Substituent effects on the structure and properties of \((para\text{-}C_5H_4X)\text{Ir(PH}_3)_3\) complexes in the ground state \((S_0)\) and first singlet excited state \((S_1)\): DFT and TD-DFT investigations

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Abstract
The ground and lowest singlet excited state geometries of selected \((para\text{-}C_5H_4X)\text{Ir(PH}_3)_3\) iridabenzene complexes \((para\text{-}substituent} = \text{NH}_2, \text{OMe}, \text{Me}, \text{H}, \text{F}, \text{Cl}, \text{CCl}_3, \text{CF}_3, \text{NO}_2)\) are optimized using the MPW1PW91 procedure employing the LanL2DZ(Ir) and 6-311G(d, p) (C, H, N, O, P, F, Cl, P) basis sets. The excited state is generated using the time-dependent density function method. The effects of electron-donating groups and electron-withdrawing groups on the energy, atomization energy, rotational constants, and frontier orbital energies in the first singlet excited state \((S_1)\) of iridabenzene are investigated and compared to those of the ground state \((S_0)\). The Ir–C and Ir–P bonds in the studied molecules are analyzed by electron localization function and localized-orbital locator methods. The correlations between the Ir–C and Ir–P bond distances, electron localization function, and localized-orbital locator values Hammett constants \((\sigma_p)\) and dual parameters \((\sigma_I\text{ and }\sigma_R)\) are given for the two studied states. The para-delocalization index is used for investigation of the aromaticity of the studied complexes.

Keywords
electron localization function, excited state, iridabenzene, localized-orbital locator, substituent effect, time-dependent density functional theory

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Introduction
Metallabenzenes are a type of metallacycle that consists of six-membered ring. Metallabenzenes are similar to benzene with one CH unit substituted by an isolobal transition-metal fragment.¹⁻⁵ Over the years, the preparation and characterization of various metallabenzenes have been reported.⁶⁻¹³ The aromaticity of metallabenzenes compared to benzene and cyclic heteroaromatics has been investigated.¹⁴⁻¹⁸

As an example, replacing a CH of benzene with isolobal fragments of iridium leads to the synthesis of different iridabenzenes.¹⁹⁻²²

Iridabenzene was the initial synthetic sample of a metallabenzenec with a structure like that suggested by Thorn and Hoffmann.²³ Crystal structures have been described for high oxidation state iridabenzenes.²⁴ These 16-electron complexes have an open coordination site at iridium. In other studies, the nonlinear optical (NLO) properties of these complexes have been explored.²⁵ The polarity effect of the solvent on the structure and electronic properties of these complexes have been reported using computational methods.²⁶ Also, in the other theoretical studies, the structure, chemical reactivity, aromaticity, and \(^{14}N\) nuclear quadrupole resonance (NQR) parameters of iridapyridine isomers have been investigated.²⁷ It is well known that 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. This is why many theoretical studies have been conducted to show how various substituents influence the properties of organometallic complexes.²⁶,²⁸⁻³⁹ Moreover, it has been shown that quantitative substituent parameter

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scales can be used to explain how molecular properties are influenced by the polar or steric effects of the substituent. For example, the Hammett constant ($\sigma_p$) explains the electronic effects of substituents on the equilibrium and rate constants of a reacting molecule. The substituent effects in the structure and the properties of the para-substituted iridabenzenes in the ground state have been studied.

Investigation of variations in the structures and properties of molecules in the electronic excited states is possible by quantum chemical methods. The time-dependent density functional theory (TDDFT) approach is one of the most commonly employed computational methods. Numerous computational studies on the excited states of molecules have been reported.

The absence of any theoretical or experimental investigations on the first singlet excited states of iridabenzenes encouraged us to study substitution effects on the structural, electronic properties, and aromaticity of para-substituted iridabenzenes at the first singlet excited state. We compare the obtained results with those of the ground states of the complexes.

**Results and discussion**

**Atomization energies**

Figure 1 displays the structures of the studied para-substituted iridabenzenes molecules in our investigations. The atomization energy is the energy difference between a molecule and its constituent ground state atoms. To compute the atomization energies of the investigated iridabenzenes molecules in the ground state ($S_0$) and first singlet excited state ($S_1$), molecules are considered as closed shell singlet and the multiplicities assumed for H, C, N, O, F, Cl, and P atoms are doublet, triplet, quartet, triplet, doublet, doublet, and quartet, respectively. The calculated atomization energies of the investigated molecules are listed in Table 1. Larger atomization energy values ($E_{\text{atom}}$) are observed for the $S_0$ state compared to the $S_1$ state.

Since in atomization processes, we break all bonds in the molecule and form separated atoms; it seems plausible that the change in electronic energy for atomization can be estimated as the sum of the energies associated with each bond in the molecule. Therefore, the atomization energy is equivalent to the total binding energy.

**Energetic aspects**

The absolute energy values of the investigated complexes in the $S_0$ and $S_1$ states are collected in Table 1. The excitation energies with respect to the ground states ($\Delta E$) are calculated (Table 1). The Hammett substituent constants ($\sigma_p$) and dual parameters ($\sigma_I$ and $\sigma_R$) are also listed in Table 1. The $\sigma_I$ and $\sigma_R$ values are the resonance and inductive constants of the substituents, respectively.

The plot of $\Delta E$ values versus the Hammett constants ($\sigma_p$) values is shown in Figure 2. Surprisingly, the $\Delta E$ values demonstrate a linear relation with respect to the $\sigma_p$ values

$$\Delta E = 0.3555 \sigma_p + 1.4201; \quad R^2 = 0.9419$$

It is found that these values are lower in the presence of electron-donating groups (EDG) compared to EWG.

**Rotational constants**

The calculated rotational constants for the investigated iridabenzenes molecules in the $S_0$ and $S_1$ states are shown in Table 2.

These values show that rotational constants in the excited state are less than those of the corresponding ground state rotational constants. Since the moment of inertia (and consequently the rotational constant) of a molecule is

![Figure 1](image_url)

**Table 1.** Total energy (E, a.u), excitation energy with respect to the ground state ($\Delta E$, eV), atomization ($E_{\text{atom}}$, kcal/mol), dipole moment ($\mu$, Debye), and para-delocalization index (PDI) values in the ground state ($S_0$) and first singlet excited state ($S_1$) of (para-C$_5$H$_4X$)Ir(PH$_3$)$_3$ iridabenzenes complexes.

| X       | $\sigma_p$ | $\sigma_I$ | $\sigma_R$ | E (GS)   | E (ES)   | $\Delta E$ | $E_{\text{atom}}$ ($S_0$) | $E_{\text{atom}}$ ($S_1$) | $\mu$ ($S_0$) | $\mu$ ($S_1$) | PDI ($S_0$) | PDI ($S_1$) |
|---------|------------|------------|------------|----------|----------|------------|-----------------------------|-----------------------------|---------------|---------------|-------------|-------------|
| NH$_3$  | −0.66      | 0.17       | −0.82      | −1383.173 | −1383.129 | 1.19       | 2237.76                     | 2210.24                     | 1.01           | 1.00          | 0.0715      | 0.0605      |
| OMe     | −0.27      | 0.3        | −0.58      | −1442.332 | −1442.287 | 1.28       | 2461.72                     | 2432.18                     | 3.09           | 2.03          | 0.0757      | 0.0671      |
| Me      | −0.17      | −0.01      | −0.16      | −1367.124 | −1367.072 | 1.42       | 2357.23                     | 2324.56                     | 3.85           | 2.46          | 0.0871      | 0.0821      |
| H       | 0.00       | 0.00       | 0.00       | −1327.805 | −1327.751 | 1.47       | 2053.80                     | 2019.93                     | 4.37           | 3.27          | 0.0929      | 0.0903      |
| F       | 0.06       | 0.54       | −0.48      | −1427.053 | −1427.002 | 1.39       | 2088.24                     | 2056.14                     | 5.72           | 4.39          | 0.0834      | 0.0771      |
| Cl      | 0.23       | 0.30       | −0.25      | −1787.440 | −1787.387 | 1.45       | 2051.84                     | 2018.31                     | 6.68           | 4.87          | 0.0851      | 0.0804      |
| CCl$_3$ | 0.46       | 0.36       | 0.08       | −2745.991 | −2745.933 | 1.59       | 2326.49                     | 2289.83                     | 8.50           | 6.47          | 0.0857      | 0.0807      |
| CF$_3$  | 0.54       | 0.40       | 0.11       | −1664.871 | −1664.812 | 1.62       | 2462.27                     | 2424.99                     | 8.11           | 6.66          | 0.0896      | 0.0903      |
| NO$_2$  | 0.78       | 0.67       | 0.10       | −1532.317 | −1532.254 | 1.71       | 2275.42                     | 2235.91                     | 10.79          | 8.54          | 0.0852      | 0.0889      |

PDI: para-delocalization index.
Hammett substituent constants ($\sigma_p$) and dual parameters ($\sigma_I$ and $\sigma_R$) for substituents.
directly related to the nuclear coordinate,\(^5\) it is reasonable that the rotational constant changes in the \(S_0\) and \(S_1\) states. By taking a closer look at the data in Table 2, it is revealed that the studied iridabenzenes are asymmetric top as expected (namely, \(A \neq B \neq C\)). With the electron number \((N_e)\) of the molecule becoming larger, the rotational constants become smaller. It is interesting to note, however, that there are good linear correlations between the A values and number of electrons

\[
A\left(S_0\right) = -0.0064 N_e + 1.6976; R^2 = 0.9233 \\
A\left(S_1\right) = -0.0055 N_e + 1.4887; R^2 = 0.9448
\]

**Dipole moment**

The dipole moment values of the studied \(para\)-substituted iridabenzenes in the \(S_0\) and \(S_1\) states are shown in Table 1. Larger dipole moment values are observed in the \(S_1\) state compared to the \(S_0\) state. Therefore, the electronic distributions of the first singlet excited state differ compared to the ground state because of the large charge transfer excitation. These electronic distributions are dependent on the substituent character.

However, the dipole moment values are larger in the presence of EWGs compared to EDGs in both the \(S_0\) and \(S_1\) states. It is interesting to note, however, that there are good linear correlations between the dipole moment values and the Hammett constants (Figure 3)

\[
\mu(S_0) = 6.7542 \sigma_p + 5.0631; R^2 = 0.9809 \\
\mu(S_1) = 5.4409 \sigma_p + 3.8232; R^2 = 0.9686
\]

**Bond distances**

The C–C and Ir–C bond distances of the studied \(para\)-substituted iridabenzenes are listed in Table 3 for the \(S_0\) and \(S_1\) states.

These values show that the Ir–C2, C3–C4, and Ir–P\(_{ax}\) bond distances are longer in the \(S_1\) state than in the \(S_0\) state. In contrast, the C2–C3 and Ir–P\(_{eq}\) bond distances are shorter in \(S_1\) state than \(S_0\) state.

The study of changes in bond distances in \(S_1\) state compared to \(S_0\) state shows that the most changes occurs in Ir–P\(_{ax}\) bond distance. These changes are larger in the presence of EWGs.

As shown, the Ir–P\(_{ax}\) bond lengths are longer in the presence of EDGs than in the EWGs in the \(S_0\) state. In contrast, the Ir–P\(_{eq}\) bond lengths are longer in the presence of EWGs compared with EDGs in the \(S_1\) state.

The \(Ir–C\) and \(C–C\) bond lengths in the ground state are compatible with the experimental data of similar compounds.\(^5\) The shorter C2–C3 bond in the \(S_1\) state compared to that in the \(S_0\) state indicates a larger contribution of the zwitterionic resonance structure to the \(S_1\) state (Figure 1(b)).

The plots of the Ir–C and Ir–P bond distances versus Hammett constants give the following equations:

\[
S_0 \text{ state} \\
r(Ir - P_{ax}) = -0.0196 \sigma_p + 2.2658; R^2 = 0.8286 \\
r(Ir - P_{eq}) = 0.0144 \sigma_p + 2.3411; R^2 = 0.9611
\]

| \(X\) | \(N_e\) | \(S_0\) | \(S_1\) |
|------|------|------|------|
|      |      | \(A\) | \(B\) | \(C\) | \(A\) | \(B\) | \(C\) |
| NH₂  | 114  | 0.9550 | 0.4401 | 0.4056 | 0.8538 | 0.4221 | 0.3963 |
| OMe  | 122  | 0.9287 | 0.3247 | 0.3035 | 0.8317 | 0.3169 | 0.2994 |
| Me   | 114  | 0.9566 | 0.4404 | 0.4042 | 0.8549 | 0.4214 | 0.3944 |
| H    | 106  | 0.9629 | 0.6276 | 0.5547 | 0.8621 | 0.5811 | 0.5287 |
| F    | 114  | 0.9592 | 0.4282 | 0.3941 | 0.8518 | 0.4103 | 0.3856 |
| Cl   | 122  | 0.9609 | 0.3133 | 0.2942 | 0.8520 | 0.3063 | 0.2922 |
| CCl\(_3\) | 162 | 0.6190 | 0.1408 | 0.1368 | 0.5692 | 0.1421 | 0.1392 |
| CF\(_3\) | 138 | 0.8259 | 0.2069 | 0.1980 | 0.7315 | 0.2051 | 0.2002 |
| NO\(_2\) | 128 | 0.9018 | 0.2675 | 0.2478 | 0.7886 | 0.2635 | 0.2496 |
S\textsubscript{1} state

\[ r(\text{Ir}-\text{P}_{\text{eq}}) = 0.10 \sigma_{\text{i}} + 0.09 \sigma_{\text{n}} + 2.95; R^2 = 0.9143 \]
\[ r(\text{Ir}-\text{P}_{\text{ax}}) = 1.35 \times 10^{-3} \sigma_{\text{i}} + 2.76 \times 10^{-3} \sigma_{\text{n}} + 2.35; R^2 = 0.9966 \]

These equations show good correlations for r(Ir–P) bonds in the S\textsubscript{0} and S\textsubscript{1} states. In these equations, the major contribution of the \( \sigma_{\text{n}} \) parameter is demonstrated in the Ir–P\textsubscript{eq} bonds.

Frontier orbital energies and HOMO-LUMO gap

The computed frontier orbitals energies and highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap energies of the studied \textit{para}-substituted iridabenzene complexes in the S\textsubscript{0} and S\textsubscript{1} states are shown in Table 4.

These values show that the energy of stability of the frontier orbitals increases in the presence of EWGs in both the S\textsubscript{0} and S\textsubscript{1} states. In comparison, the stability of the frontier orbitals decreased in the presence of EDGs in both the S\textsubscript{0} and S\textsubscript{1} states.

Good linear correlations can be observed between the frontier orbital energy values and Hammett constants in both the S\textsubscript{0} and S\textsubscript{1} states:

\[ S\textsubscript{0} \text{ state} \]
\[ E(\text{HOMO}) = -0.029 \sigma_{\text{i}} - 0.1837; R^2 = 0.9917 \]
\[ E(\text{LUMO}) = -0.0375 \sigma_{\text{i}} - 0.0503; R^2 = 0.9400 \]

\[ S\textsubscript{1} \text{ state} \]
\[ E(\text{HOMO}) = -0.0278 \sigma_{\text{i}} - 0.172; R^2 = 0.9865 \]
\[ E(\text{LUMO}) = -0.0373 \sigma_{\text{i}} - 0.0952; R^2 = 0.9656 \]

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Table 3. Selected bond distances (in Å) in the ground state (\( S_0 \)) and first singlet excited state (\( S_1 \)) of (\textit{para}-C\textsubscript{6}H\textsubscript{4}X)Ir(PH\textsubscript{3})\textsubscript{3} iridabenzene complexes.

| X     | \( S_0 \) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| \( \text{Ir-C2} \) | \( \text{C2-C3} \) | \( \text{C3-C4} \) | \( \text{Ir-P}_{\text{ax}} \) | \( \text{Ir-P}_{\text{eq}} \) | \( \text{Ir-C2} \) | \( \text{C2-C3} \) | \( \text{C3-C4} \) | \( \text{Ir-P}_{\text{ax}} \) | \( \text{Ir-P}_{\text{eq}} \) | \( \text{Ir-C2} \) | \( \text{C2-C3} \) | \( \text{C3-C4} \) | \( \text{Ir-P}_{\text{ax}} \) | \( \text{Ir-P}_{\text{eq}} \) |
| \( \text{NH}_2 \)  | 1.994 | 1.373 | 1.406 | 2.279 | 2.331 | 2.028 | 1.361 | 1.419 | 2.912 | 2.326 |
| \( \text{OMe} \)   | 2.001 | 1.368 | 1.406 | 2.276 | 2.337 | 2.028 | 1.363 | 1.412 | 2.926 | 2.336 |
| \( \text{Me} \)    | 1.987 | 1.381 | 1.397 | 2.263 | 2.341 | 2.019 | 1.373 | 1.406 | 2.934 | 2.342 |
| \( \text{H} \)     | 1.988 | 1.383 | 1.392 | 2.259 | 2.343 | 2.020 | 1.374 | 1.401 | 2.944 | 2.346 |
| \( \text{F} \)     | 1.989 | 1.381 | 1.386 | 2.268 | 2.340 | 2.024 | 1.372 | 1.394 | 2.942 | 2.341 |
| \( \text{Cl} \)    | 1.986 | 1.382 | 1.390 | 2.264 | 2.344 | 2.017 | 1.369 | 1.402 | 2.959 | 2.343 |
| \( \text{CCl}_3 \) | 1.973 | 1.389 | 1.388 | 2.257 | 2.348 | 2.004 | 1.377 | 1.400 | 2.984 | 2.354 |
| \( \text{CF}_3 \)  | 1.984 | 1.382 | 1.393 | 2.255 | 2.349 | 2.010 | 1.372 | 1.403 | 3.017 | 2.355 |
| \( \text{NO}_2 \)  | 1.987 | 1.380 | 1.390 | 2.250 | 2.352 | 2.010 | 1.367 | 1.403 | 3.038 | 2.358 |
However, there are larger HOMO-LUMO gap values in the presence of EDGs compared with EWGs in both the $S_0$ and $S_1$ states. This trend is due to an electron-withdrawing inductive effect which concentrates the electronic density over the substituted region of the complex. The HOMO-LUMO gap values are larger in the $S_0$ state compared to the $S_1$ state.

**Electron localization function analysis**

We analyzed the nature of the chemical bonding in the Ir–C and Ir–P bonds on the basis of the electron localization function (ELF)\(^{58}\) distribution, which is indicative for concentrations of valence electron density in regions of chemical bonds.

A large ELF value corresponds to largely localized electrons which indicates that a covalent bond, a lone pair, or inner shells of the atom are involved. Table 5 reveals larger ELF values for the Ir–C bond compared to Ir–P bonds. There are larger ELF values for the Ir–C bond in the presence of EWGs. However, the ELF values of the Ir–C bond are larger in the $S_0$ state than the $S_1$ state. There are larger ELF values for the Ir–P\(_{ax}\) bond compared to the Ir–P\(_{eq}\) bond in the $S_0$ state. The plots of ELF values of the Ir–C and Ir–P bonds versus the Hammett constants give the following equations:

### Table 4. Frontier orbital energies and HOMO-LUMO gap energies (eV) in the ground state ($S_0$) and first singlet excited state ($S_1$) of (para-C$_5$H$_4$X)Ir(PH$_3$)$_3$ iridabenzen complexes.

| X     | $S_0$ | $S_1$ |
|-------|-------|-------|
|       | HOMO  | LUMO  | $\Delta E$ | HOMO  | LUMO  | $\Delta E$ |
| NH$_2$ | −4.46 | −0.84 | 3.62       | −4.21 | −2.01 | 2.20       |
| OMe   | −4.75 | −1.03 | 3.72       | −4.42 | −2.23 | 2.19       |
| Me    | −4.90 | −1.23 | 3.68       | −4.56 | −2.46 | 2.10       |
| H     | −5.01 | −1.31 | 3.70       | −4.68 | −2.58 | 2.10       |
| F     | −5.07 | −1.33 | 3.74       | −4.75 | −2.61 | 2.14       |
| Cl    | −5.17 | −1.54 | 3.63       | −4.84 | −2.78 | 2.07       |
| CCl$_3$ | −5.41 | −1.92 | 3.49       | −5.06 | −3.11 | 1.95       |
| CF$_3$ | −5.39 | −1.78 | 3.61       | −5.02 | −3.01 | 2.01       |
| NO$_2$ | −5.59 | −2.35 | 3.24       | −5.31 | −3.51 | 1.80       |

HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital.

### Table 5. ELF and LOL values of selected bonds in the ground state ($S_0$) and first singlet excited state ($S_1$) of (para-C$_5$H$_4$X)Ir(PH$_3$)$_3$ iridabenzen complexes.

| X     | $S_0$ | $S_1$ |
|-------|-------|-------|
|       | Ir–C$_2$ | Ir–P$_{ax}$ | Ir–P$_{eq}$ | Ir–C$_2$ | Ir–P$_{ax}$ | Ir–P$_{eq}$ |
| (a) ELF |       |       |       |       |       |       |
| NH$_2$ | 0.47753 | 0.43372 | 0.33439 | 0.43003 | 0.22769 | 0.32469 |
| OMe   | 0.48374 | 0.43756 | 0.33803 | 0.43720 | 0.22274 | 0.32038 |
| Me    | 0.49132 | 0.45144 | 0.33019 | 0.44521 | 0.22048 | 0.31739 |
| H     | 0.49208 | 0.45639 | 0.32921 | 0.44778 | 0.21745 | 0.31650 |
| F     | 0.48083 | 0.44818 | 0.33169 | 0.43275 | 0.21742 | 0.31941 |
| Cl    | 0.48596 | 0.45418 | 0.32997 | 0.43932 | 0.21225 | 0.32478 |
| CCl$_3$ | 0.49445 | 0.46380 | 0.32628 | 0.45144 | 0.20535 | 0.31485 |
| CF$_3$ | 0.49457 | 0.46516 | 0.32768 | 0.45101 | 0.18394 | 0.31973 |
| NO$_2$ | 0.49709 | 0.47423 | 0.32682 | 0.45209 | 0.18951 | 0.32763 |
| (b) LOL |       |       |       |       |       |       |
| NH$_2$ | 0.48877 | 0.46675 | 0.41482 | 0.46485 | 0.35200 | 0.40950 |
| OMe   | 0.49188 | 0.46868 | 0.41680 | 0.46848 | 0.34878 | 0.40712 |
| Me    | 0.49567 | 0.47569 | 0.41252 | 0.47253 | 0.34729 | 0.40546 |
| H     | 0.49605 | 0.47818 | 0.41199 | 0.47383 | 0.34529 | 0.40496 |
| F     | 0.49042 | 0.47405 | 0.41335 | 0.46623 | 0.34527 | 0.40658 |
| Cl    | 0.49299 | 0.47707 | 0.41240 | 0.46956 | 0.34182 | 0.40955 |
| CCl$_3$ | 0.49723 | 0.48191 | 0.41038 | 0.47703 | 0.33714 | 0.40404 |
| CF$_3$ | 0.49729 | 0.48259 | 0.41115 | 0.47546 | 0.32204 | 0.40676 |
| NO$_2$ | 0.49855 | 0.48713 | 0.41067 | 0.47600 | 0.32607 | 0.41112 |

ELF: electron localization function; LOL: localized-orbital locator.
It can be seen that there are poor Hammett correlations for these equations.

We also studied the multiple linear regression which considers the inductive ($\sigma_I$) and resonance ($\sigma_R$) dual parameters. The results of these correlations are:

**S_0 state**

\[
\text{ELF} \left( \text{Ir} - \text{C} \right) = 0.0122 \sigma_I + 0.4873; R^2 = 0.6401
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{ax}} \right) = 0.0277 \sigma_I + 0.4509; R^2 = 0.9074
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{eq}} \right) = -0.0068 \sigma_I + 0.3312; R^2 = 0.6486
\]

**S_1 state**

\[
\text{ELF} \left( \text{Ir} - \text{C} \right) = 0.0153 \sigma_I + 0.4416; R^2 = 0.6091
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{ax}} \right) = -0.0305 \sigma_I + 0.214; R^2 = 0.8212
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{eq}} \right) = 0.0007 \sigma_I + 0.3205; R^2 = 0.0059
\]

**S_0 state**

\[
\text{ELF} \left( \text{Ir} - \text{C} \right) = -4.8 \times 10^{-2} \sigma_I + 1.96 \times 10^{-2} \sigma_R
\]
\[
+ 0.4930; R^2 = 0.9340
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{ax}} \right) = 1.72 \times 10^{-2} \sigma_I + 3.44 \times 10^{-2} \sigma_R
\]
\[
+ 0.4562; R^2 = 0.9730
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{eq}} \right) = -1.60 \times 10^{-3} \sigma_I - 9.72 \times 10^{-3} \sigma_R
\]
\[
+ 0.3288; R^2 = 0.7874
\]

**S_1 state**

\[
\text{ELF} \left( \text{Ir} - \text{C} \right) = -1.43 \times 10^{-3} \sigma_I + 2.51 \times 10^{-3} \sigma_R
\]
\[
+ 0.4492; R^2 = 0.9180
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{ax}} \right) = -3.26 \times 10^{-3} \sigma_I - 3.10 \times 10^{-3} \sigma_R
\]
\[
+ 0.2138; R^2 = 0.8317
\]
\[
\text{ELF} \left( \text{Ir} - P_{\text{eq}} \right) = 9.79 \times 10^{-3} \sigma_I - 4.42 \times 10^{-3} \sigma_R
\]
\[
+ 0.3167; R^2 = 0.3322
\]
These equations show good correlations of ELF(Ir–C) for the \( S_0 \) and \( S_1 \) states and ELF(Ir–P\(_{eq}\)) for the \( S_0 \) state. In these equations, the major contribution of the \( \sigma_R \) parameter is demonstrated.

Figure 4 presents shaded surface maps with projections of the ELF in the \((para-C_5H_5)Ir(PH_3)_3\) iridabenzene complex for \( S_0 \) and \( S_1 \) states.

**Localized-orbital locator analysis**

A developed descriptor for electron localization is the localized-orbital locator (LOL).\(^{39,60}\) The LOL gives simple, recognizable patterns in classic chemical bonds and proves useful in interpreting the structures of unusual materials. LOL analysis focuses on the topological properties of kinetic energy density.\(^{61}\)

A large LOL value corresponds to largely localized electrons which indicates that a covalent bond, a lone pair, or inner shells of the atom are involved. Table 5 reveals larger LOL values for Ir–C bonds compared to Ir–P bonds. There are larger LOL values for the Ir–C bond compared to the Ir–P\(_{ax}\) bond in the \( S_0 \) state. In contrast, there are larger LOL values for the Ir–P\(_{ax}\) bond compared to the Ir–P\(_{eq}\) bond in the \( S_1 \) state.

The plots of the LOL values of the Ir–C and Ir–P bonds versus Hammett constants give the following equations:

**\( S_0 \) state**

\[
\text{LOL (Ir–C)} = 0.0061\sigma_p + 0.4937; R^2 = 0.6397
\]

\[
\text{LOL (Ir–P\(_{eq}\))} = 0.014\sigma_p + 0.4754; R^2 = 0.9074
\]

\[
\text{LOL (Ir–P\(_{ax}\))} = -0.0037\sigma_p + 0.4131; R^2 = 0.6498
\]

**\( S_1 \) state**

\[
\text{LOL (Ir–C)} = 0.0078\sigma_p + 0.4707; R^2 = 0.6092
\]

\[
\text{LOL (Ir–P\(_{eq}\))} = -0.0208\sigma_p + 0.3429; R^2 = 0.8101
\]

\[
\text{LOL (Ir–P\(_{ax}\))} = 0.0004\sigma_p + 0.4072; R^2 = 0.0057
\]

It is observed that there are poor Hammett correlations for these equations.

Studying the multiple linear regression, which considers the inductive (\( \sigma_i \)) and resonance (\( \sigma_R \)) dual parameters, gave the following correlations:

**\( S_0 \) state**

\[
\text{LOL (Ir–C)} = -2.5 \times 10^{-4}\sigma_i + 9.83 \times 10^{-5}\sigma_R
+ 0.4966; R^2 = 0.9340
\]

\[
\text{LOL (Ir–P\(_{eq}\))} = 8.62 \times 10^{-3}\sigma_i + 1.73 \times 10^{-2}\sigma_R
+ 0.4781; R^2 = 0.9705
\]

\[
\text{LOL (Ir–P\(_{ax}\))} = -8.8 \times 10^{-4}\sigma_i - 5.3 \times 10^{-5}\sigma_R
+ 0.4118; R^2 = 0.7884
\]

These equations show good correlations for LOL(Ir–C) in the \( S_0 \) and \( S_1 \) states and for LOL(Ir–P\(_{eq}\)) in the \( S_0 \) state. In these equations, the major contribution from the \( \sigma_R \) parameter is demonstrated.

Figure 4 reveals shaded surface maps with projection of the LOL in the \((para-C_5H_5)Ir(PH_3)_3\) iridabenzene complex for \( S_0 \) and \( S_1 \) states.

**Aromaticity.** The \( para \)-delocalization index (PDI) is a quantity for measuring the aromaticity of six-membered rings.\(^{62,63}\) PDI is fundamentally the averaged \( para \)-delocalization index (para-DI) in six-membered rings. In the studied systems, this parameter is calculated as

\[
PDI = \frac{DI(1,4) + DI(2,5) + DI(3,6)}{3}
\]

The foundation of PDI was laid according to a study by Bader et al., who believed that the DI in benzene is greater for \( para \)-related than for \( meta \)-related carbon atoms. It is obvious that the PDI would mean a larger delocalization and stronger aromaticity. The main limitation of the definition of PDI is its applicability for studying the aromaticity of six-membered rings only; it was reported that the PDI is unsuitable for cases in which the ring plane has an out-of-plane distortion.

The PDI values of the studied molecules are listed in Table 1. These values show larger PDI values for EWGs compared to EDGs. This result is consistent with nucleus-independent chemical shift (NICS) values in previous studies on \( para \)-substituted iridabenzenes.\(^{34}\)

**Conclusion**

Computational investigations of the substitution effects on the structures and properties of \( para \)-substituted iridabenzenes in the ground state and first singlet excited state showed the following:

1. Atomization energy values (\( E_{atom} \)) for the \( S_1 \) state were larger compared to the \( S_0 \) state.
2. The energy difference values of the ground state and first singlet excited state were lower in the presence of EDGs compared to EWGs.
3. The rotational constants in the excited state were less than those of the corresponding ground state rotational constants.
4. The dipole moment values were larger in the presence of EWGs compared to EDGs in both the \( S_0 \)
and $S_1$ states. There were good linear correlations between the dipole moment values and the Hammett constants.

5. The Ir–P$_{ax}$ bond lengths were longer in the presence of EDGs compared with EWGs in the $S_0$ state. In contrast, the Ir–P$_{ax}$ bond lengths were longer in the presence of EWGs compared with EDGs in the $S_1$ state.

6. The ELF and LOL values for the Ir–C bond are larger compared to the Ir–P bonds. There are larger ELF and LOL values for the Ir–C bond in the presence of EWGs. However, the ELF and LOL values of Ir–C bond are larger in the $S_0$ state than the $S_1$ state.

7. The larger PDI values for EWGs compared to EDGs indicate their enhanced aromatic properties in the presence of EWGs.

### Computational methods

All calculations were carried out with the Gaussian (Version 09) software package$^{64}$ using the standard 6-311G (d, p) basis set computations for systems involving the main group elements.$^{65,66}$ For Ir, the standard LANL2DZ basis set$^{67–69}$ is applied and Ir is explained by the effective core potential (ECP)$^{70}$ with a double-$ξ$ valence using the LANL2DZ basis set.

The ground state and first singlet state geometry optimizations were carried out by applying the parametric hybrid functional with adapted Perdew–Wang exchange and correlation (MPW1PW91)$^{71}$ According to the results of computations for transition-metal complexes, the MPW1PW91 functional outperformed B3LYP.$^{72–75}$ 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 the TD-DFT method.$^{41}$

The Multiwfn 3.5 program was used for topological analysis of the ELF, the LOL, and for calculation of the PDI.$^{76}$

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### References

1. Bleeke JR. Chem Rev 2001; 101: 1205.
2. Wright LJ. J Chem Soc Dalton Trans 2006: 1821.
3. He G, Xia H and Jia G. Chin Sci Bull 2004; 49: 1543.
4. Haley MM and Landorf CW. Angew Chem Int Ed 2006; 45: 3914.
5. Wright LJ. Metallabenzenes: an expert view. Auckland, New Zealand: John Wiley & Sons Ltd., 2017.
6. Jacob V, Landorf CW, Zakharov LN, et al. Organometallics 2009; 28: 5183.
7. Landorf CW, Jacob V, Weakley TJ, et al. Organometallics 2004; 2: 1174.
8. Lin R, Lee K-H, Poon KC, et al. Chem Eur J 2014; 20: 14885.
9. Vivancos A, Paneque M, Poveda ML, et al. Angew Chem Int Ed 2013; 52: 10068.
10. Poon KC, Liu LX, Guo TX, et al. Angew Chem Int Ed 2010; 49: 2759.
11. Clark GR, Ferguson LA, McIntosh AE, et al. J Am Chem Soc 2010; 132: 13443.
12. Hua Y, Lan Q, Fei J, et al. Chem: Eur J 2018; 24: 14531.
13. Wang T, Han F, Huang H, et al. Sci Rep 2015; 5: 9584.
14. Iron MA, Lucassen ACB, Cohen H, et al. J Am Chem Soc 2004; 126: 11699.
15. Proft FD and Geerlings P. Phys Chem Chem Phys 2004; 6: 242.
16. Camizo JA, Morgado J and Sosa P. Organometallics 1993; 12: 5005.
17. Zhu C, Zhou X, Xing H, et al. Angew Chem Int Ed 2015; 54: 3102.
18. Zhu C, Luo M, Zhu Q, et al. Nat Commun 2014; 5: 3265.
19. Paneque M, Posadas CM and Poveda ML. J Am Chem Soc 2003; 125: 9898.
20. Gilbertson RD, Lau TLS and Lanza S. Organometallics 2003; 22: 3279.
21. Gilbertson RD, Weakley TJR and Haley MM. J Am Chem Soc 1999; 121: 2597.
22. Gilbertson RD, Weakley TJR and Haley MM. Chem Eur J 2000; 6: 437.
23. Thorn DL and Hoffmann R. Nouv J Chim 1979; 3: 39.
24. Chase DT, Zakharov LN and Haley MM. Acta Crystallograr Sect E: Cryst Commun 2015; 71: 1315.
25. Karton A, Iron MA, Boom MEvd, et al. J Phys Chem A 2005; 109: 5454.
26. Ghiasi R and Amini E. J Struct Chem 2015; 56: 1483.
27. Ghiasi R and Amini E. J Struct Chem 2015; 56: 1458.
28. Shamami MK, Ghiasi R and Asli MD. J Chin Chem Soc 2017; 64: 522.
29. Ghobadi H, Ghiasi R and Jamehzbozorgi S. J Chin Chem Soc 2017; 64: 522.
30. Ghiasi R, Pasdar H and Fereidoni S. Russ J Inorg Chem 2016; 61: 327.
31. Ghiasi R and Heydarbeighi A. Russ J Inorg Chem 2016; 61: 985.
32. Ghiasi R, Pasdar H and Irajizadeh F. J Chil Chem Soc 2015; 60: 2740.
33. Peikari A, Ghiasi R and Pasdar H. Russ J Phys Chem A 2015; 89: 250.
34. Fashami MZ and Ghiasi R. J Struct Chem 2015; 56: 1474.
35. Ghiasi R and Pasdar H. Russ J Phys Chem A 2013; 87: 973.
36. Ghiasi R and Boshak A. J Mex Chem Soc 2013; 57: 8.
37. Pasdar H and Ghiasi R. Main Group Chem 2009; 8: 143.
38. Ghiasi R, Saraf SH and Pasdar H. Monatsh Chem: Chem Mon 2018; 149: 2167.
39. Ghiasi R and Zamani A. J Chin Chem Soc 2017; 64: 1340.
40. Hammett L.P. J Am Chem Soc 1937; 59: 96.
41. Runge E and Gross EKU. Phys Rev Lett 1984; 52: 997.
42. Yang D, Yang Y and Liu Y. Comput Theor Chem 2012; 997.
43. Ganguly A, Paul BK, Ghosh S, et al. Comput Theor Chem 2016; 1095.
44. Bhattacharyya PK. Comput Theor Chem 2015; 1057.
45. Annaraj B, Pan S, Neelakantan MA, et al. Comput Theor Chem 2014; 1028.
46. Karaca S and Elmacı N. *Comput Theor Chem* 2011; 964.
47. Aguilera-Porta N, Granucci G, Munoz-Muriedas J, et al. *Comput Theor Chem* 2019; 1151.
48. Cui Y, Zhao H, Jiang L, et al. *Comput Theor Chem* 2015; 1074.
49. Fan G-H, Li X, Liu J-Y, et al. *Comput Theor Chem* 2014; 1030.
50. Kiani M, Ghiasi R, Pasdar H, et al. *J Mol Liq* 2020; 300: 112327.
51. Kiani M, Ghiasi R, Pasdar H, et al. *Russ J Phys Chem A* 2020; 94: 345.
52. Shalmani GG, Ghiasi R and Marjani A. *Chem Methodol* 2019; 3: 752.
53. Xie L-M, Bai F-Q, Li W, et al. *Phys Chem Chem Phys* 2015; 17: 10014.
54. Bai F-Q, Wang J, Xia B-H, et al. *Dalton Trans* 2012; 41: 8441.
55. Hansch C, Leo A and Taft RW. *Chem Rev* 1991; 91: 165.
56. Levine N. *Molecular spectroscopy*. New York: Wiley, 1975.
57. Bleeke JR, Xie Y-F, Peng W-J, et al. *J Am Chem Soc* 1989; 111: 4118.
58. Becke AD and Edgecombe KE. *J Chem Phys* 1990; 92: 5397.
59. Schmidt H-L and Becke AD. *J Mol Struct: Theochem* 2000; 527: 51.
60. Schmidt H-L and Becke AD. *J Chem Phys* 2002; 116: 3184.
61. Schmidt MW, Baldridge KK, Boatz JA, et al. *J Comput Chem* 1993; 14: 1347.
62. Poater J, Fradera X, Duran M, et al. *Chem Eur J* 2003; 9: 400.
63. Poater J, Duran M, Solà M, et al. *Chem Rev* 2005; 105: 3911.
64. Frisch MJ, Trucks GW, Schlegel HB, et al. *Gaussian 09, revision A.02*. Wallingford, CT: Gaussian, Inc., 2009.
65. Hariharan PC and Pople JA. *Theo Chim Acta* 1973; 28: 213.
66. Hariharan PC and Pople JA. *Mol Phys* 1974; 27: 209.
67. Hay PJ and Wadt WR. *J Chem Phys* 1985; 82: 299.
68. Hay PJ and Wadt WR. *J Chem Phys* 1985; 82: 284.
69. Schaefer A, Horn H and Ahlrichs R. *J Chem Phys* 1992; 97: 2571.
70. Hay PJ and Wadt WR. *J Chem Phys* 1985; 82: 270.
71. Adamo C and Barone V. *J Chem Phys* 1998; 108: 664.
72. Dunbar RC. *J Phys Chem A* 2002; 106: 7328.
73. Porembski M and Weisshaar JC. *J Phys Chem A* 2001; 105: 6655.
74. Porembski M and Weisshaar JC. *J Phys Chem A* 2001; 105: 4851.
75. Zhang Y, Guo Z and You X-Z. *J Am Chem Soc* 2001; 123: 9378.
76. Lu T and Chen F. *J Mol Graph Model* 2012; 38: 314.