3	1.414	1.446(16)	C^{12}-C^{13}	1.366	1.328(14)
C^3-C^4	1.386	1.403(14)	C^{13}-C^{14}	1.437	1.409(13)
C^4-C^5	1.442	1.393(13)	C^{14}-C^{15}	1.424	1.435(12)
C^4-C^{15}	1.437	1.417(13)	C^{15}-C^{16}	1.428	1.434(12)
C^5-C^6	1.358	1.337(15)			

† This Work

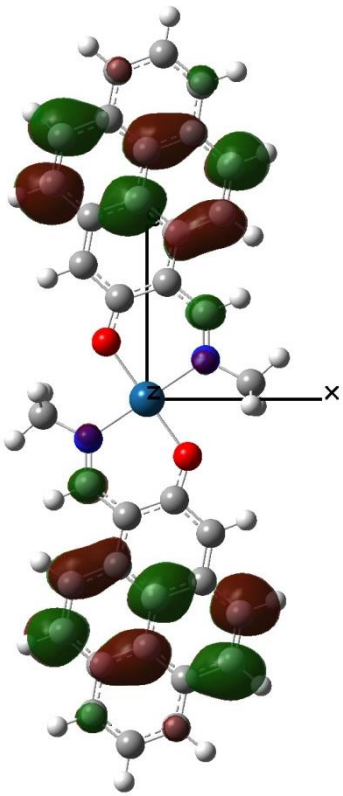
†† This Work, n-Heptyl

Comparison of the Important Bond Angles (degree)

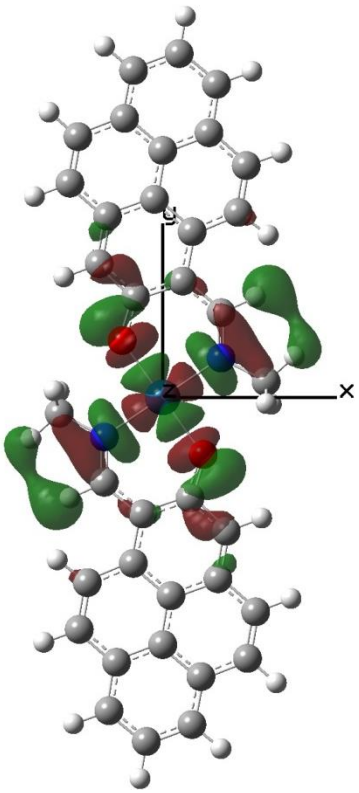


Angle	Theoretical Study†	Diffraction Study††
		Molecule #1
N-Pt-O ($\angle\theta^1$)	91.21	93.0(3)
N-Pt-O ($\angle\theta^2$)	88.78	87.0(3)
Pt-O-C^2	127.64	125.6(6)
O-C^2-C^1	125.58	126.9(10)
C^2-C^1-C^{17}	121.76	120.2(10)
C^1-C^{17}-N	129.39	130.7(9)
C^{17}-N-Pt	124.07	121.8(6)
C^{17}-N-C^{18}	117.50	117.6(8)
C^{18}-N-Pt	118.42	120.3(6)
C^{14}-C^1-C^2	119.37	120.4(9)
C^1-C^2-C^3	118.84	117.2(10)

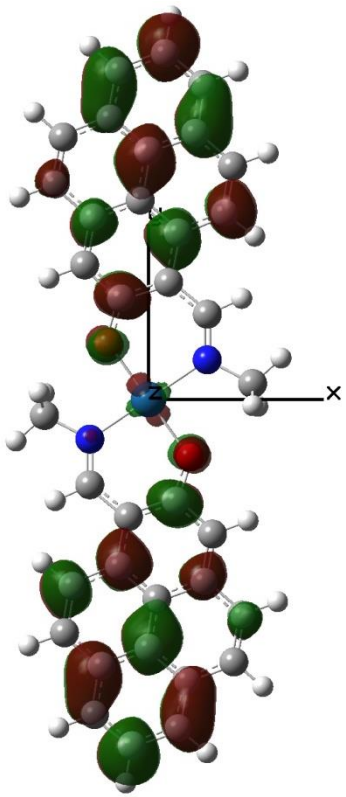
† This Work
†† This Work, n-Heptyl



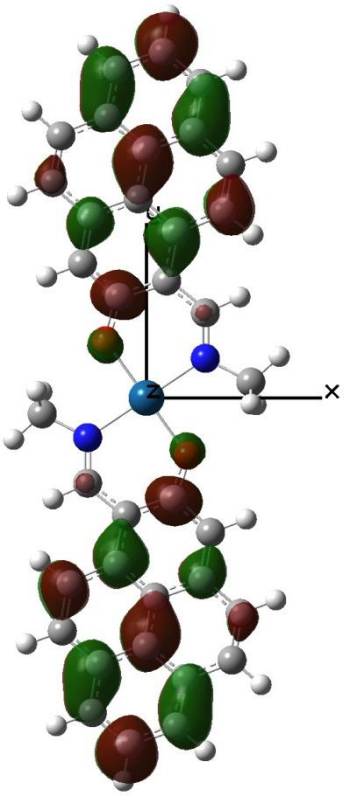
a_u, ϕ_{152}
+0.00 eV



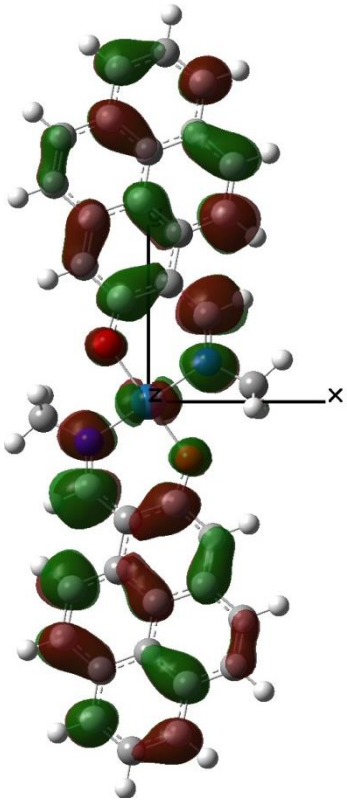
a_g, ϕ_{151}
-0.05 eV



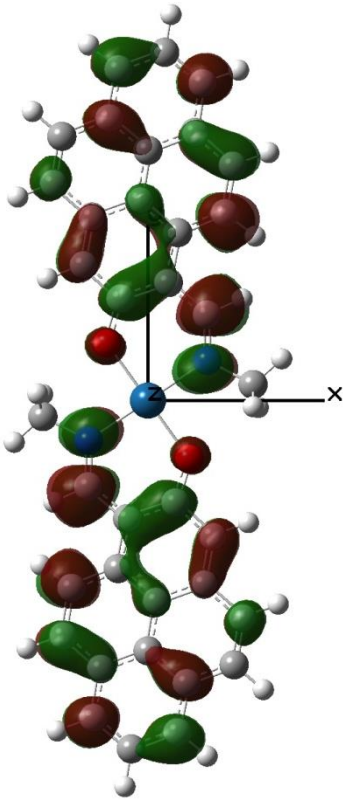
a_g, ϕ_{150}
-0.32 eV



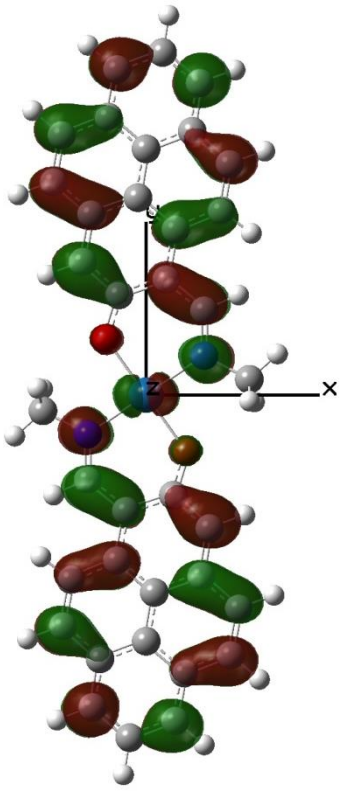
a_u, ϕ_{149}
-0.38 eV



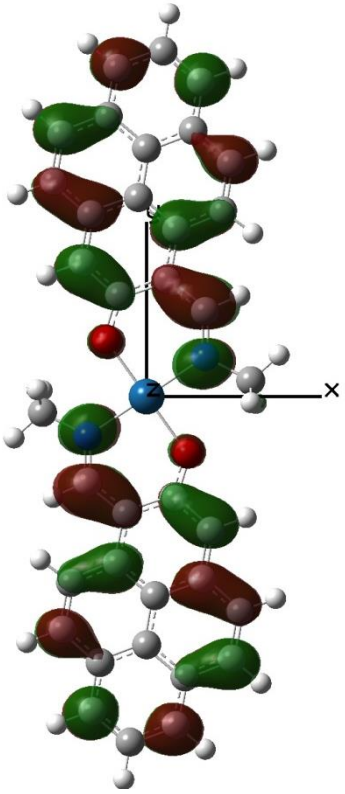
a_g, ϕ_{148}
-0.48 eV



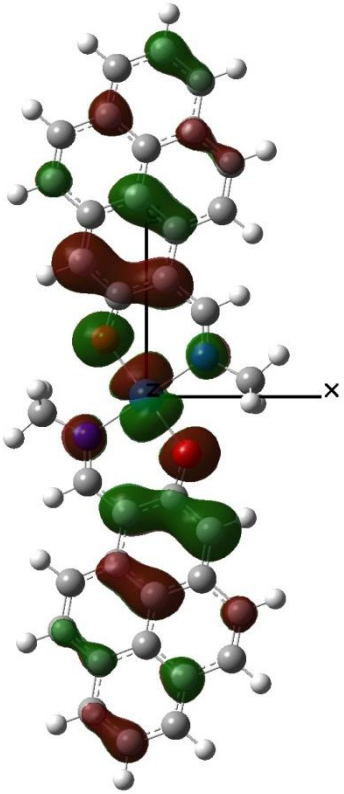
a_u, ϕ_{147}
-0.68 eV



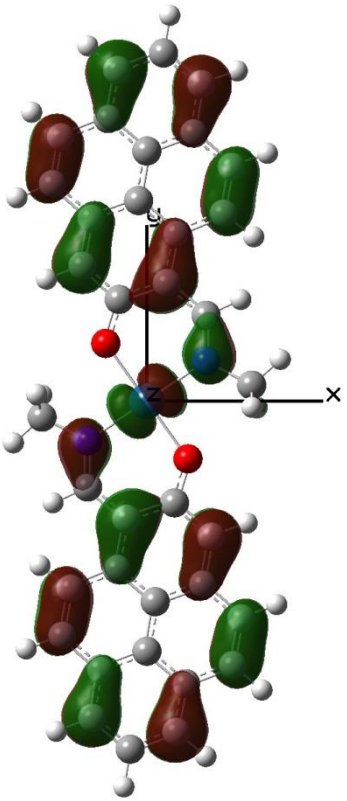
a_g, ϕ_{146}
-1.89 eV
LUMO+1



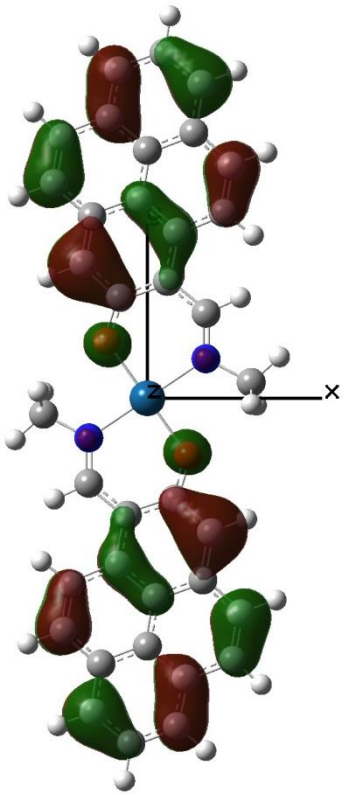
a_u, ϕ_{145}
-2.07 eV
LUMO



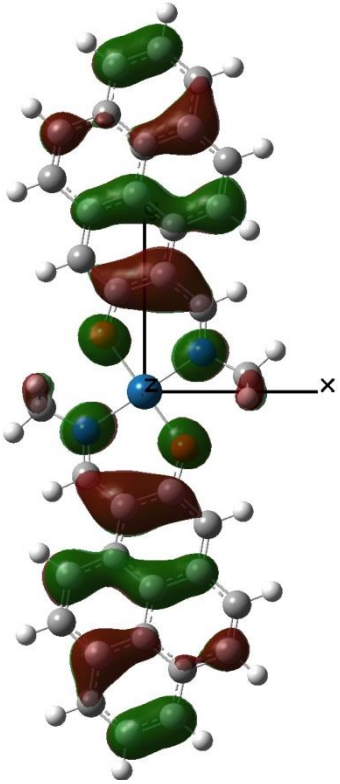
a_g, ϕ_{144}
-4.89 eV
HOMO



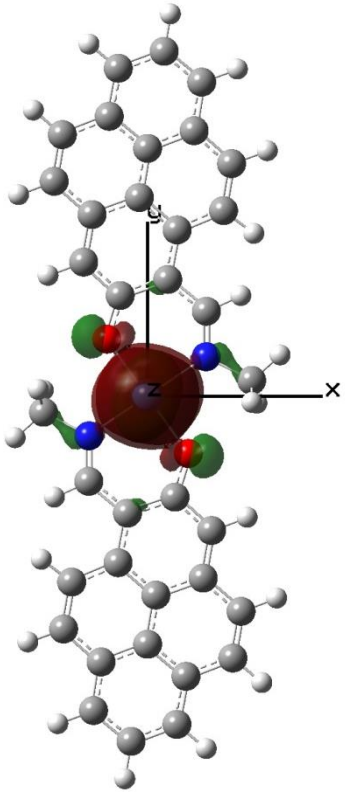
a_g, ϕ_{143}
-5.28 eV
HOMO-1



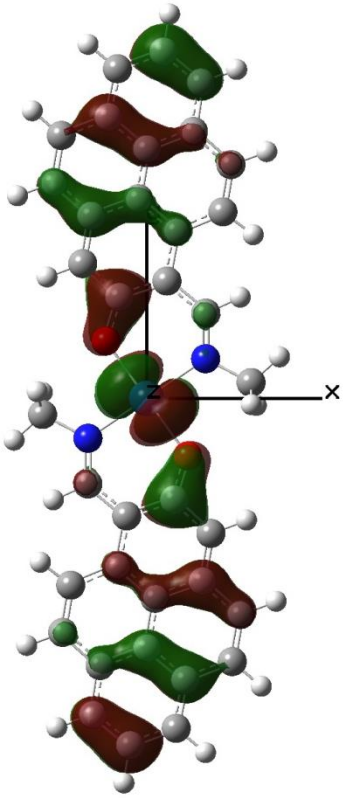
a_u, ϕ_{142}
-5.36 eV



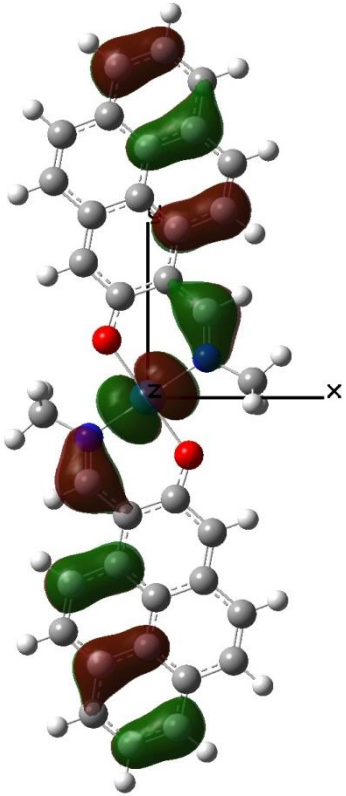
a_u, ϕ_{141}
-5.65 eV



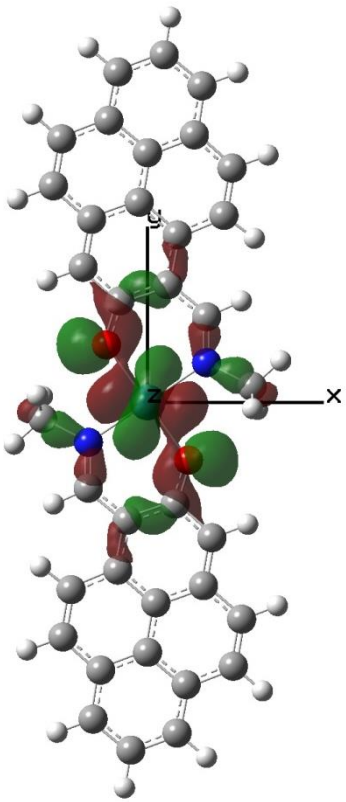
a_g, ϕ_{140}
-6.16 eV



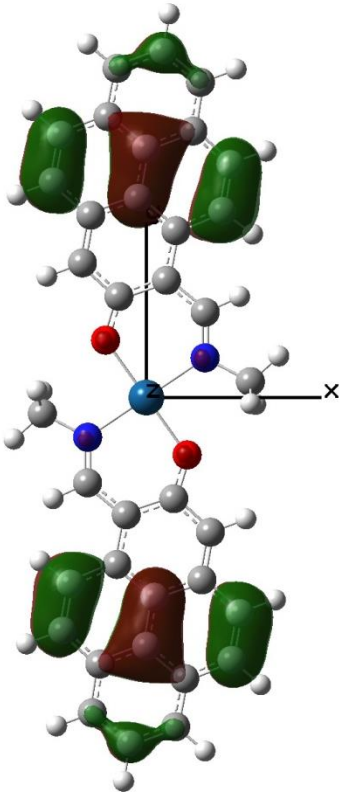
a_g, ϕ_{139}
-6.50 eV



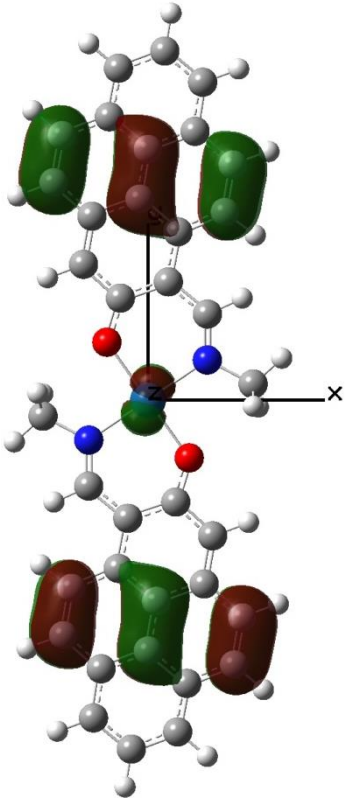
a_g, ϕ_{138}
-6.54 eV



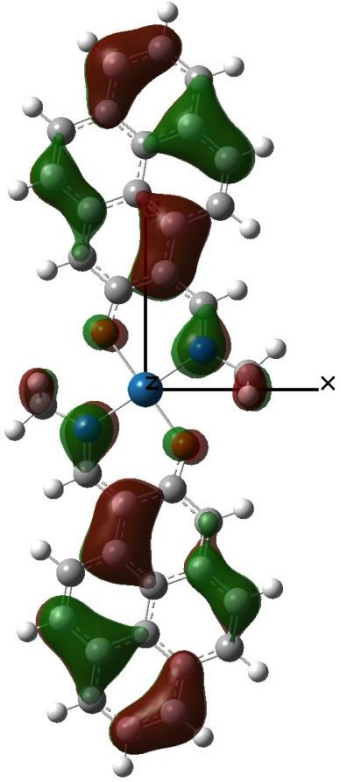
a_g, ϕ_{137}
-6.84 eV



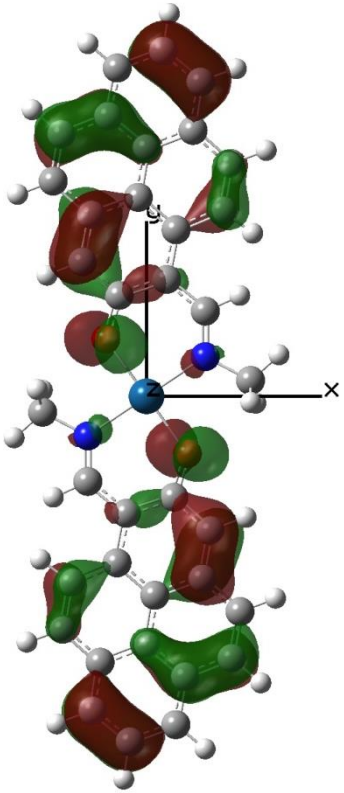
a_u, ϕ_{136}
-6.87 eV



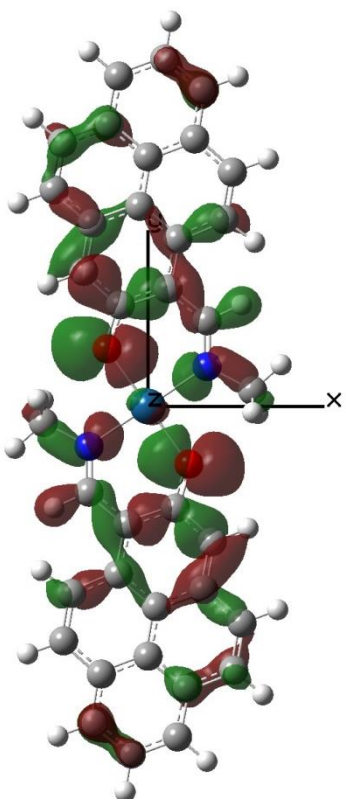
a_g, ϕ_{135}
-6.91 eV



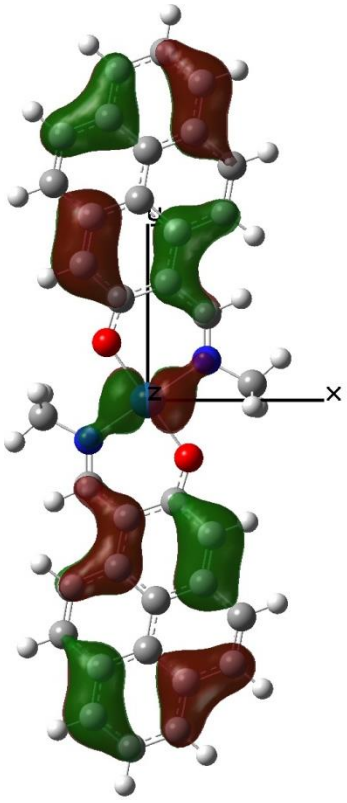
a_u, ϕ_{134}
-7.32 eV



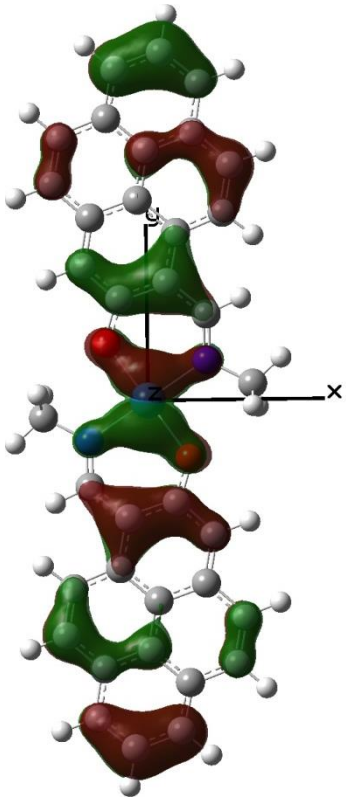
a_u, ϕ_{133}
-7.37 eV



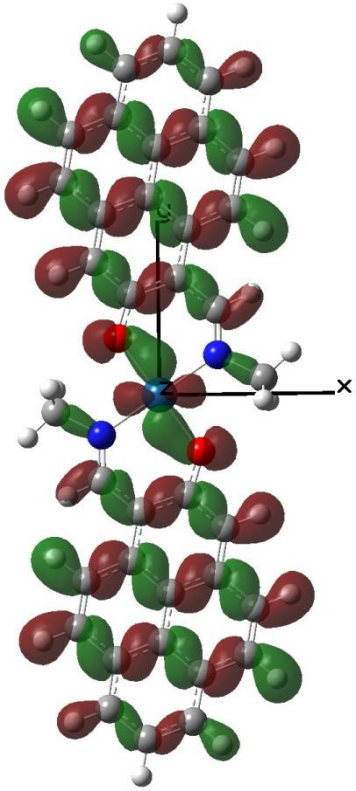
a_u, ϕ_{132}
-7.40 eV



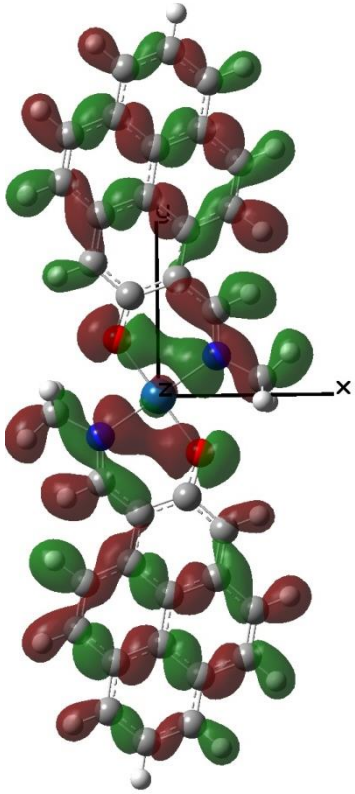
a_g, ϕ_{131}
-7.53 eV



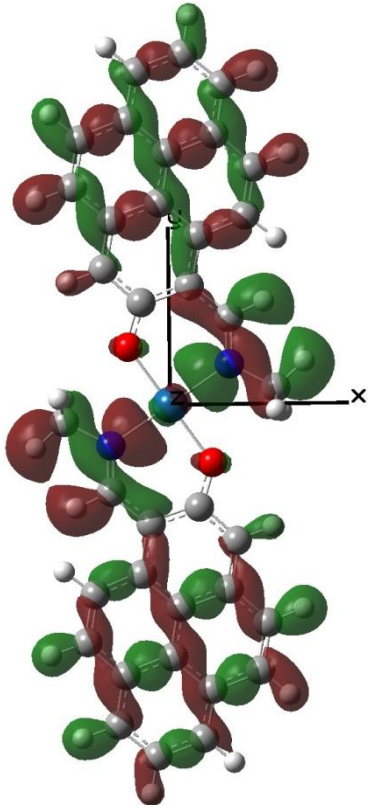
a_g, ϕ_{130}
-7.75 eV



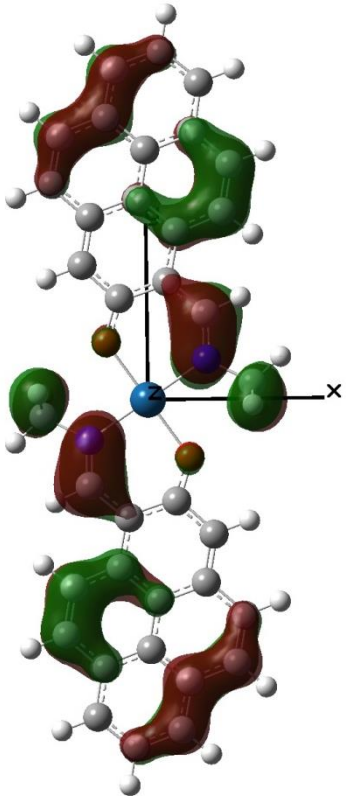
a_g, ϕ_{129}
-8.56 eV



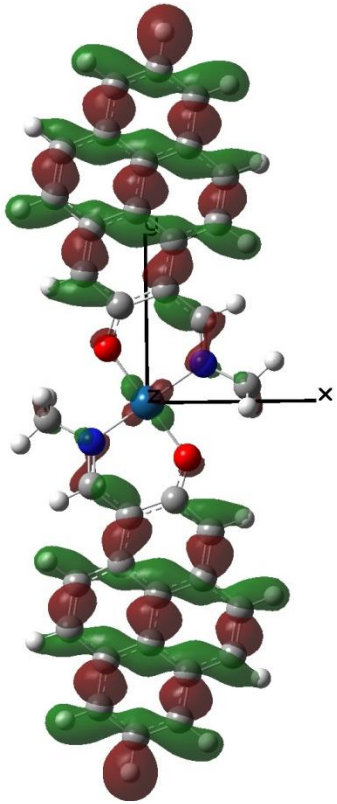
a_u, ϕ_{128}
-8.67 eV



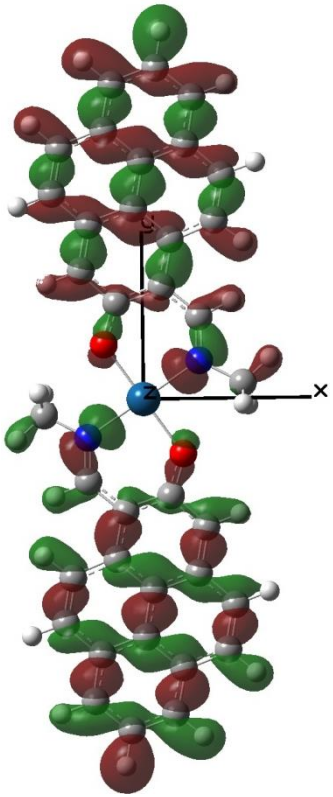
a_u, ϕ_{127}
-8.85 eV



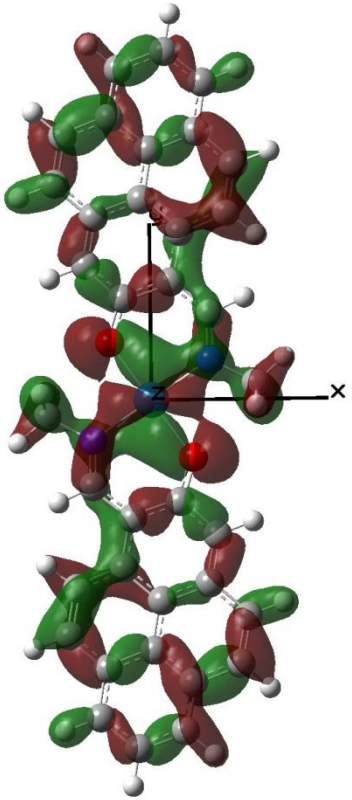
a_u, ϕ_{126}
-8.96 eV



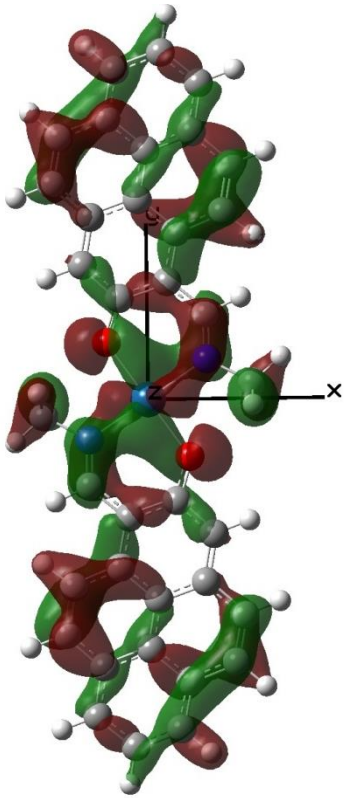
a_g, ϕ_{125}
-9.08 eV



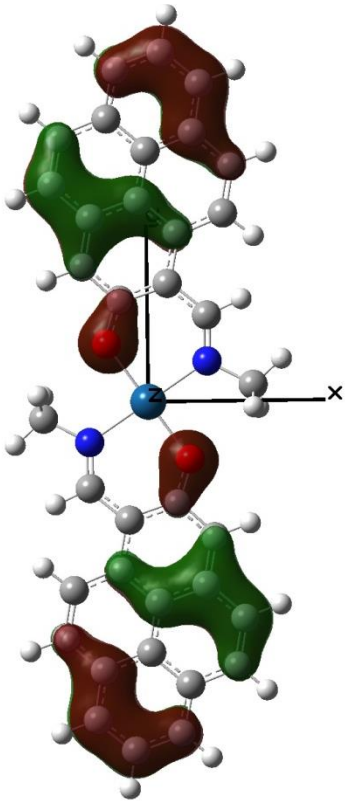
b_g, ϕ_{124}
-9.11 eV



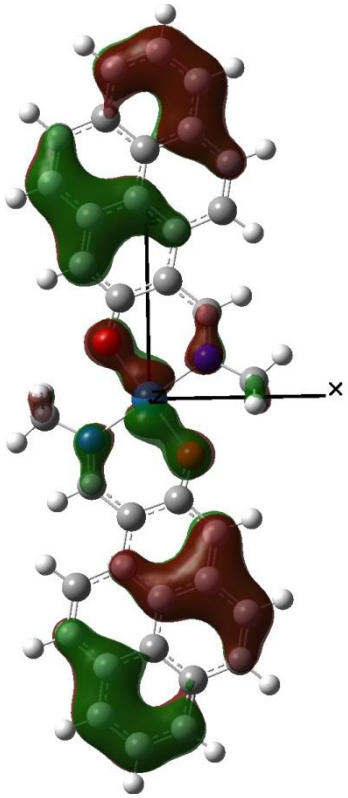
a_u, ϕ_{123}
-9.12 eV



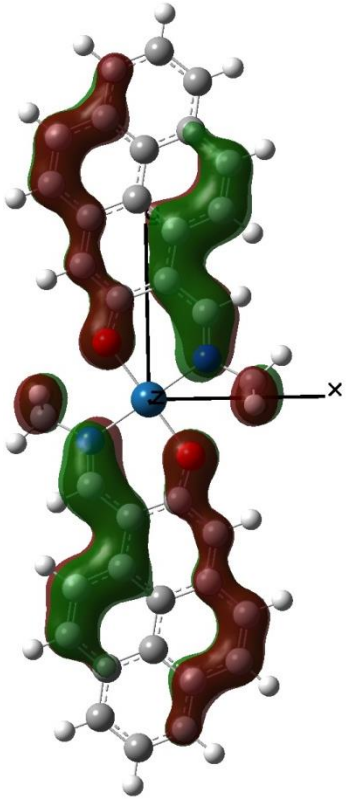
a_u, ϕ_{122}
-9.14 eV



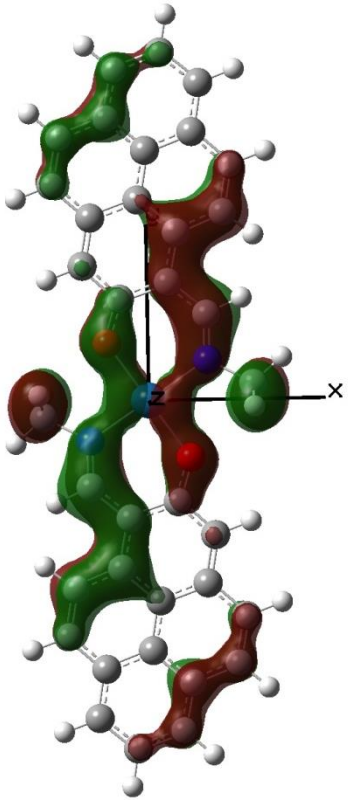
a_u, ϕ_{121}
-9.23 eV



a_g, ϕ_{120}
-9.36 eV

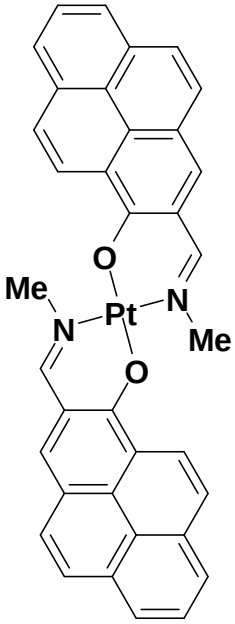


b_g, ϕ_{119}
-9.48 eV



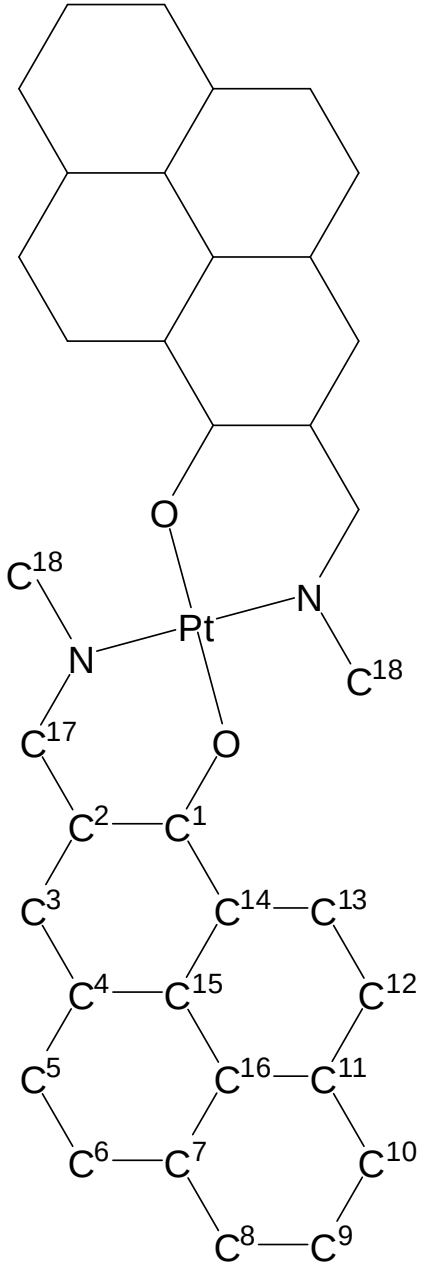
a_u, ϕ_{118}
-9.55 eV

Part-2
Theoretical Studies of *anti*-**2** (Old Pt complex)



Program:	Gaussian R-09W Ver.7 + Gauss View Ver.5
Method:	B3LYP
Basis Set:	Hay-Wadt's ECP for Pt, 6-31G(d) for C, H, N, and O
Optimized Structure:	C_{2h}
Comment#1:	Considering the cost of the calculation, alkyl groups on the nitrogens, *n*-C_8H_{17} of **1(Pt)**, are replaced by methyl groups.

Comparison of the Bond Distances (Å)

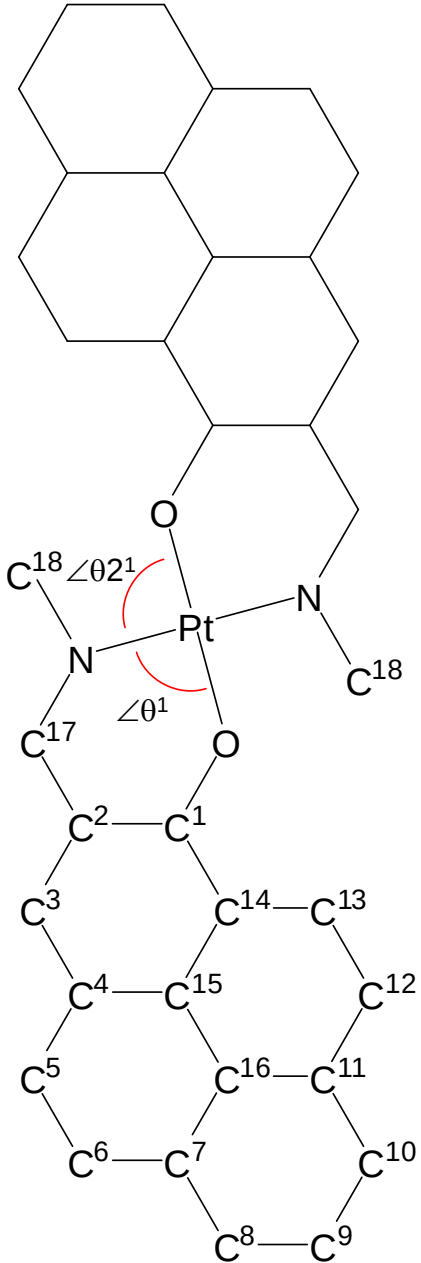


Bond	Theoretical Study†	Diffraction Study for **2**†† Molecule #1	Diffraction Study for **2**†† Molecule #2	Bond	Theoretical Study	Diffraction Study for **2**†† Molecule #1	Diffraction Study for **2**†† Molecule #2
Pt-N	2.036	2.008(8)	2.014(8)	C^6-C^7	1.442	1.450(14)	1.441(14)
Pt-O	2.020	1.996(6)	1.991(7)	C^7-C^8	1.401	1.403(14)	1.393(15)
O-C^1	1.306	1.291(10)	1.292(10)	C^7-C^{16}	1.431	1.441(13)	1.405(13)
N-C^{17}	1.299	1.295(11)	1.288(11)	C^8-C^9	1.398	1.392(14)	1.353(15)
N-C^{18}	1.466	1.479(11)	1.479(12)	C^9-C^{10}	1.390	1.378(14)	1.400(16)
C^1-C^2	1.429	1.430(12)	1.394(13)	C^{10}-C^{11}	1.409	1.400(14)	1.372(16)
C^1-C^{14}	1.438	1.434(12)	1.440(13)	C^{11}-C^{12}	1.433	1.419(13)	1.435(13)
C^2-C^3	1.414	1.408(12)	1.405(12)	C^{11}-C^{16}	1.429	1.424(13)	1.429(14)
C^2-C^{17}	1.434	1.445(13)	1.434(14)	C^{12}-C^{13}	1.365	1.359(12)	1.329(14)
C^3-C^4	1.386	1.390(13)	1.367(14)	C^{13}-C^{14}	1.431	1.414(12)	1.443(13)
C^4-C^5	1.439	1.407(12)	1.452(12)	C^{14}-C^{15}	1.419	1.422(13)	1.437(12)
C^4-C^{15}	1.436	1.410(13)	1.435(13)	C^{15}-C^{16}	1.429	1.415(13)	1.419(14)
C^5-C^6	1.359	1.343(13)	1.313(14)				

† This Work

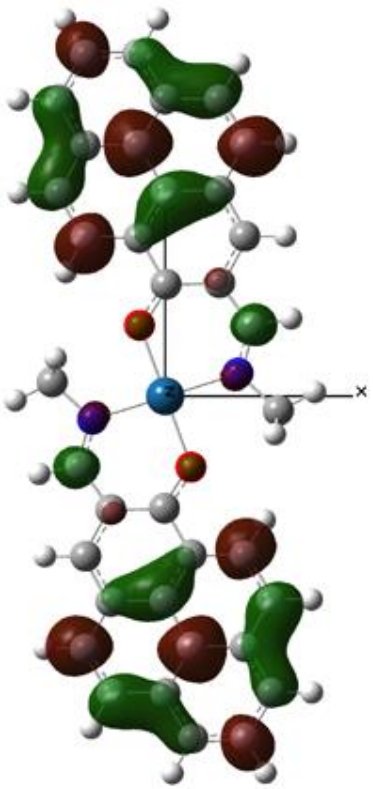
†† This Work, n-Octyl

Comparison of the Important Bond Angles (degree)

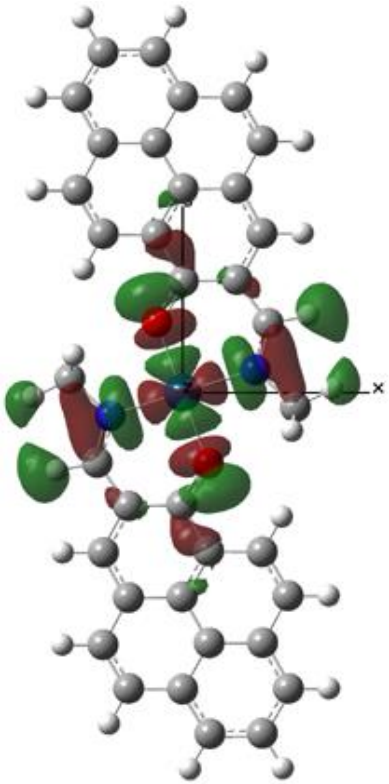


Angle	Theoretical Study†	Diffraction Study††	
		Molecule #1	Molecule #2
N-Pt-O ($\angle\theta^1$)	92.20	92.4(3)	91.8(3)
N-Pt-O ($\angle\theta^2$)	87.80	87.6(3)	88.2(3)
Pt-O-C^1	127.29	126.7(6)	127.1(6)
O-C^1-C^2	124.45	124.9(8)	125.3(9)
C^1-C^2-C^{17}	123.96	123.0(8)	123.7(9)
C^2-C^{17}-N	129.05	128.0(9)	128.0(9)
C^{17}-N-Pt	123.04	123.5(7)	123.7(7)
C^{17}-N-C^{18}	117.56	115.3(8)	115.4(8)
C^{18}-N-Pt	119.39	121.2(6)	120.9(6)
C^{14}-C^1-C^2	118.19	117.2(8)	118.3(9)
C^1-C^2-C^3	119.84	120.3(8)	120.6(10)

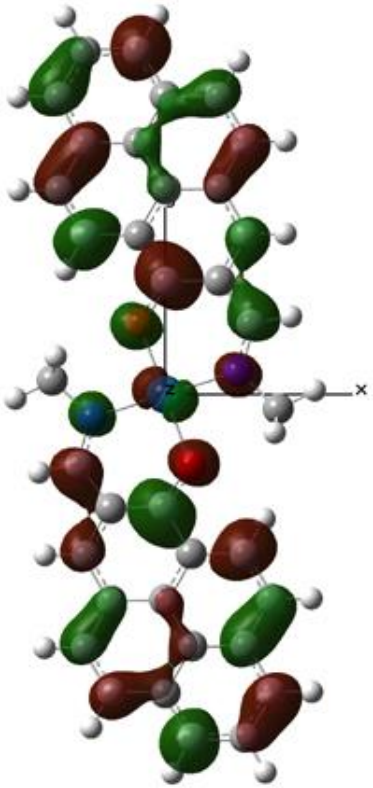
† This Work
†† This Work



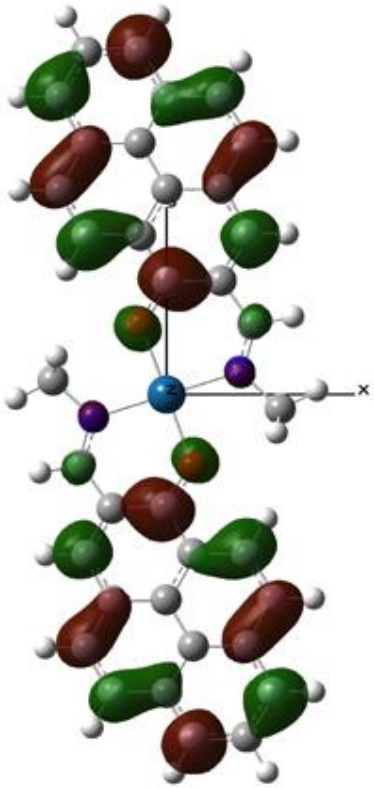
a_u, ϕ_{150}
+0.00 eV



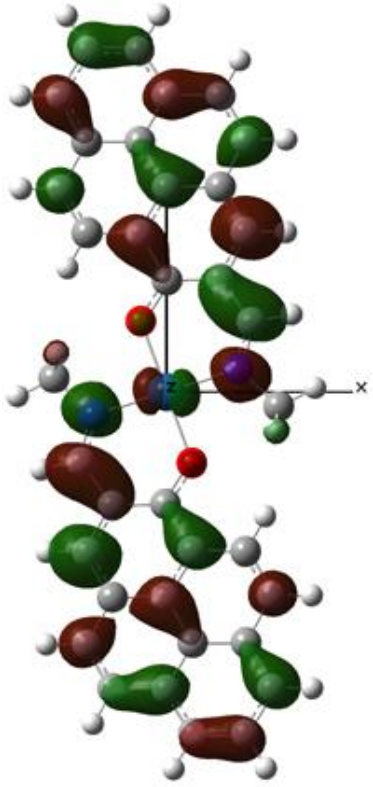
a_g, ϕ_{149}
-0.44 eV



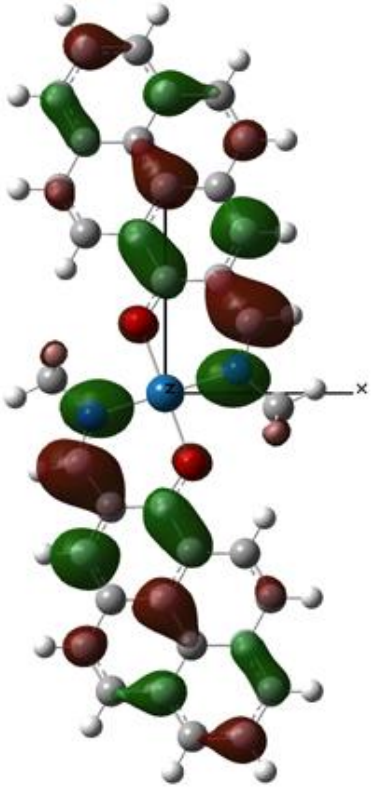
b_g, ϕ_{148}
-1.11 eV



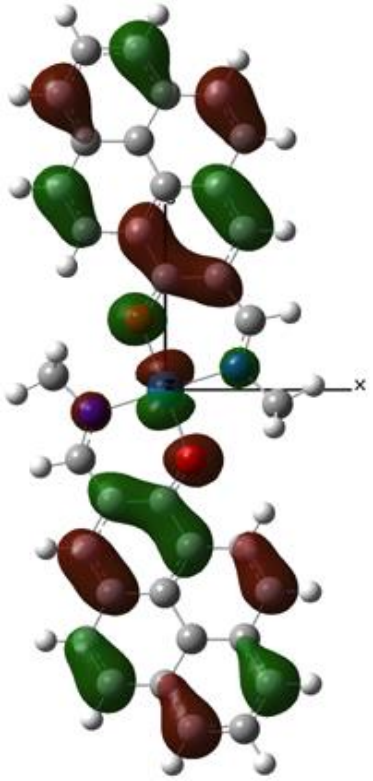
a_u, ϕ_{147}
-1.25 eV



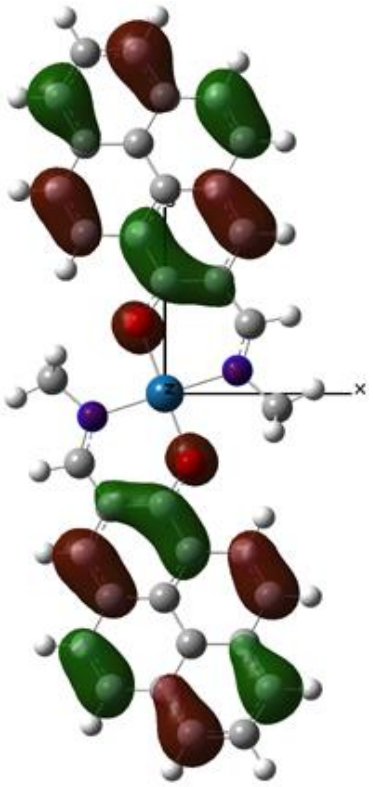
b_g, ϕ_{146}
-1.58 eV
LUMO+1



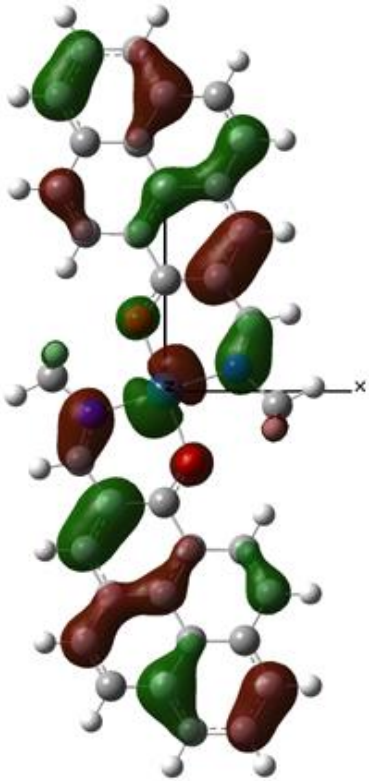
a_u, ϕ_{145}
-1.84 eV
LUMO



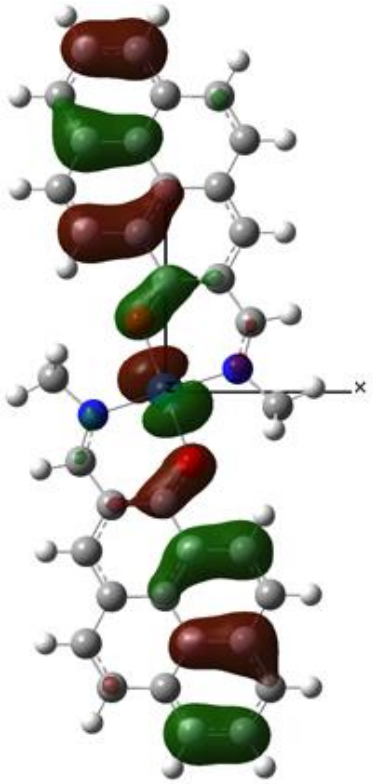
b_g, ϕ_{144}
-4.69 eV
HOMO



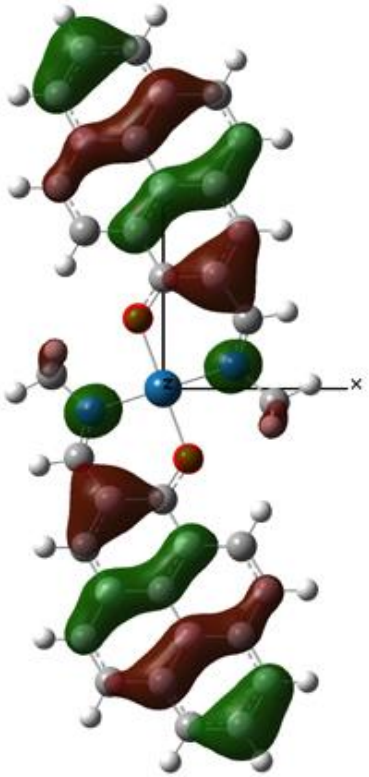
a_u, ϕ_{143}
-4.93 eV
HOMO-1
bonding combination of
HOMO(ϕ_{68}) of the ligand



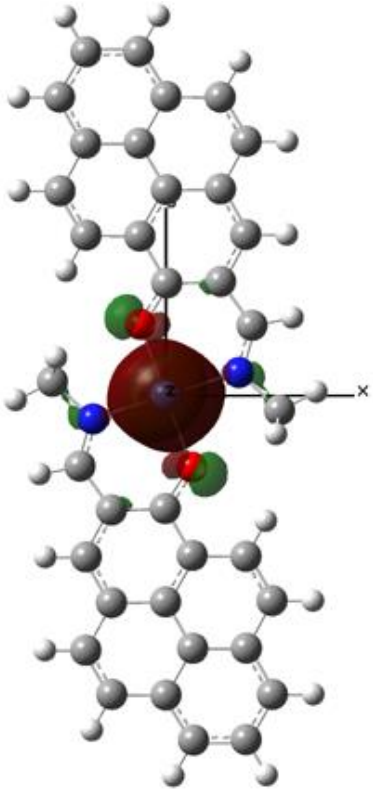
b_g, ϕ_{142}
-5.84 eV



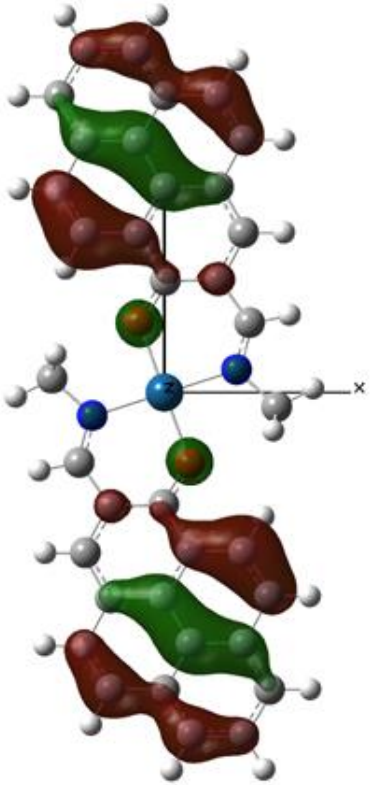
b_g, ϕ_{141}
-6.23^5 eV



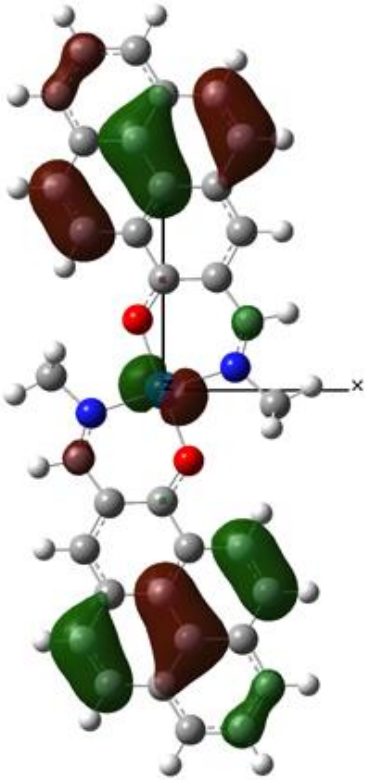
a_u, ϕ_{140}
-6.24^1 eV
bonding combination
of ϕ_{67} of the ligand



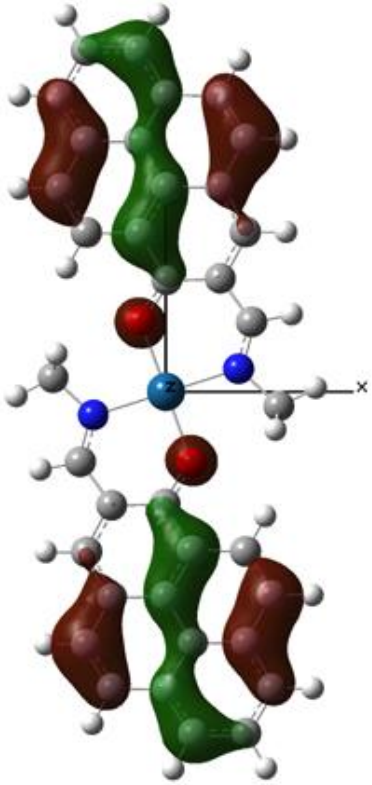
a_g, ϕ_{139}
-6.42 eV



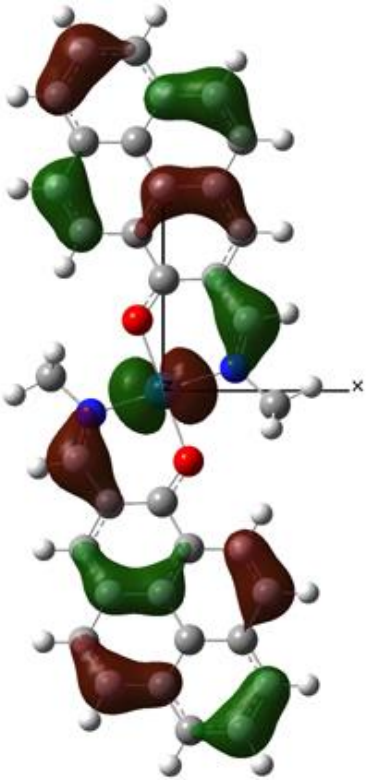
a_u, ϕ_{138}
-6.72 eV



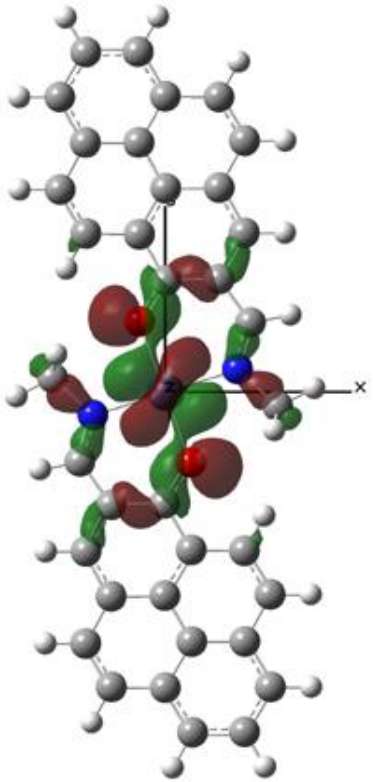
b_g, ϕ_{137}
-6.78 eV



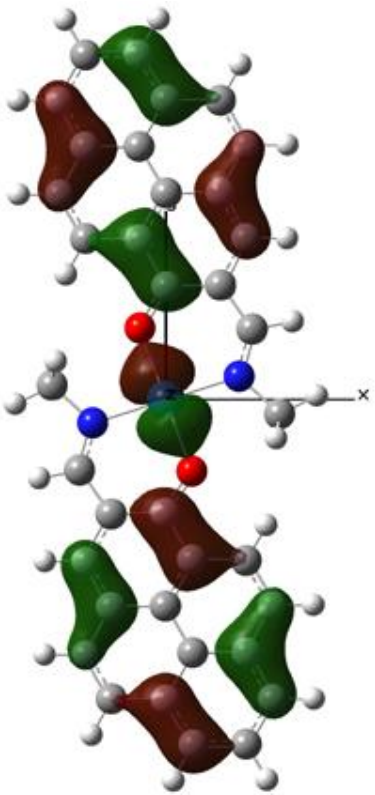
a_u, ϕ_{136}
-6.93^6 eV



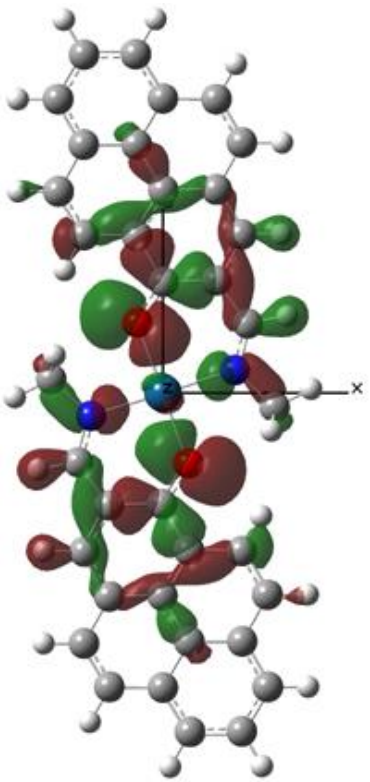
b_g, ϕ_{135}
-6.94^4 eV



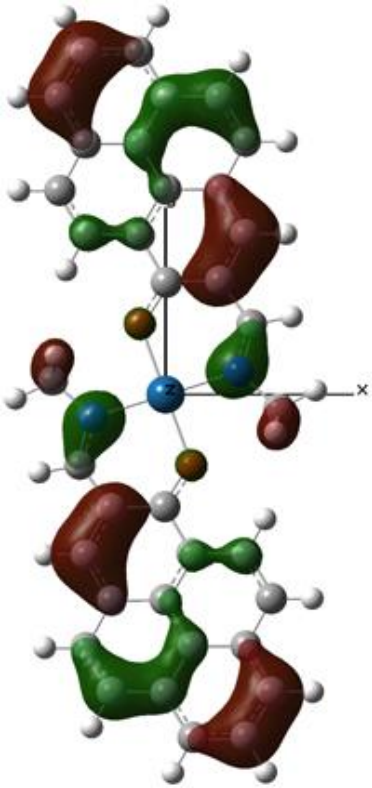
a_g, ϕ_{134}
-7.12 eV



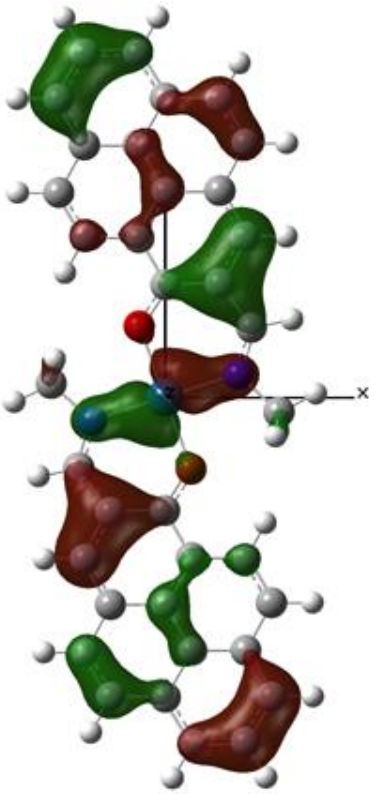
b_g, ϕ_{133}
-7.32 eV



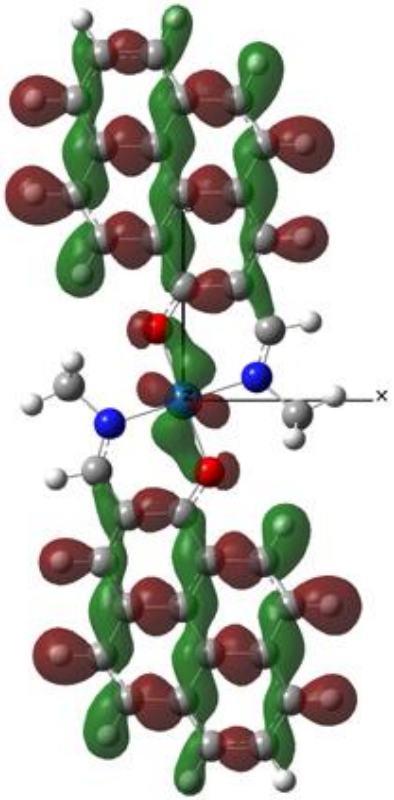
b_u, ϕ_{132}
-7.66 eV



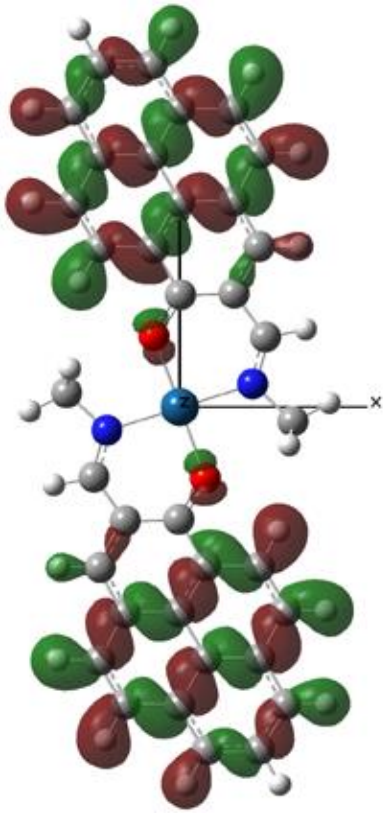
a_u, ϕ_{131}
-7.72 eV



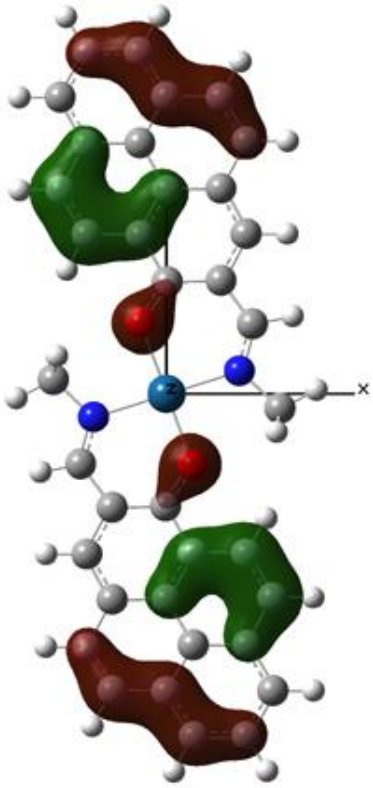
b_g, ϕ_{130}
-8.05 eV
bonding interaction of d_{yz} with the ligand



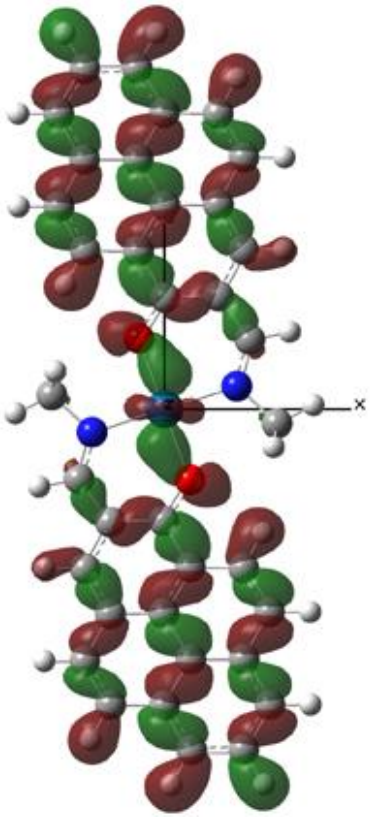
a_g, ϕ_{129}
-8.60 eV
bonding interaction of dxy with the ligand



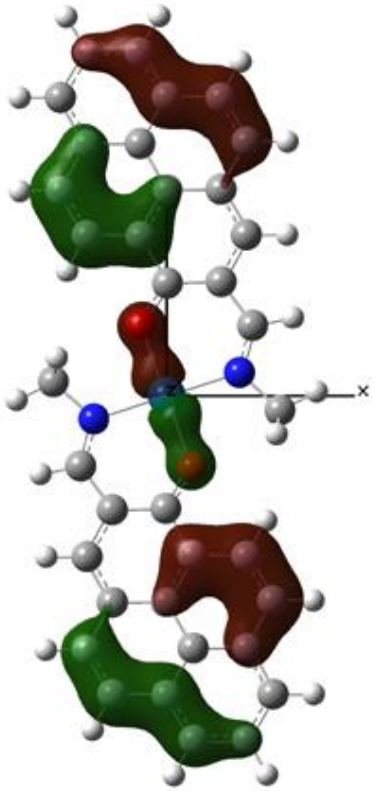
b_u, ϕ_{128}
-8.64 eV
antibonding interaction of ϕ_{xxx} of the ligand



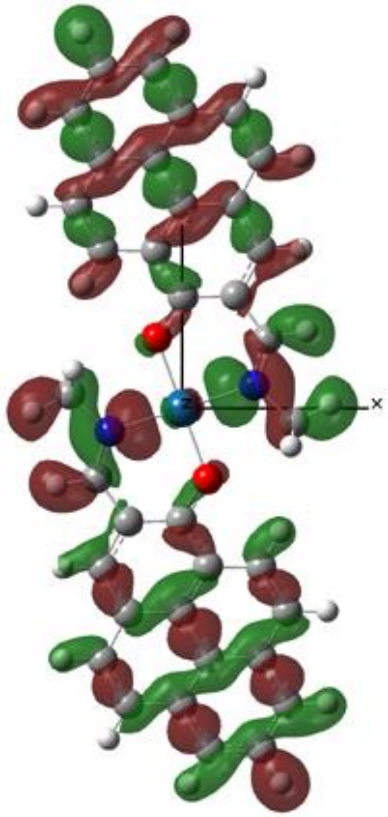
a_u, ϕ_{127}
-8.86 eV
bonding interaction of ϕ_{xxx} of the ligand



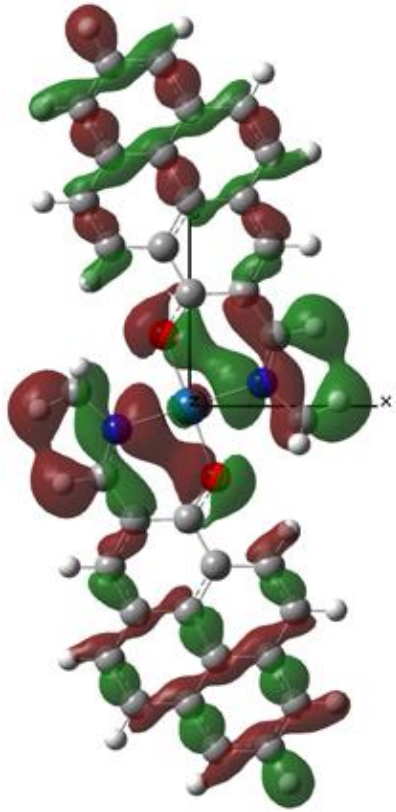
a_g, ϕ_{126}
-8.88 eV
bonding interaction of d_{xy} with the ligand



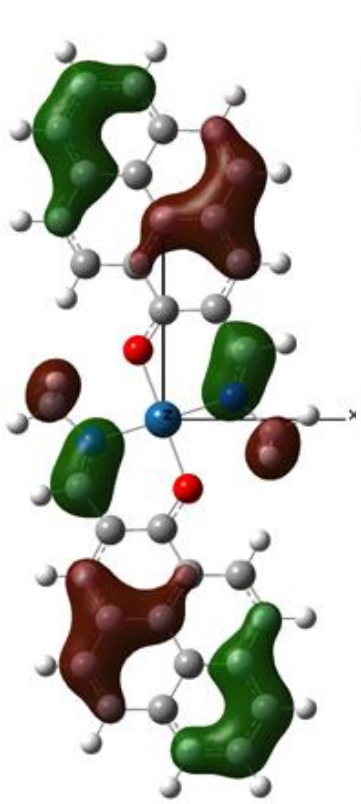
b_g, ϕ_{125}
-8.99 eV
bonding interaction of d_{zx} with the ligand



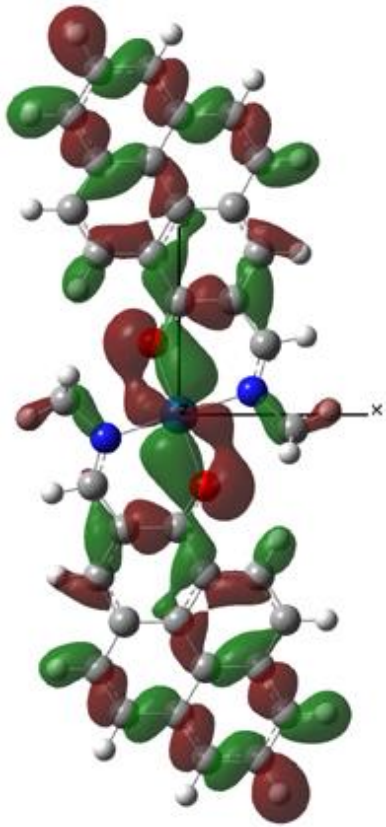
b_u, ϕ_{124}
-9.00 eV
antibonding interaction of ϕ_{XXX} of the ligand



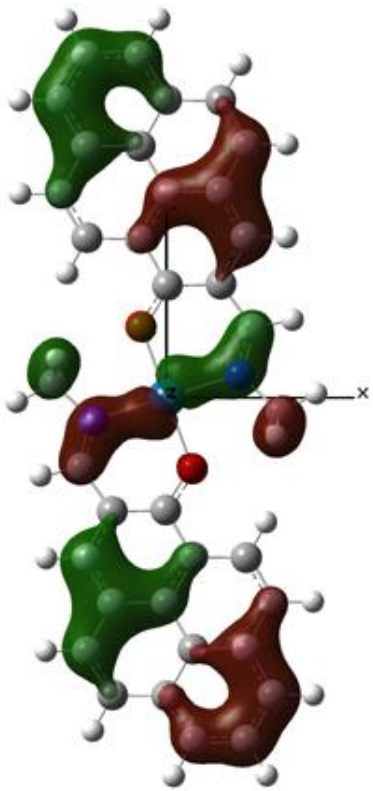
b_u, ϕ_{123}
-9.10 eV
antibonding interaction of ϕXXX of the ligand



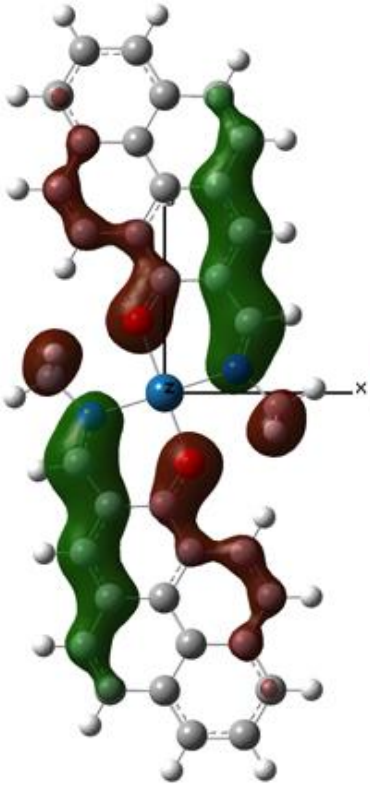
a_u, ϕ_{122}
-9.22 eV
bonding interaction of ϕ_{XXX} of the ligand



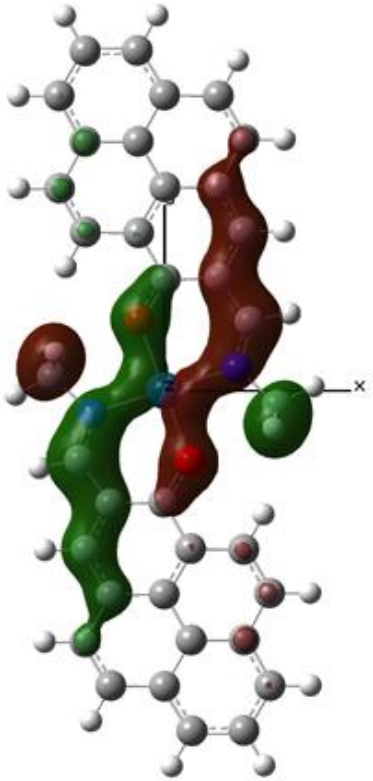
a_g, ϕ_{121}
-9.35 eV
bonding interaction of d_{xy} with the ligand



b_g, ϕ_{120}
-9.37 eV
bonding interaction of d_{yz} with the ligand

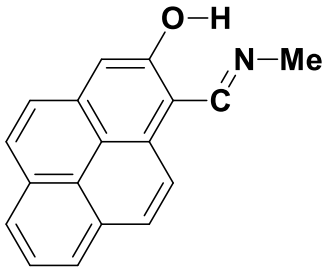


a_u, ϕ_{119}
-9.64 eV
bonding interaction of ϕ_{XXX} of the ligand



b_g, ϕ_{118}
-9.75 eV
bonding interaction of d_{yz} with the ligand

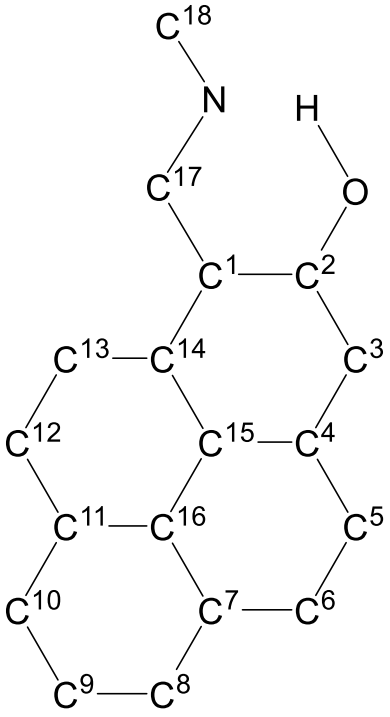
Part-3
Theoretical† Studies of New Pyrene Ligand)



OH-form
Energy: - -823.76078722 HR

Program:	Gaussian R-09W Ver.7 + Gauss View Ver.5
Method:	B3LYP
Basis Set:	6-31G(d)
Optimized Structure:	

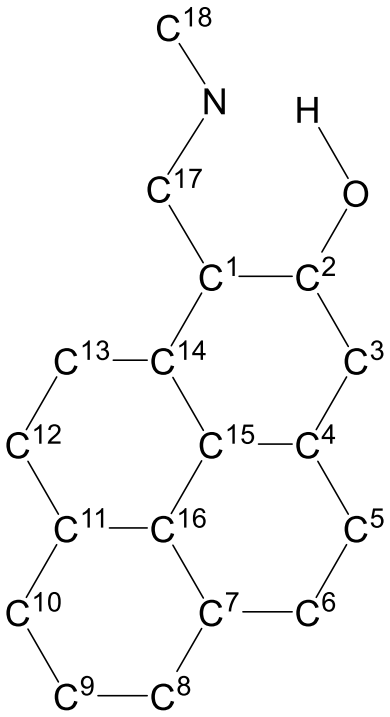
Bond Distances of the Optimized Structure (Å)



Bond	Theoretical Study†	Bond	Theoretical Study†
O-H	1.004	C^5-C^6	1.360
N···H	1.678	C^6-C^7	1.438
O-C^2	1.341	C^7-C^8	1.402
N-C^{17}	1.288	C^7-C^{16}	1.430
N-C^{18}	1.448	C^8-C^9	1.396
C^1-C^2	1.426	C^9-C^{10}	1.391
C^1-C^{14}	1.430	C^{10}-C^{11}	1.406
C^2-C^3	1.398	C^{11}-C^{12}	1.430
C^1-C^{17}	1.456	C^{11}-C^{16}	1.426
C^3-C^4	1.394	C^{12}-C^{13}	1.364
C^4-C^5	1.439	C^{13}-C^{14}	1.439
C^4-C^{15}	1.433	C^{14}-	1.428

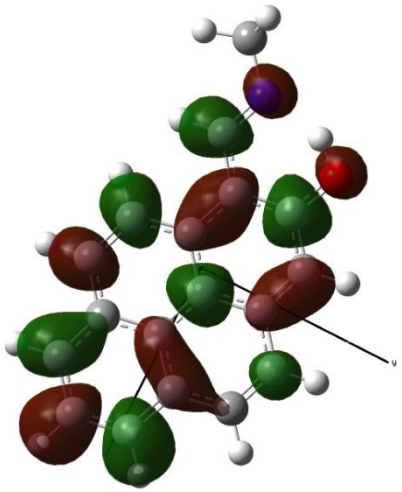
† This Work

Important Bond Angles of the Optimized Structure (Å)

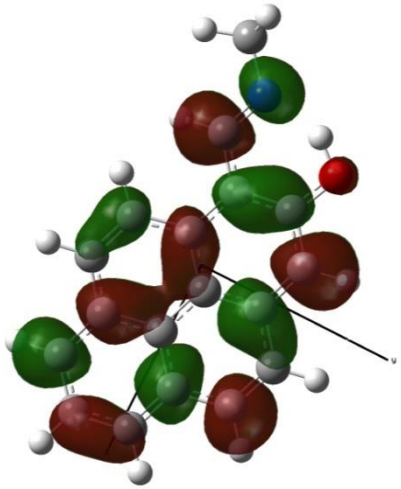


Angle	Theoretical Study†
N-H-O	148.1
H-O-C^2	107.4
O-C^2-C^1	122.2
C^2-C^1-C^{17}	119.2
C^1-C^{17}-N	122.9
C^{17}-N-H	100.2

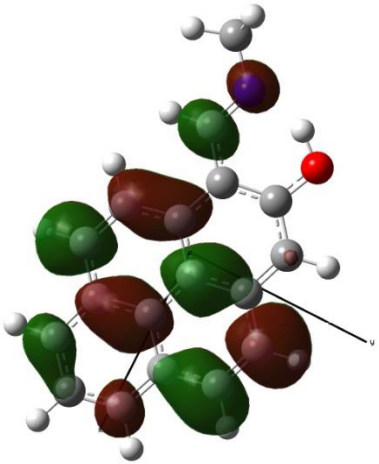
† This Work



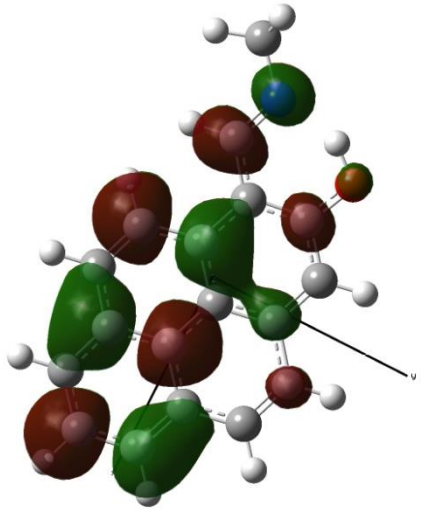
a” (= π), ϕ_{74},
+2.04 eV



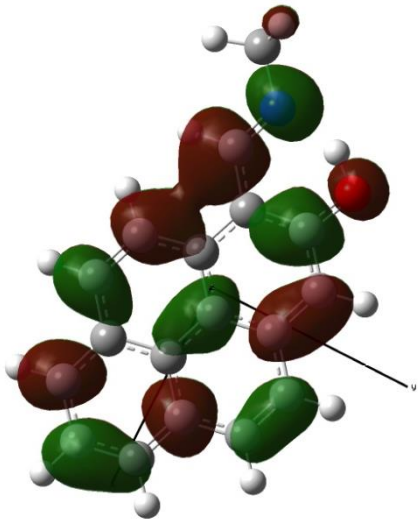
a” (= π), ϕ_{73}
0.97 eV



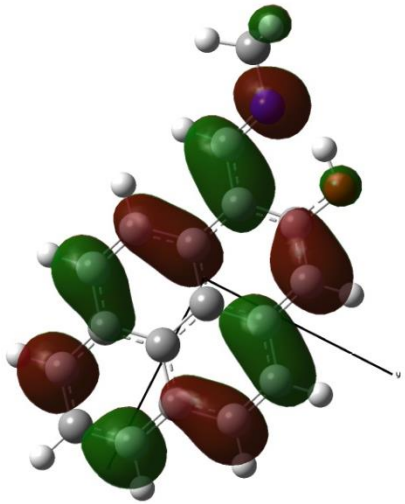
a” (= π), ϕ_{72}
-0.01 eV



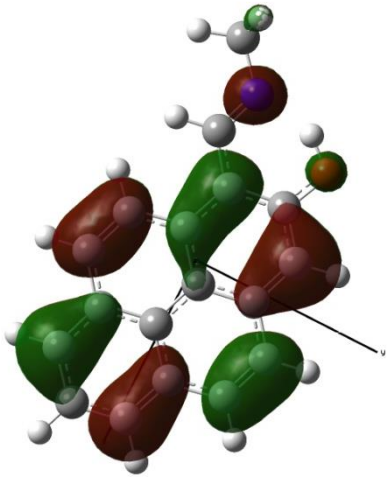
a” (= π), ϕ_{71}
-0.39 eV



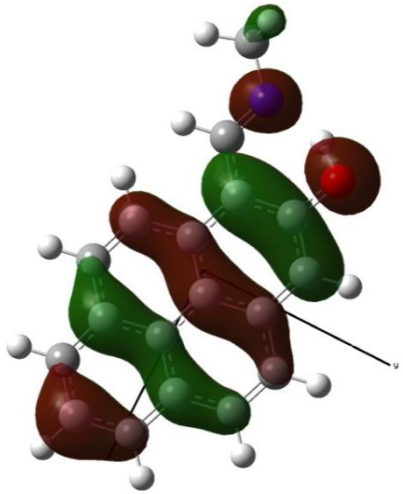
a˝ (= π), ϕ_{70},
-0.58 eV
LUMO+1



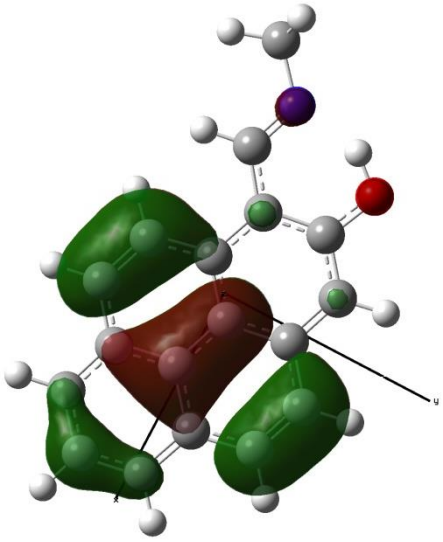
a” (= π), ϕ_{69}
-1.94 eV
LUMO



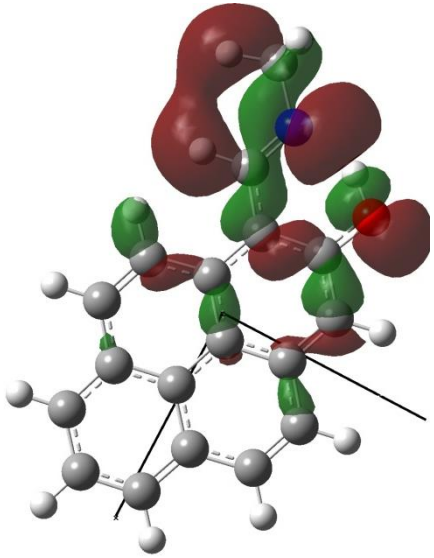
a” (= π), ϕ_{68}
-5.41 eV
HOMO



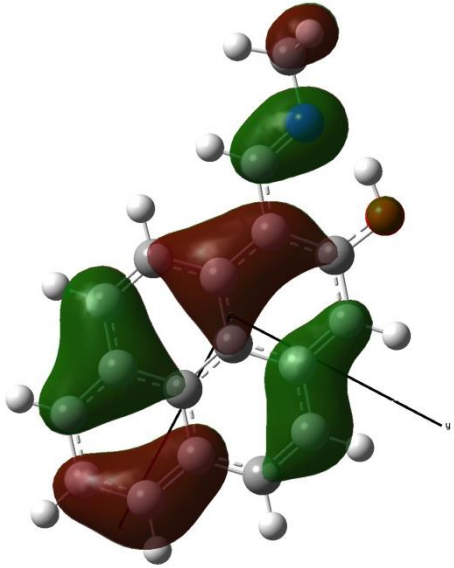
a” (= π), ϕ_{67}
-5.67 eV
HOMO-1



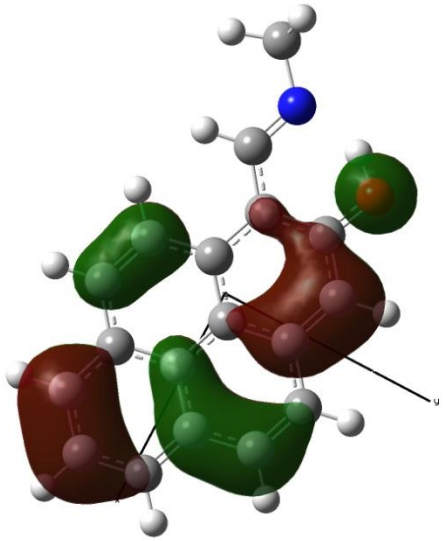
a” (= π), ϕ_{66}
-6.92 eV



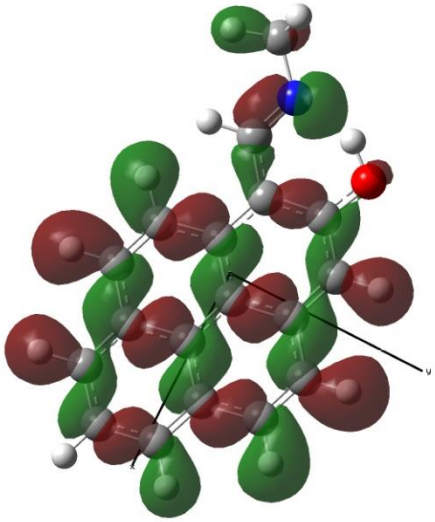
a” (= σ), ϕ_{65}
-7.22 eV



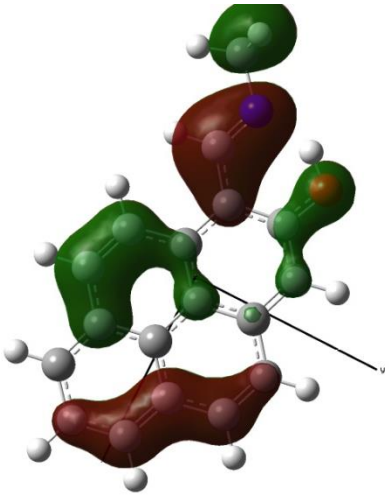
a’ (= π), ϕ_{64}
-7.30 eV



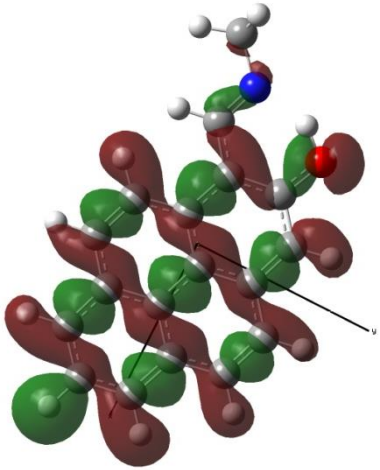
a” (= π), ϕ_{63}
-7.45eV



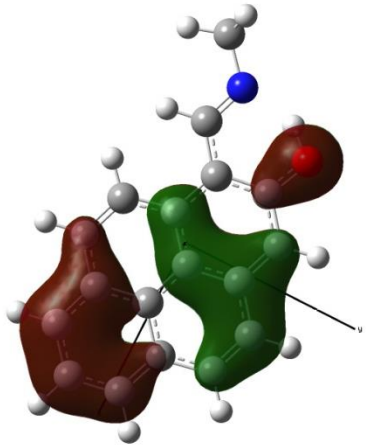
a’ (= σ), ϕ_{62}
-8.75 eV



a” (= π), ϕ_{61}
-8.80 eV

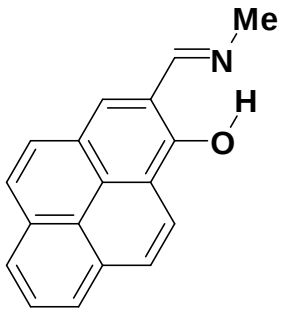


a’ (= π), ϕ_{60}
-9.11 eV

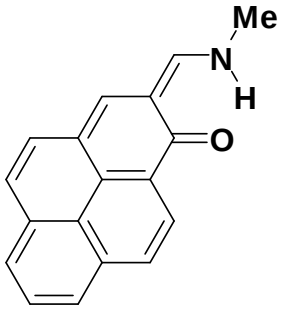


a” (= π), ϕ_{59}
-9.30 eV

Part-2
Theoretical† Studies of **1** (Pyrene Ligand)



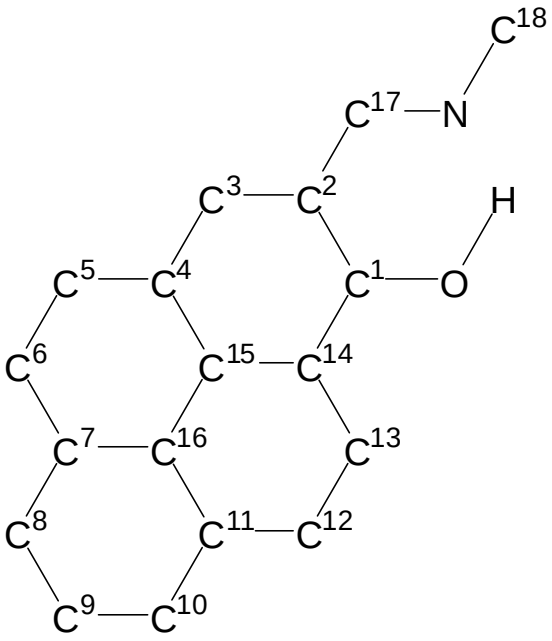
OH-form
Energy: -823.76512992 HR



NH-form
Energy: -823.76177316 HR

Program:	Gaussian R-09W Ver.7 + Gauss View Ver.5
Method:	B3LYP
Basis Set:	6-31G(d)
Optimized Structure:	C_s
Comment #1:	For this ligand, two forms are possible, *i.e.*, OH-form and NH-form. Theoretical studies on these two forms suggest that OH-form is more stable than NH-form, about 2.11 kcal mol^{-1}. This *Supporting Information* only describes the structure and properties of OH-form.

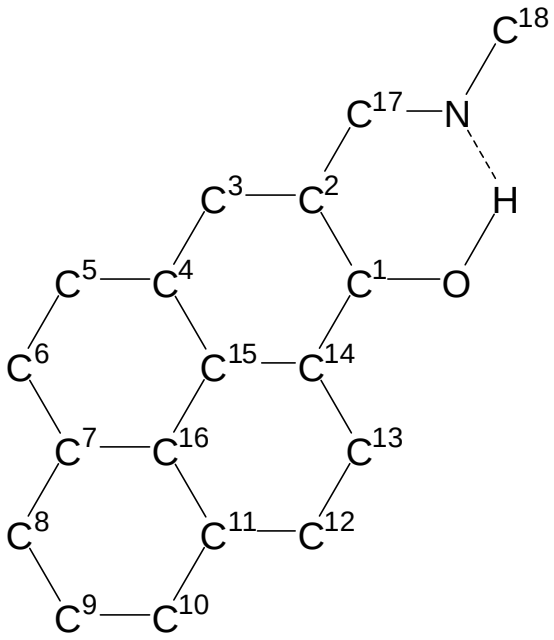
Bond Distances of the Optimized Structure (Å)



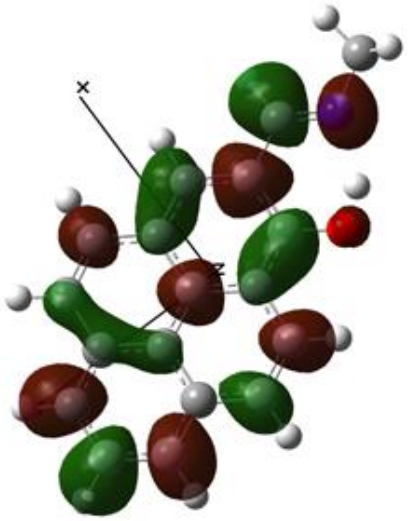
Bond	Theoretical Study†	Bond	Theoretical Study†
O-H	1.003	C^5-C^6	1.360
N···H	1.718	C^6-C^7	1.440
O-C^1	1.341	C^7-C^8	1.403
N-C^{17}	1.284	C^7-C^{16}	1.430
N-C^{18}	1.448	C^8-C^9	1.396
C^1-C^2	1.421	C^9-C^{10}	1.392
C^1-C^{14}	1.416	C^{10}-C^{11}	1.406
C^2-C^3	1.403	C^{11}-C^{12}	1.436
C^2-C^{17}	1.457	C^{11}-C^{16}	1.429
C^3-C^4	1.395	C^{12}-C^{13}	1.363
C^4-C^5	1.438	C^{13}-C^{14}	1.434
C^4-	1.433	C^{14}-C^{15}	1.423

† This Work
†† This Work

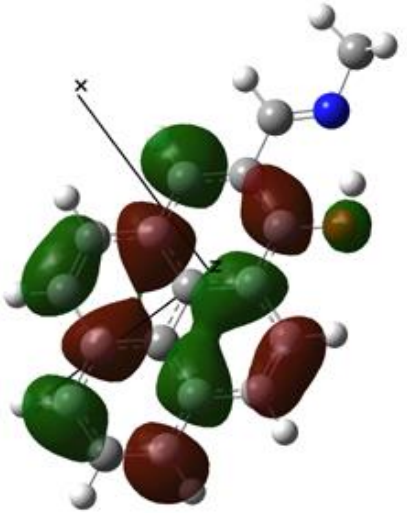
Important Bond Angles of the Optimized Structure (Å)



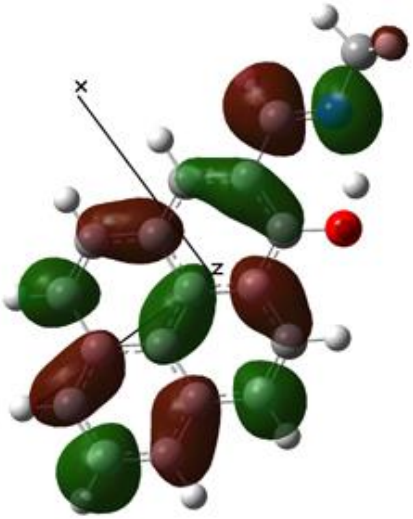
Angle	Theoretical Study†
N-H-O	148.15
H-O-C^1	107.30
O-C^1-C^2	121.59
C^1-C^2-C^{17}	120.89
C^2-C^{17}-N	122.79
C^{17}-N-H	99.27



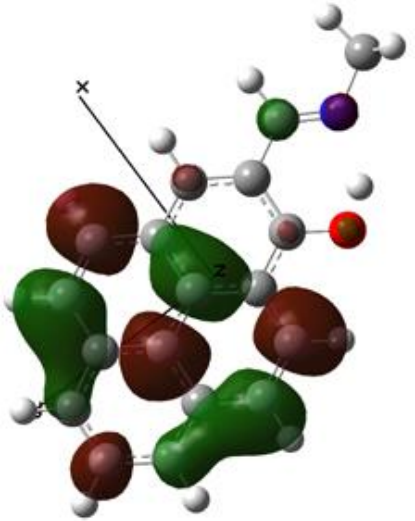
a” (= π), ϕ_{74},
+2.28 eV



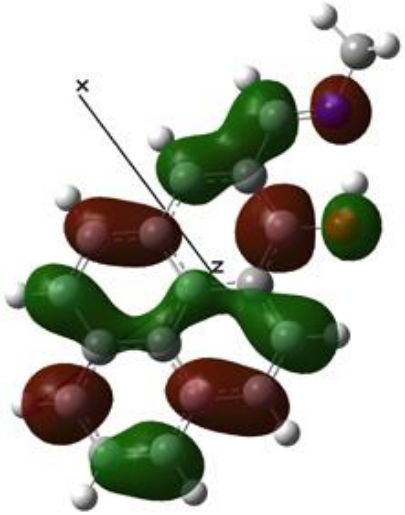
a” (= π), ϕ_{73}
0.73 eV



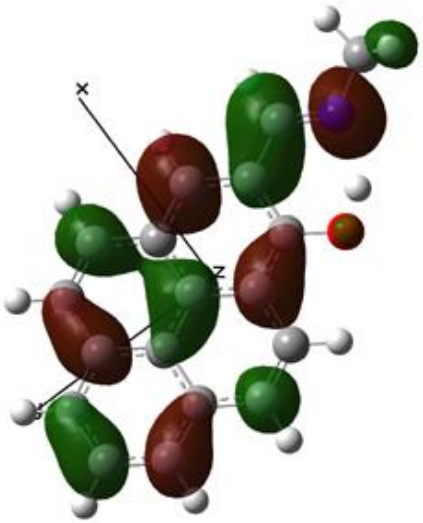
a” (= π), ϕ_{72}
0.29 eV



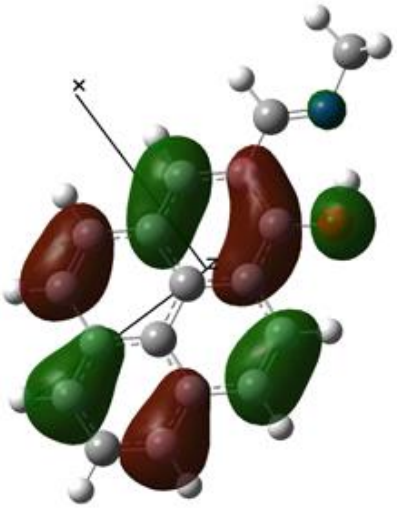
a” (= π), ϕ_{71}
0.02 eV



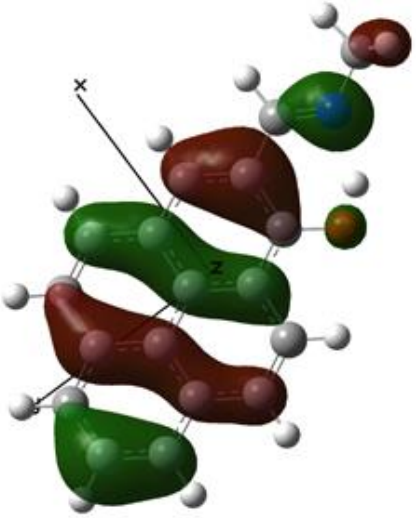
a” (= π), ϕ_{70},
-1.24 eV
LUMO+1



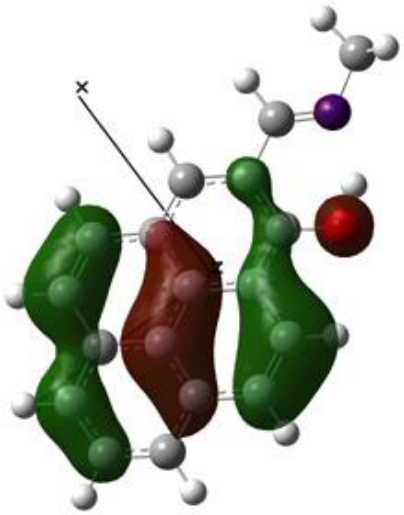
a” (= π), ϕ_{69}
-1.50 eV
LUMO



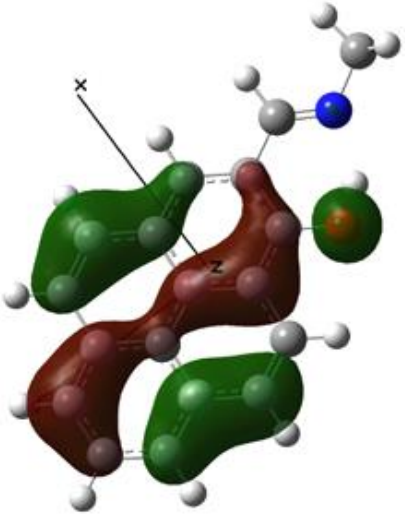
a” (= π), ϕ_{68}
-4.99 eV
HOMO



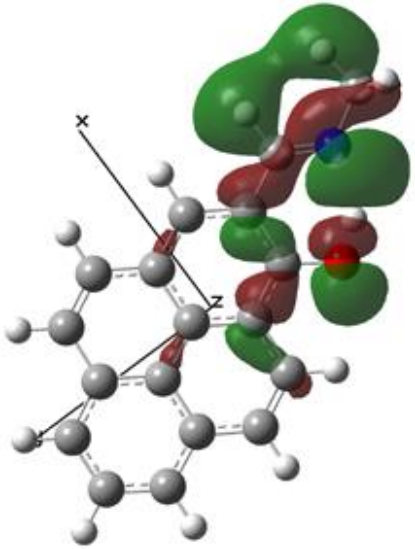
a” (= π), ϕ_{67}
-6.13 eV
HOMO-1



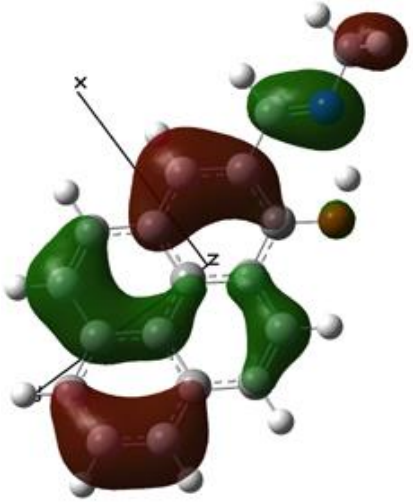
a” (= π), ϕ_{66}
-6.75 eV



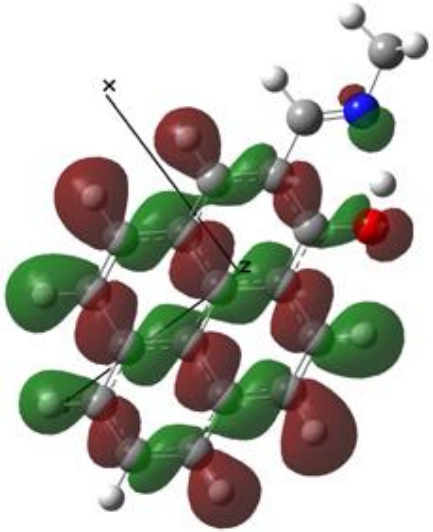
a” (= π), ϕ_{65}
-6.98 eV



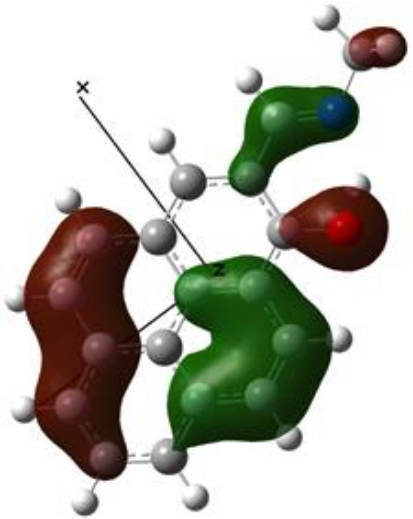
a’ (= σ), ϕ_{64}
-7.41 eV



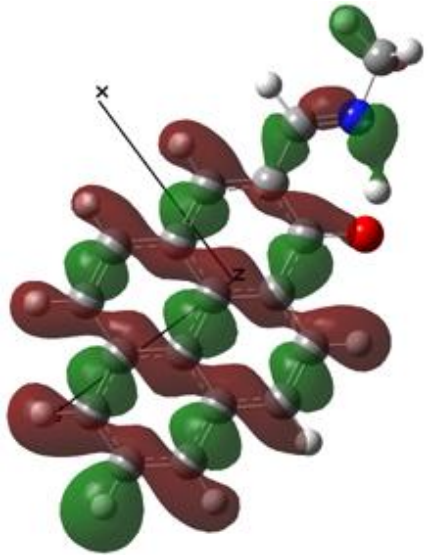
a” (= π), ϕ_{63}
-7.63 eV



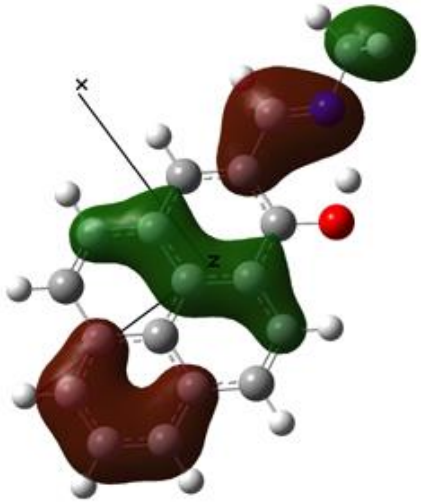
a’ (= σ), ϕ_{62}
-8.61 eV



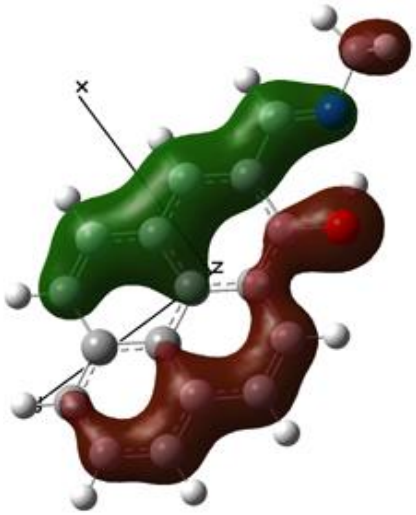
a” (= π), ϕ_{61}
-8.86 eV



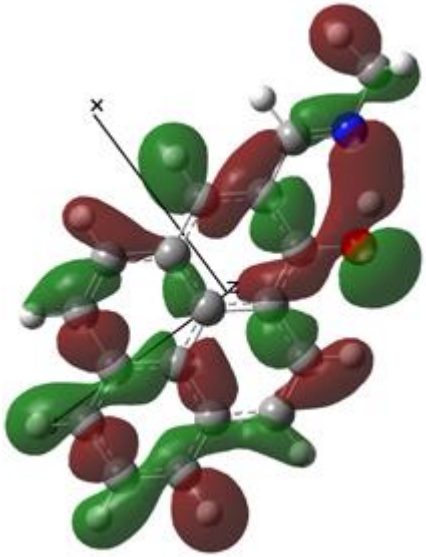
a’ (= σ), ϕ_{60}
-8.98 eV



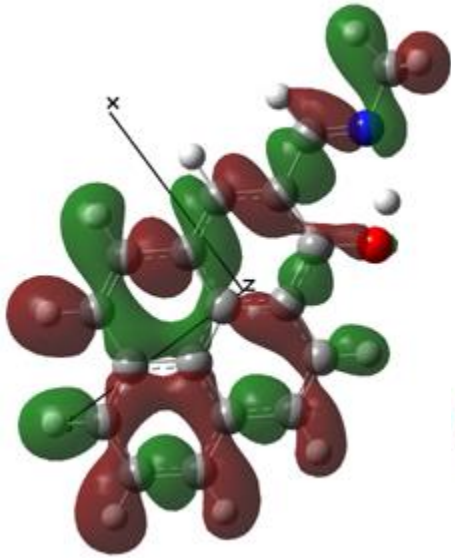
a” (= π), ϕ_{59}
-9.06 eV



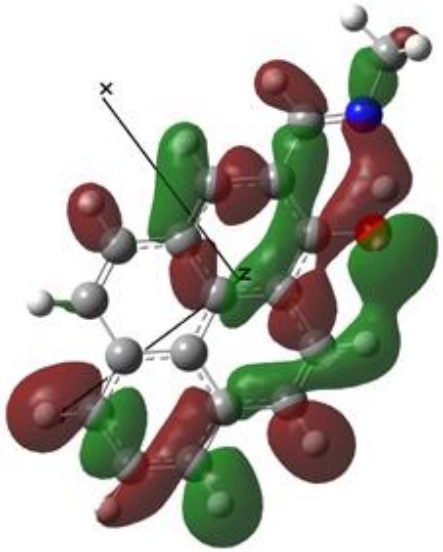
a” (= π), ϕ_{58}
-9.50 eV



a’ (= σ), ϕ_{57}
-9.68 eV



a’ (= σ), ϕ_{56}
-10.05 eV



a’ (= σ), ϕ_{55}
-10.41 eV

Part-6
Comparison of Kohn-Sham Orbital Energies

Kohn-Sham Frontier Orbital Energies of **2** and **4**