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Theoretical Study of First Singlet Excited State of *Para*-Substituted Platinabenzene Complexes

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ABSTRACT

The structure, electronic properties, and aromaticity of the *para*-substituted platinabenzenes were illustrated by applying the hybrid density functional MPW1PW91 theory. The electron donor groups (EDG) and electron withdraw groups (EWG) effects on geometry, frontier orbital energies, reactivity indices and aromaticity in the first singlet excited state of platinabenzene were investigated and compared to ground state. The contribution of the fragments of the studied complexes in the frontier orbitals were calculated both in terms of the ground state and the first singlet excited state. Linear correlations between the studied parameters with Hammett's constants (σ_p) were given in the two studied states.

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Graphical Abstract

First Singlet Excited State

EDG ——┐
                ├—— *Substituent effect* ——→ [X / Pt / Cp structure]
EWG ——┘

→ Dipole moment

→ Aromaticity

→ Frontier orbitals
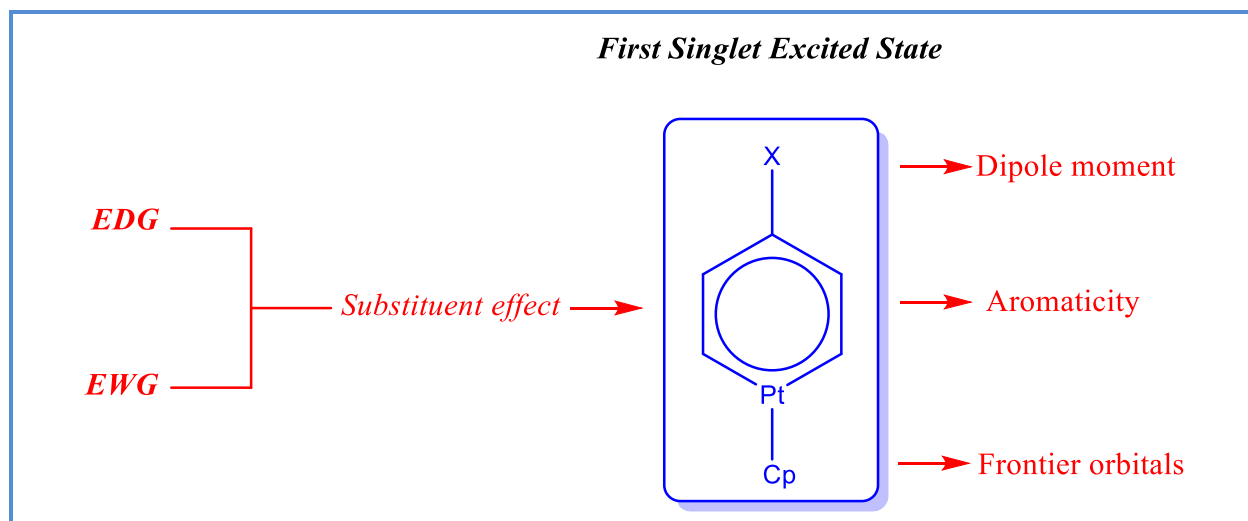
Introduction

Metallabenzenes belong to metallacycles that consist of six members and are similar to benzene for which one CH unit was substituted by an isolobal transition-metal fragment [1-4]. Recently, preparations and characterizations of various metallabenzenes have been reported [5-10]. One of the transition metals to be incorporated into stable metallabenzene complexes is platinum [6-11]. The experimental and theoretical investigations on the structure and properties of platinabenzenes have been reported [12-18]. The reduced aromaticity of metallabenzenes [14-19] relative to benzene and heteroaromatic rings has been investigated [20]. In addition, the nonlinear optical (NLO) properties of these complexes have been studied [21].

It is well-known that the electron withdrawing groups (EWGs) and electron-releasing groups (ERGs) influence molecular behavior. In other words, the presence of different substituents affects the physical, electronic, and spectroscopic features of molecules. That is why many theoretical studies have been conducted to show how various substituents influence the organometallic complexes [17, 22-33]. Moreover, it has been shown that quantitative substituent parameter scales can be used to explain how molecular properties are influenced by the polar or steric effects of the substituent. For example, Hammett constant (σ_p) [34] explained the electronic effects of substituents on the equilibrium and rate constants of a reacting molecule. The substituted effects on the structure and properties of the *para*-substituted platinabenzene in the ground state have been studied [17].

Structure and properties of molecules in their electronically excited states can be investigated by quantum chemical methods. The most generally used computational methods are the single configurational procedures like CI-Singles (CIS) [35], coupled-cluster (CC) techniques [36], the TDDFT (time-dependent density functional theory) approach [37] and the more sophisticated multi-configurational treatments, with particular emphasis on perturbation theory, the CASPT2 approach [38]. Many computational investigations on the structure and properties of molecules in their electronically excited states have been reported [39-46].

In the presented study, we aim at illustrating the substitution effect on the structural, electronic properties and aromaticity *para*-substituted platinabenzenes at the first singlet excited state. Then, we compare the results to the ground state of the complexes.

Computational methods

All calculations were carried out with the Gaussian (Version, 09) software package [47] using the standard 6-311G (d, p) basis set computations of systems involving the main group elements [48, 49]. For Pt element standard LANL2DZ basis set [50-52] have been applied and Pt was explained by effective core potential (ECP) [53] with a doublet-ξ valance using the LANL2DZ.

Ground state and first singlet state geometry optimizations were carried out by applying one parameter hybrid functional with the adapted Perdew-Wang exchange and correlation (MPW1PW91) [54]. According to the results of computations for transition metal complexes, MPW1PW91 functional out performed B3LYP [55-58]. A vibrational analysis at each stationary point verified its identity as an energy minimum. The first singlet excited states of the target compounds were determined by TD-DFT method [37].

The percentage of contributions of atomic orbitals in the HOMO and LUMO (frontier orbitals) was determined by applying GaussSum (Version, 3.0) software package [59].

The nucleus independent chemical shift (NICS) was applied to explain the aromaticity from the magnetic feature. The indicator is specified as the negative value of the absolute magnetic shielding determined at the ring center [60] or another suitable point of the system [61]. Rings having highly negative values of NICS are determined as aromatic by definition, but those with positive values are anti-aromatic.

Results and discussion

Energetic aspects

Figure 1 displays the structure of the studied *para*-substituted platinabenzene molecules in our investigation. The absolute energy values of the investigated complexes molecules in the ground state and first singlet-excited state are gathered in Table 1. The excitation energy with respect to the ground state (ΔE) are calculated (Table 1). It can be found that these values are larger in the presence of the electron-donor groups (EDG) as compared to electron-withdrawing groups (EWG). Linear correlation between these values and Hammett's constant are:

$$X=EDG: \Delta E = 16.031 \, \sigma_p + 44.047; \, R^2=0.9759$$

$$X=EWG; \Delta E = -1.1269 \, \sigma_p + 4.3619; \, R^2=0.8460$$

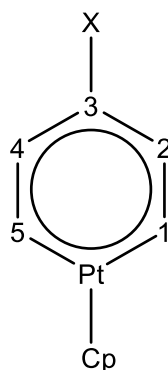Therefore, a better linear correlation in the presence of EDGs can be observed as compared to EDGs.

Figure 1. The structure of studied *para*-substituted platinabenzene (cp=η^5-C_5H_5)

Table 1. Absolute energy (E, a. u), excitation energy with respect to the ground state (ΔE, kcal/mol), dipole moment (μ, Debye) values of the para substituted platinabenzene complexes at the ground state and first singlet excited state. σ_p is Hammett's constant of the substitutions

X	σ_p	E(G.S)	E(E.S)	ΔE	μ(G.S)	μ(E.S)
NH$_2$	-0.66	-561.5908	-561.5372	33.62	3.42	8.93
OH	-0.37	-581.4517	-581.3910	38.09	1.35	7.10
OMe	-0.27	-620.7489	-620.6868	39.01	1.75	8.50
Me	-0.17	-545.5370	-545.4702	41.90	0.19	7.16
H	0.00	-506.2166	-506.2102	4.04	1.06	0.46
F	0.06	-605.4645	-605.4575	4.39	2.31	1.84
Cl	0.23	-965.8507	-965.8443	4.03	2.99	2.30
COOH	0.45	-694.7990	-694.7931	3.71	3.45	3.01
CN	0.66	-598.4551	-598.4491	3.73	6.72	6.06

Dipole moment

Dipole moment values of the studied *para*-substituted platinabenzene molecules in the ground state and first singlet-excited state are shown in Table 1. Directions of the dipole moment values are presented in Figure 2. Accordingly, the larger dipole moment values in the first singlet-excited state in the presence of EDGs can be observed as compared to ground stat. In contrast, dipole moment values of the first singlet-excited state decrease in the presence of the EWGs as compared to ground stat.

Therefore, the electronic distributions of the first singlet-excited state differ as compared to ground state because of the large charge transfer excitation. These electronic distributions are dependent on the substituent character.
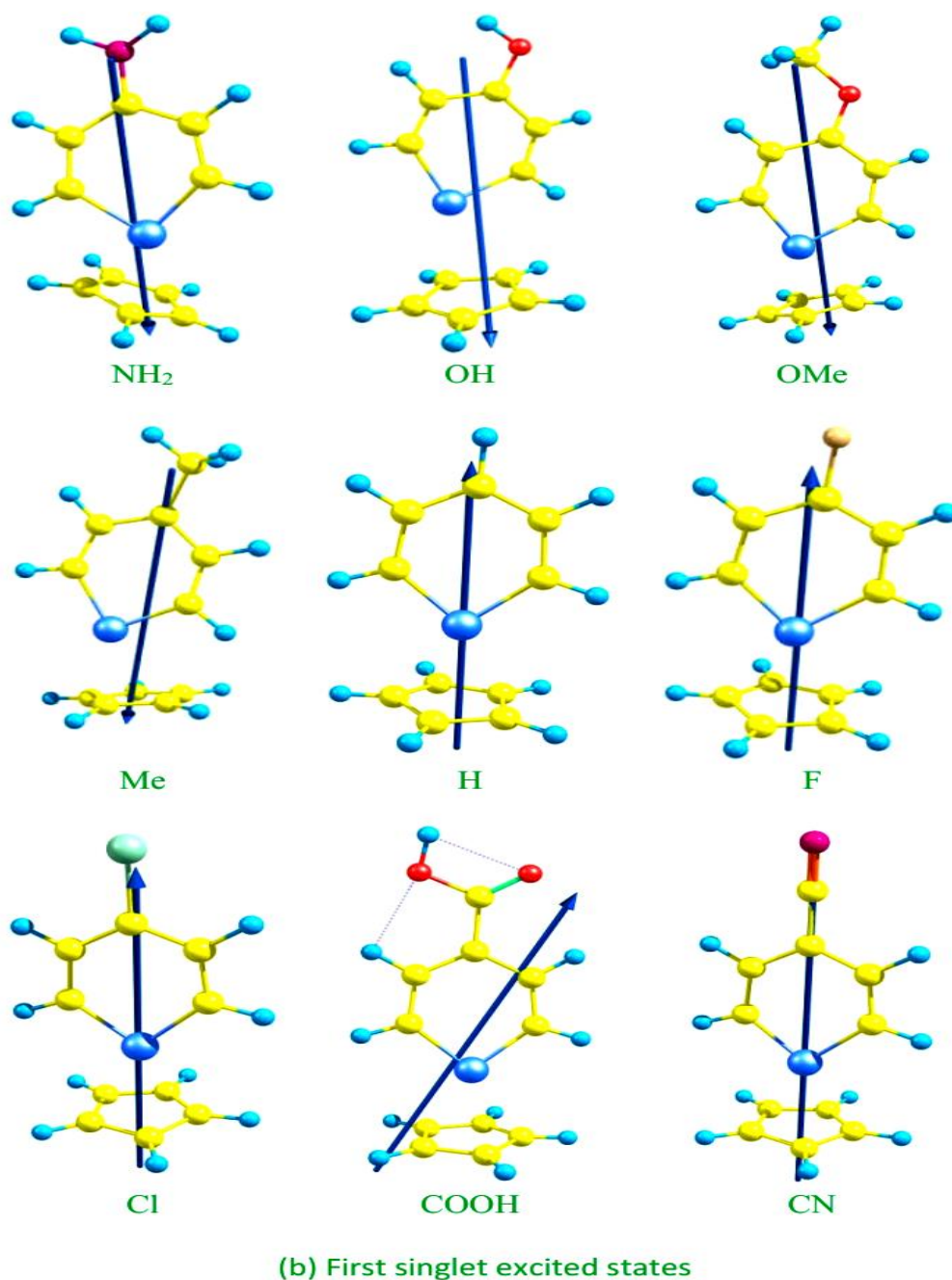

(a)Ground state

(b) First singlet excited states
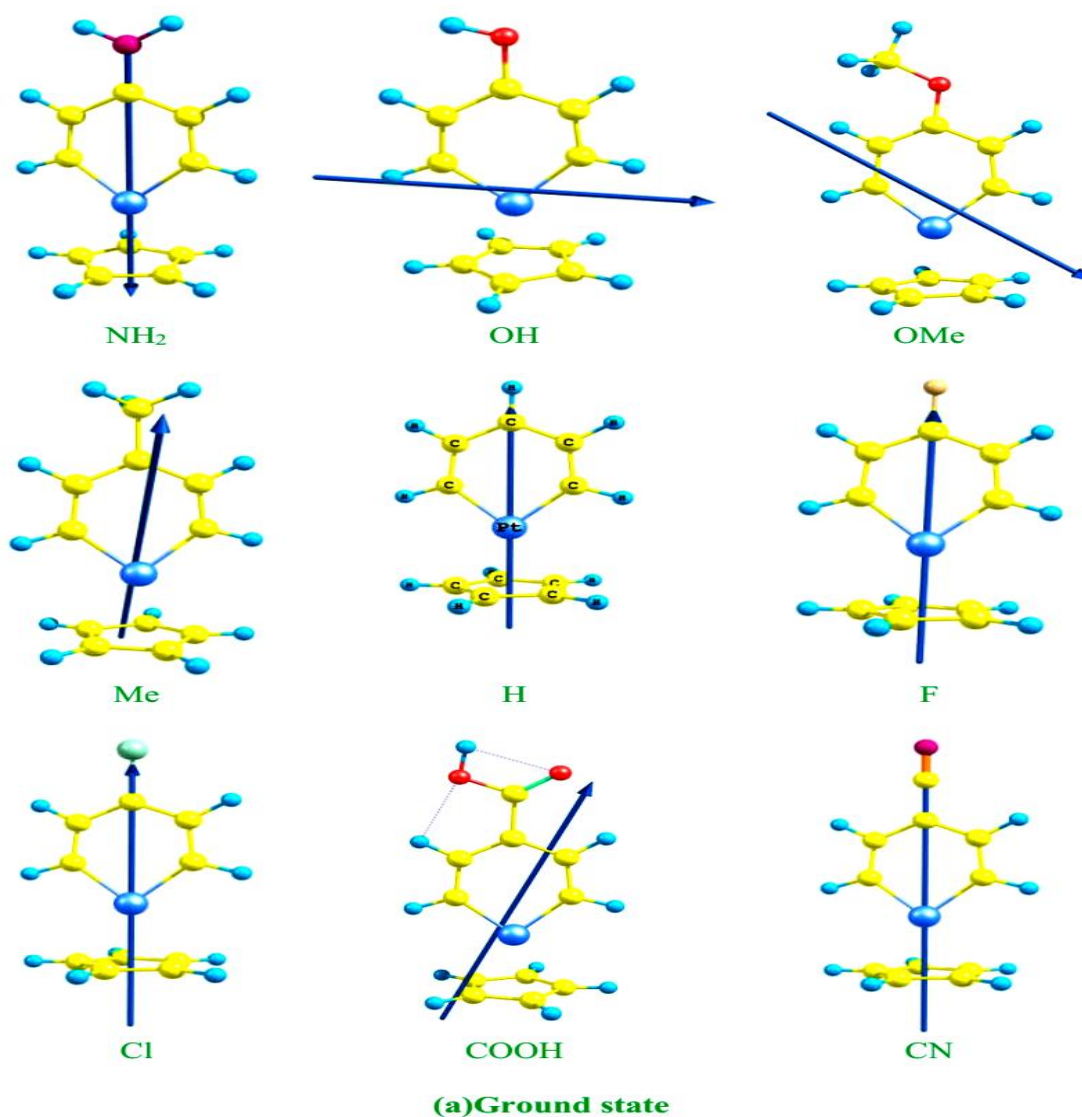
Figure 2. Directions of the dipole moment values in the (a) ground and (b) first singlet excited states of studied *para*-substituted platinabenzene complexes

Frontier orbital energies and chemical hardness

The computed frontier orbitals energies, HOMO-LUMO gap energy, hardness, chemical potential, and electrophilicity values of the studied *para*-substituted platinabenzene molecules in the ground state and first singlet-excited state are shown in Table 2.

These values show the energy of the stability of the HOMO decrease in the presence of EDGs in the first singlet-excited state. Meanwhile, the stability of the HOMO increased in the presence of EWGs in the first singlet-excited state.

Table 2. Frontier orbital energies (Hartree), HOMO-LUMO gap energy (eV), hardness (eV), chemical potential (eV), and electrophilicity (ω) of para substituted platinabenzene complexes at the ground state and first singlet excited state

(a)Ground state

X	HOMO	LUMO	ΔE	η	μ	ω
NH$_2$	-0.191	-0.057	3.630	1.815	-3.376	3.140
OH	-0.207	-0.072	3.693	1.847	-3.798	3.906
OMe	-0.205	-0.070	3.674	1.837	-3.733	3.793
Me	-0.215	-0.079	3.695	1.847	-3.994	4.318
H	-0.221	-0.084	3.738	1.869	-4.144	4.594
F	-0.221	-0.084	3.732	1.866	-4.158	4.633
Cl	-0.225	-0.092	3.614	1.807	-4.307	5.132
COOH	-0.232	-0.104	3.477	1.739	-4.568	6.002
CN	-0.239	-0.112	3.442	1.721	-4.781	6.641

(b) First singlet excited state

| X	HOMO	LUMO	ΔE	η	μ	ω
NH$_2$	-0.177	-0.109	1.853	0.927	-3.891	8.168
OH	-0.183	-0.125	1.597	0.798	-4.190	10.996
OMe	-0.179	-0.123	1.524	0.762	-4.101	11.034
Me	-0.182	-0.134	1.300	0.650	-4.308	14.269
H	-0.225	-0.094	3.575	1.787	-4.344	5.278
F	-0.226	-0.096	3.547	1.773	-4.375	5.396
Cl	-0.229	-0.102	3.458	1.729	-4.492	5.837
COOH	-0.236	-0.114	3.311	1.656	-4.760	6.842
CN	-0.242	-0.122	3.276	1.638	-4.955	7.493

Besides, these values show the energy of the stability of the LUMO increase in the presence of EDGs and EWGs in the first singlet-excited state.

The good linear correlation can be observed between frontier orbital energy values with Hammett's constants in the ground state (Figure 3(a)):
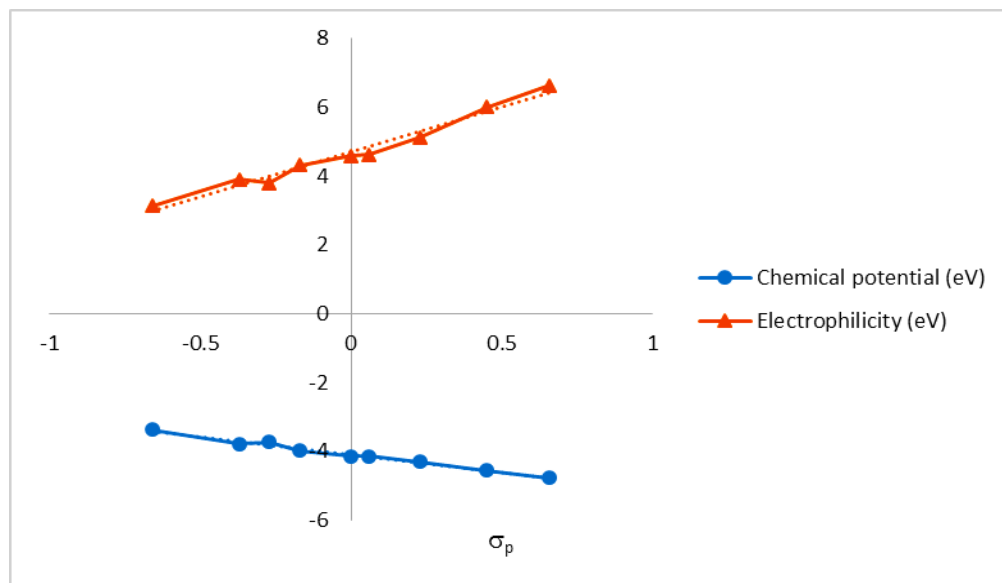
$$E \text{ (HOMO)} = -0.035 \ \sigma_p - 0.2176; R^2 = 0.9655$$

$$E \text{ (LUMO)} = -0.0413 \ \sigma_p - 0.0841; R^2 = 0.9845$$

It can be found that HOMO-LUMO gap values were decreased in the presence of EDGs and EWGs in the first singlet-excited state.
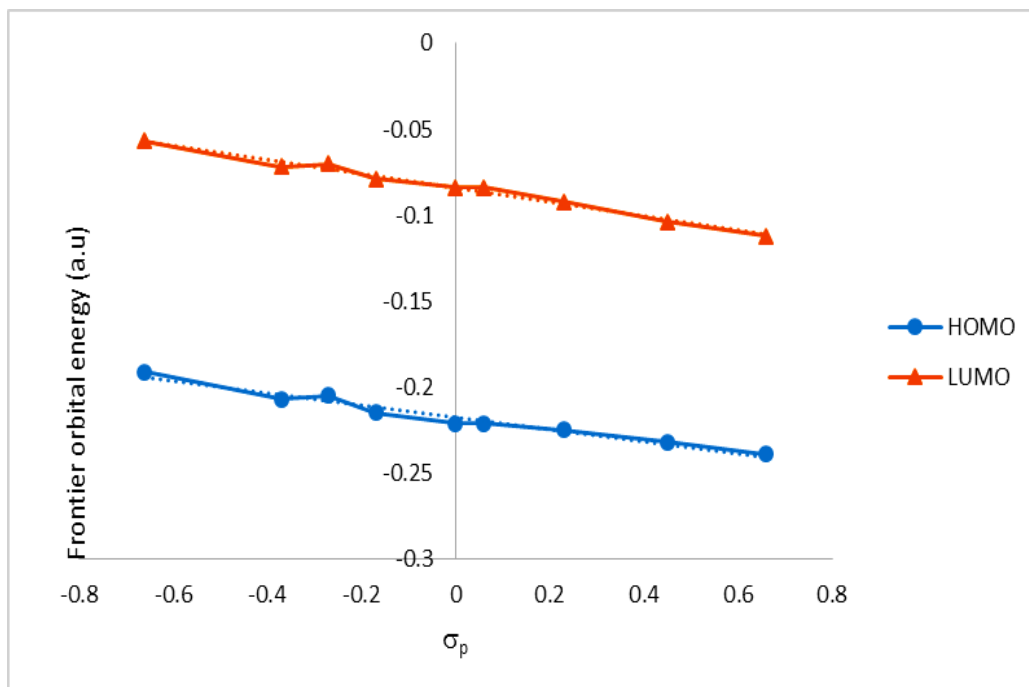
(a)

(b)

Figure 3. Linear correlation between (a) frontier orbital energy values, (b) electrophilicity and chemical potential with Hammett's constant of the substitutions in the ground state of studied *para* substituted platinabenzene complexes

To evaluate the hardness and chemical potential of these complexes, these values can be determined from the HOMO and LUMO orbital energies by applying the following approximate expression:

$$\mu = (E_{HOMO} + E_{LUMO})/2$$

$$\eta = (E_{HOMO} - E_{LUMO})/2$$

Where μ denotes the chemical potential and η denotes the hardness [62, 63].

The hardness values in Table 2 show the decrease of these values in the presence of EDGs and EWGs in the first singlet-excited state.

The collected values of the chemical potential in Table 2 show that these values were decreased in the presence of EDGs and EWGs in the first singlet-excited state. The good linear correlation can be observed between chemical potential values with Hammett's constants in the ground state and first singlet-excited state (Figure 3(b)):

$$\mu \text{ (G.S) } = -1.0359 \, \sigma_p - 4.1034; \, R^2 = 0.9841$$

$$\mu \text{ (E.S)} = -0.7721 \, \sigma_p - 4.3854; \, R^2 = 0.9629$$

To determine the electrophilicity of these complexes, the electrophilicity index, ω, for each complex was determined by applying the following expression [64]:

$$\omega = \mu^2/2\eta$$

The values of electrophilicity index in Table 2 show that these values were increasedin the presence of EDGs and EWGs in the first singlet-excited state. The good linear correlation can be observed in electrophilicity values with Hammett's constants in the ground state (Figure 3(b)):

$$\omega = 2.6268 \, \sigma_p + 4.7047; \, R^2 = 0.9738$$

Figure 4 presents Plots of frontier orbitals in the studied molecules in the ground state (X=H) and first singlet-excited state (X=Me, H, COOH). Moreover, π^*-overlap between Pt and ligands in LUMO and in the presence of EWGs and EDGs can be observed for ground state. In HOMO, there is a significant orbital overlapping between metal and ligands in the presence of EWGs and EDGs. For first singlet exited state, π^*-overlap between Pt and ligands in LUMO can be observed in the presence of EWGs. Nevertheless, there is not an orbital overlap between Pt and cp ligand in the presence of EDGs. In HOMO, there is a significant orbital overlapping between metal and ligands in the presence of EWGs. In contrast, there is a significant orbital overlapping between metal and cp ligand in the presence of EDGs.
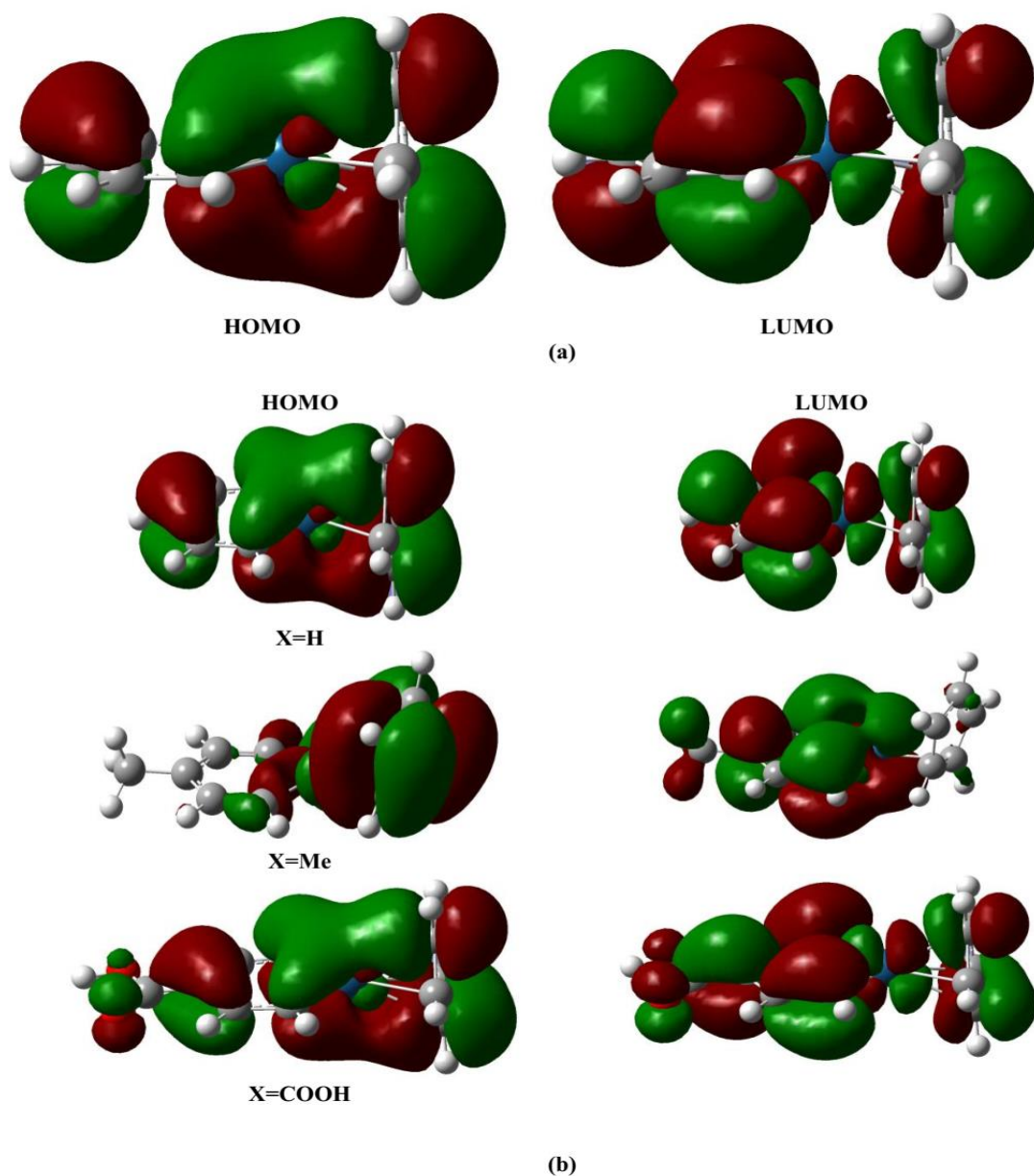
HOMO   **LUMO**

(a)

HOMO   **LUMO**

X=H

X=Me

X=COOH

(b)

Figure 4. Plots of frontier orbitals in the studied molecules in (a) the ground state (X=H) and (b) first singlet excited states of studied *para* substituted platinabenzene complexes. (X=Me, H, COOH)

The contribution of the Pt, cp and carbon atoms of six-membered ring (bz) in frontier orbitals in the ground and first singlet states are listed in Table 3. The contribution trend of the fragment in the ground state in the frontier orbitals can be found as:

HOMO: Cp>bz>Pt

LUMO: bz>Pt>cp

On the other hand, in the first singlet-excited state, it can be found as:

<div align="center">HOMO: Cp> Pt>bz</div>

<div align="center">LUMO: bz>Pt>cp</div>
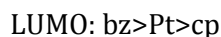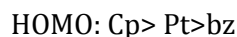
Therefore, both ground state and first singlet-excited state cp and bz ligands have most contribution in the HOMO and LUMO, respectively.

Nucleus-independent chemical shift analysis (NICS)

The nucleus-independent chemical shift (NICS) method has been extensively used to describe the aromaticity [54]. To highlight the use of NICS as a measure of aromaticity for the six-membered one, we have determined NICS values along the *z*-axis to the ring plane starting on the middle of the ring up to 2.0 Å in the ground state and first singlet-excited state. According to these calculations, the shape of NICS profile regarding the distance from the ring center is similar. Moreover, for all species, we have localized the highest and lowest NICS and calculated the distances to the center of the ring at which they occur (Table 4).

For all the molecules, the highest absolute value of NICS is 1.0 Å above the center of the ring. It is likely that induced magnetic fields made by the π-aromaticity indicate a minimum NICS at the certain distance from the center of the ring.

As shown in Table 4, the six-membered ring compounds have larger negative NICS values in ground state in comparison to the first singlet-excited state, indicating their enhanced aromatic properties in ground state.

Table 3. The contribution of the fragments of para substituted platinabenzene complexes in the frontier orbitals at the ground state and first singlet excited state

X	Pt	HOMO cp	bz	Pt	LUMO cp	bz	Pt	HOMO cp	bz	Pt	LUMO cp	bz
NH$_2$	24	43	32	17	12	71	14	81	5	18	1	81
OH	23	45	32	19	14	68	12	83	6	19	1	80
OMe	23	44	33	19	14	68	10	84	5	19	1	80
Me	21	45	34	20	16	64	10	84	6	20	1	79
H	20	46	34	21	17	63	17	52	30	21	15	64
F	21	46	33	20	15	65	19	52	30	20	14	66
Cl	20	44	36	20	16	64	18	50	32	20	15	65
COOH	19	43	38	20	18	62	16	48	35	21	17	63
CN	18	42	40	20	18	61	16	48	36	21	17	62

Table 4. The NICS (0.0), NICS (0.5), NICS (1.0), NICS (1.5), and NICS (2.0) (ppm) values of para substituted platinabenzene complexes at the ground state and first singlet excited state

X	NICS (0.0)	NICS (0.5)	G.S NICS (1.0)	NICS (1.5)	NICS (2.0)	NICS (0.0)	NICS (0.5)	E.S NICS (1.0)	NICS (1.5)	NICS (2.0)
NH$_2$	-3.02	-4.27	-5.12	-4.18	-2.88	-1.56	-1.25	-2.10	-2.07	-1.65
OH	-3.83	-5.14	-5.95	-4.81	-3.30	-2.35	-1.60	-2.63	-2.49	-1.95
OMe	-4.26	-5.75	-6.49	-5.11	-3.47	-0.18	-1.67	-3.03	-2.58	-1.83
Me	-4.04	-5.87	-6.98	-5.60	-3.81	0.82	0.94	-1.27	-1.92	-1.69
H	-3.58	-5.50	-6.87	-5.65	-3.89	-2.84	-4.79	-6.32	-5.32	-3.74
F	-4.61	-4.61	-5.93	-6.67	-5.33	-3.65	-4.94	-5.83	-4.84	-3.42
Cl	-4.59	-4.59	-6.19	-7.12	-5.69	-3.06	-4.61	-5.82	-4.94	-3.53
COOH	-5.59	-7.56	-8.48	-6.58	-4.39	-3.12	-5.14	-6.79	-5.78	-4.10
CN	-4.19	-6.01	-7.28	-5.99	-4.13	-3.60	-5.44	-6.86	-5.76	-4.05

Bond distances

C-C and Pt-C bond distances of the studied *para*-substituted platinabenzene molecules are listed in Table 5. for the ground state and first singlet-excited state. As shown, in the Pt–C bond, the lengths of the lowest energy singlet-excited state were decreased in the presence of EWGs as compared to ground state. In contrast, these Pt–C bond lengths were increased in the presence of EDGs as compared to the ground state.

On the other hand, the C-C bond lengths of the lowest energy singlet-excited state were increased in the presence of EWGs as compared to the ground state. In contrast, these C-C bond lengths were decreased in the presence of EDGs compared to ground state.

Also, it can be found that C1-C2 and C4-C5 bond distances are shorter than C2-C3 and C3-C4, both in ground state and singlet excited state, except in the presence of X=H, F, Cl. These changes in the bond lengths show a larger contribution of the zwitterionic quinonoid resonance structure to the ground state or first singlet excited state of these derivatives (Figure 5). It can be deduced that resonance forms have more contribution in the presence of X=H, F, Cl.

The Pt-C and C-C bonds length of ground state are compatible with experimental data of similar compounds [55].

Table 5. Bond distances values (in Å) of para substituted platinabenzene complexes at the ground state and first singlet excited state

(a) Ground state

X	Pt-C1	C1-C2	C2-C3	C3-C4	C4-C5	C5-Pt
NH$_2$	1.934	1.365	1.412	1.412	1.364	1.934
OH	1.930	1.370	1.402	1.399	1.368	1.933
OMe	1.926	1.374	1.401	1.406	1.364	1.935
Me	1.929	1.374	1.399	1.399	1.373	1.929
H	1.930	1.376	1.393	1.393	1.376	1.929
F	1.931	1.373	1.389	1.389	1.373	1.931
Cl	1.929	1.374	1.393	1.393	1.374	1.928
COOH	1.930	1.373	1.396	1.397	1.375	1.928
CN	1.929	1.374	1.401	1.401	1.373	1.929

(b) Excited state

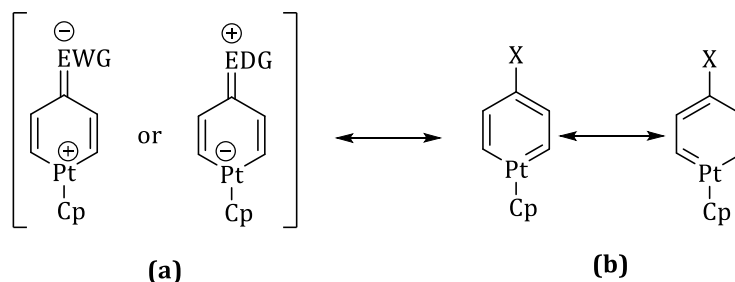| X	Pt-C1	C1-C2	C2-C3	C3-C4	C4-C5	C5-Pt
NH₂	1.945	1.356	1.416	1.417	1.355	1.949
OH	1.942	1.354	1.409	1.407	1.359	1.936
OMe	1.939	1.351	1.414	1.406	1.363	1.931
Me	1.931	1.361	1.408	1.413	1.355	1.939
H	1.919	1.402	1.398	1.399	1.401	1.917
F	1.923	1.401	1.384	1.402	1.393	1.926
Cl	1.920	1.400	1.394	1.403	1.397	1.920
COOH	1.919	1.396	1.405	1.409	1.393	1.918
CN	1.921	1.394	1.410	1.412	1.393	1.920

(a)   **(b)**

Figure 5. The resonance forms of studied *para* substituted platinabenzenes. Where X represents an electron donor group (EDG) or electron withdraw group (EWG). (a) zwitterionic, non-aromatic quinonoid structure (b) aromatic structures

Conclusions

The computational investigation of the substitution effect on the structural, electronic properties and aromaticity *para*-substituted platinabenzenes in the first singlet-excited state of the complexes showed that:

1. Energy difference values of ground state and first singlet-excited state values were larger in the presence of EDGs in comparison to EWGs. It can be found that there are good linear correlations between these values and Hammett's constants.

2. Dipole moment values in the first singlet-excited state were larger in the presence of EDGs as compared to ground stat. In contrast, dipole moment values of the first singlet-excited state were decreased in the presence of the EWGs as compared to ground stat.

3. Cp and bz ligands have the most valuable contribution in the HOMO and LUMO, respectively, both ground state and first singlet excited state.

4. Larger negative NICS values in ground state as compared to first singlet-excited stateindicate their enhanced aromatic properties in ground state.

The Pt–C bond lengths of the lowest energy singlet-excited state were decreased in the presence of EWGs as compared to ground state. In contrast, these Pt–C bond lengths were increased in the presence of EDGs as compared to ground state. C1-C2 and C4-C5 bond distances are shorter than

C2-C3 and C3-C4, both in ground state and singlet-excited state, except in the presence of X=H, F, Cl. Therefore, there is a larger contribution of the zwitterionic quinonoid resonance structure to the ground state or first singlet-excited state of these derivatives.

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