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An Iridatropylium Cation: Investigation of Electronic Structure

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Abstract

A study of the $[C_6H_6Ir(PH_3)_3]^+$ iridatropylium cation structure based on frontier orbital analysis, thermodynamic analysis, and natural bond orbital (NBO) theory is the main aim of the present research. Also, HOMO, LUMO energies, hardness, electrophilicity and chemical potential were calculated. Structural analysis indicated the optimized geometry shows a good agreement with the experimental results in iridabenzene.The thermodynamic properties at different temperatures were calculated, revealing the correlations between standard heat capacity, standard entropy, standard enthalpy changes and temperature. Quantum theory of atoms in molecule analysis (QTAIM) was used for characterizing of Ir-P and Ir-c bonds.

Keywords: *Iridatropylium cation, Molecular orbital analysis, NBO analysis, Thermodynamic parameters, QTIAM analysis.*

Introduction

Metallatropyliums cations are seven-membered metallacycles analogous to tropylium cation for which one CH unit has been replaced by an isolobal transition-metal fragment. The suitable synthetic, structural, spectral, and reactivity data have been not reported about for them. We studied theoretically the solvent and substitution on the structure and properties of iridatropylium cations [1]. Aromaticity of the seven-membered rings has been carried out using density functional theory calculations with the B_3LYP functional [2-5]. Aromaticity of the rings include the $C_7H_7^+$ cation and its hetero derivatives by replacing C, CH or CC units by B, Al, Ga, Si, Ge, N, P, As and BN group, the B_8^{2-} dianion, the CB_{7-} anion, the neutral S_3N_4 ring and its derivatives by substituting one or

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two N atoms by CH group, the $S_4N_3^+$ cation and the all-metallic cycles M_7^{3-} and M_7T with M = Cu, Ag, Au and T = Y, Sc have been investigated [6]. The present work reports a computational study on $[C_6H_6Ir(PH_3)_3]^+$ iridatropylium cation. The structural parameters, molecular orbital, natural bond orbital have been analyzed. Also, theromdynamic parameters have been calculated in different temperatures.

Computational method

All calculations were carried out with the Gaussian 2003 suite of program [7] using the standard 6-311G(d,p) basis set [8-11] for C, H, and P atoms. For Ir element standard LANL2DZ basis set [12-14] is used and Ir described by effective core potential (ECP) of Wadt and Hay pseudopotential[15]with a double-ξ valance using the LANL2DZ. Geometry optimization was performed utilizing one parameter hybrid functional with modified Perdew-Wang exchange and correlation (mpw1pw91) [16]. A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum. The population analysis has also been performed by the natural bond orbital method [17] using the natural bond orbital (NBO) program [18] under Gaussian 2003 program package. The information of the MOs was evaluated by total, partial and overlap population density of states (DOS) using the GaussSum 3.0 [19]. The isotropic polarizability <α> is calculated as the mean value as given in the following equation [20]:

$$\langle\alpha\rangle = \frac{(\alpha_x + \alpha_y + \alpha_z)}{3}$$

and the polarizability anisotropy invariant is:

$$\Delta\alpha = \left[\frac{(\alpha_x - \alpha_y)^2 + (\alpha_y - \alpha_z)^2 + (\alpha_z - \alpha_x)^2}{2}\right]^{\frac{1}{2}}$$

Geometries were optimized at this level of theory without any symmetry constraints followed by the calculations of the first order hyperpolarizabilities. The total static first hyperpolarizability β was obtained from the relation:

$$\beta_t = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

upon calculating the individual static components:

$$\beta_i = \beta_{ii} + \frac{1}{3}\sum_{i \neq j}(\beta_i + \beta_j + \beta_j)$$

Due to the Kleinman symmetry[21]:

$$\beta_{xyy} = \beta_{yxy} = \beta_{yyx}\,;\ \beta_{yyz} = \beta_{yzy} = \beta_{zyy}, \ldots$$

one finally obtains the equation that has been employed:

$$\beta_t = \sqrt{(\beta_x + \beta_x + \beta_x)^2 + (\beta_y + \beta_y + \beta_y)^2 + (\beta_z + \beta_z + \beta_z)^2}$$

The AIM2000 program was used for topological analysis of electron density [22]. The following characteristics of ring critical points (RCPs) are taken into account: density at RCP ($\rho(r_c)$), its Laplacian ($\nabla^2(r_c)$), total electron energy density, H(ρ), kinetic energy density, G(ρ), and potential energy density, V(ρ).

Result and discussion

Molecular geometry

Figure 1 indicates the structure of $[C_6H_6Ir(PH_3)_3]^+$ iridatropylium cation. The absolute energy and dipole moment of the optimized molecule have been gathered in Table 1. The optimized structural parameters of iridatropylium cation are listed in Table 2 and the atom numbering scheme also given in Figure 1.

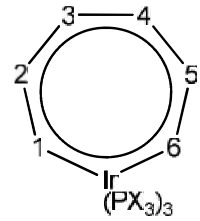


Figure 1. The structureof $[C_6H_6Ir(PH_3)_3]^+$ iridatropylium cation.

Table 1. Absolute energy, Zero point vibration energy, energy, Molar capacity at constant volume, Entropy, Dipole moment of iridatropylium cation.

Parameters			
Absolute energy (Hartree)	-1366.2818641		
Zero point vibration energy (Joules/Mol)	488760.0		
Rotational constants(GHZ)	0.94838	0.51798	0.43151
Rotational temperature (K)	0.04552	0.02486	0.02071
Energy (KCal/Mol)			
Translational	0.889		
Rotational	0.889		
Vibrational	167.891		
Total	169.668		
Molar capacity at constant volume (Cal/Mol-Kelvin)			
Translational	2.981		
Rotational	2.981		
Vibrational	49.104		
Total	55.066		
Entropy (Cal/Mol-Kelvin)			
Translational	43.642		
Rotational	31.695		
Vibrational	54.605		
Total	129.942		
Dipole moment (Debye)	4.1280		

Table 2. Structural parameters of iridatropylium (in Å).

X	Ir-C1	C1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-Ir	Ir-Peq	Ir-Peq	Ir-Pax
Gas	1.992	1.375	1.409	1.375	1.409	1.375	1.993	2.412	2.412	2.223

The selected bond distances of iridatropylium molecule in gas phase have been collected in Table 2. According to the theoretical results, three phosphine, and two carbon atoms form a square pyramidal environment around iridium. The M-C bond length are on the border between experimentally determined M-C (2.0-2.1 Å) and M=C (1.8-2.0 Å) bond lengths for iridabenzene. Although theoretical results are close to the experimental values [23] for the title molecule. The minor differences may due to the fact that the theoretical calculations were aimed at the isolated molecule in gaseous phase and the experimental results were aimed at the molecule in the solid state, the calculated geometric parameters also represents good approximation and they can be used as foundation to calculate the other parameters for the compound. On the other hand, these values show that Ir-P_{ax} bonds are shorter than Ir-P_{eq} bonds.

Analysis of frontier molecular orbitals (FMOs)

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor[24]. The MOs are defined as Eigen functions of the Fock operator, which exhibits the full symmetry of the nuclear point group, they necessarily form a basis for irreducible representations of full point-group symmetry. The energies of HOMO, LUMO, and their orbital energy gaps, have been gathered in Table 3.The pictorial illustration of the frontier molecular orbitals and their respective positive and negative regions are shown in Figure 2. Molecular orbitals, when viewed in a qualitative graphical representation, can provide insight into the nature of reactivity, and some of the structural and physical properties of molecules. The positive and negative phase is represented in gray and black color, respectively. The region of HOMO, LUMO levels spread over the Ir, PH3 and ring.

Global reactivity descriptors

Global reactivity descriptors[25-28] electronegativity (χ), chemical potential (μ), global hardness (η), global softness (S), and electrophilicity index (ω), determined on the basis of Koopman's theorem[29] are listed in Table 3.

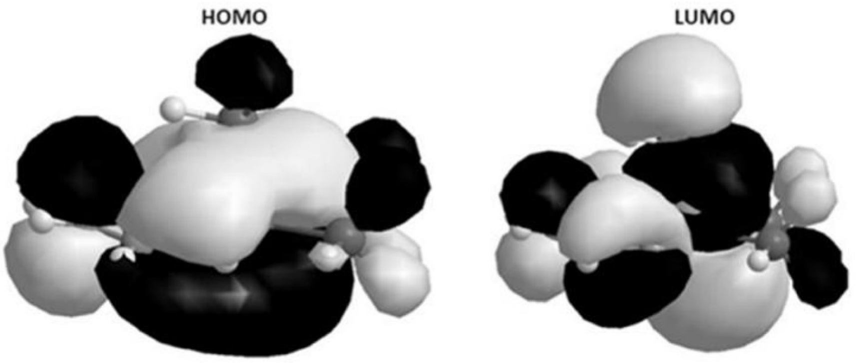
$$\eta=(E_{LUMO}-E_{HOMO})/2$$

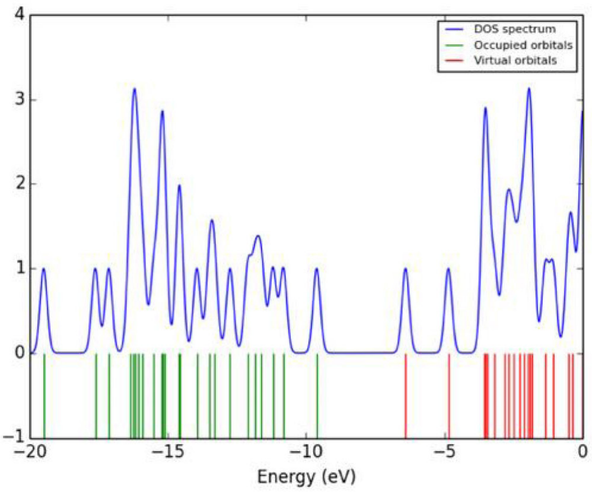
$$-\chi=\mu=(E_{HOMO}+E_{LUMO})/2$$

where I and A which are called ionization potential and electron affinity, respectively and is I = -E(HOMO) and A = - E(LUMO). The chemical hardness and softness of a molecule is a good indicator of the chemical stability of a molecule. From the HOMO–LUMO energy gap, one can find whether the molecule is hard or soft. The molecules having large energy gap are known as hard and molecules having a small energy gap are known as soft molecules. The soft molecules are more polarizable than the hard ones because they need small energy to excitation.

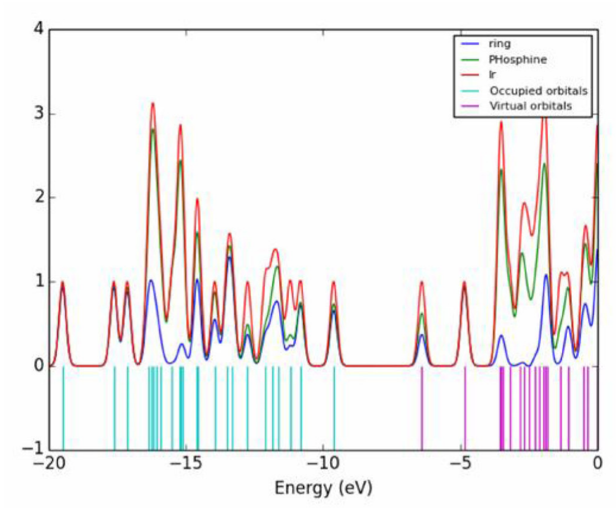
Table 3. The frontier orbitals energies (Hartree), HOMO-LUMO gap (eV), Hardness (eV), softness (eV^{-1}), chemical potential and electrophilicity of iridatropylium cation.

E(HOMO)	**E(LUMO)**	ΔE	η	**S**	ε	μ	ω
-0.35322	19.95072	-8.00552	0.622601	1.606165	3.212329	-0.23517	-0.35322

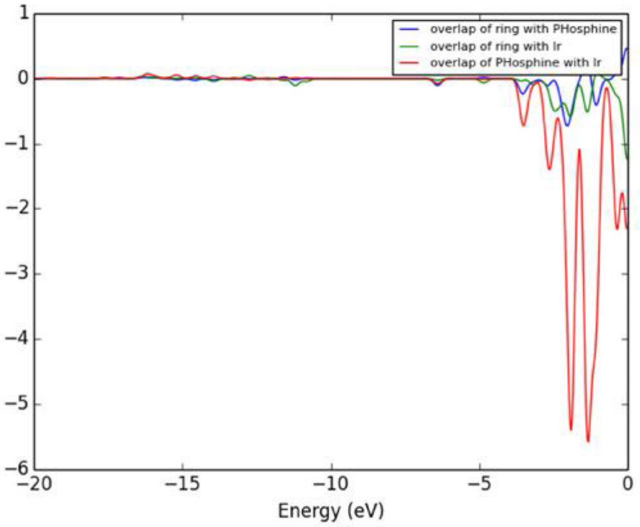




DOS



PDOS



COOP

Figure 2. Frontier molecular orbitals (MOs),DOS, PDOS and COOP diagrams of their idatropylium cation.

To understand the central features of bonding interactions of iridatropylium cation, we performed density of states of the total (TDOS), partial (PDOS), and crystal orbital overlap population (COOP). The DOS, PDOS, and COOP of studied molecules are presented in Figure 2. The PDOS essentially indicates the composition of the fragment orbitals contributing to the molecular orbitals. As clearly shown in this figure, the PDOS reveals that the HOMO and LUMO are fairly localized on Ir, phosphine and ring. The COOP illustrates the nonbonding, bonding and antibonding nature of the interaction of the two atoms, orbitals or groups. Zero value of the OPDOS indicates nonbonding interactions. The positive and negative values indicate the bonding and anti-bonding interaction. In addition, the COOP diagrams permit us to the resolve and comparison of the donor–acceptor features of the ligand and determine the bonding, non-bonding.

Temperature dependence of thermodynamic properties

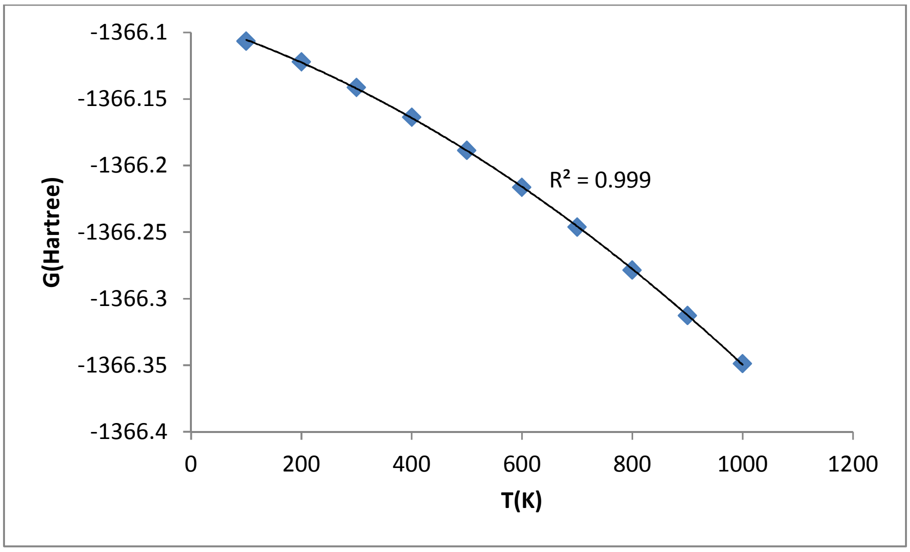
The thermodynamic parameters of iridatropylium cation have been tabulated in Tables 1 and 4. Also, the temperature dependence of the thermodynamic properties heat capacity at constant pressure (Cp), entropy (S) and enthalpy change for iridatropylium cation were also determined and listed in Table 4. Figure 3 depicts the correlation of heat capacity at constant pressure (Cp), entropy (S) and enthalpy change with temperature along with the correlation equations. From Table 4, one can find that the entropies, heat capacities, and enthalpy changes are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. These observed relations of the thermodynamic functions vs. temperatures were fitted by quadratic formulas, and the corresponding fitting regression factors (R^2) are all not less than 0.988. The corresponding fitting equations for iridatropylium cation are:

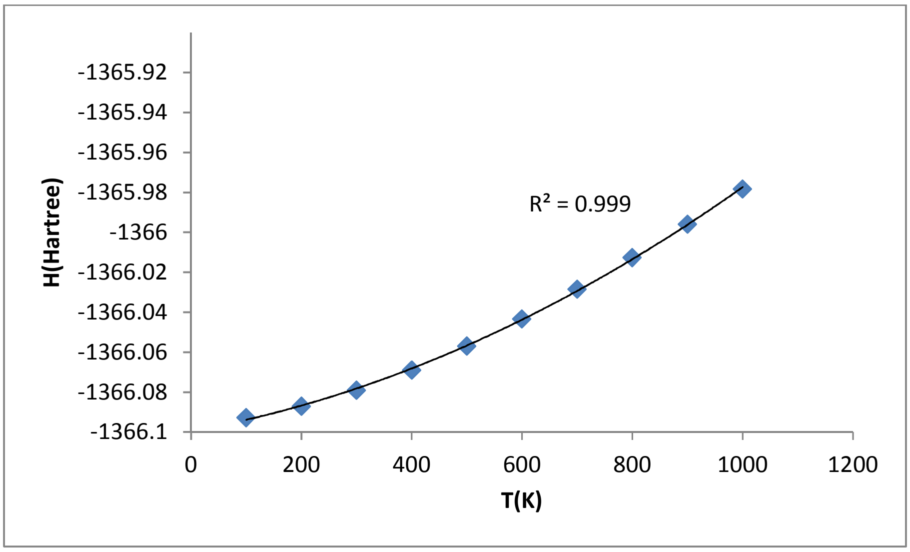
$G = -1\times10^{-7}\,T^2 - 1366.$

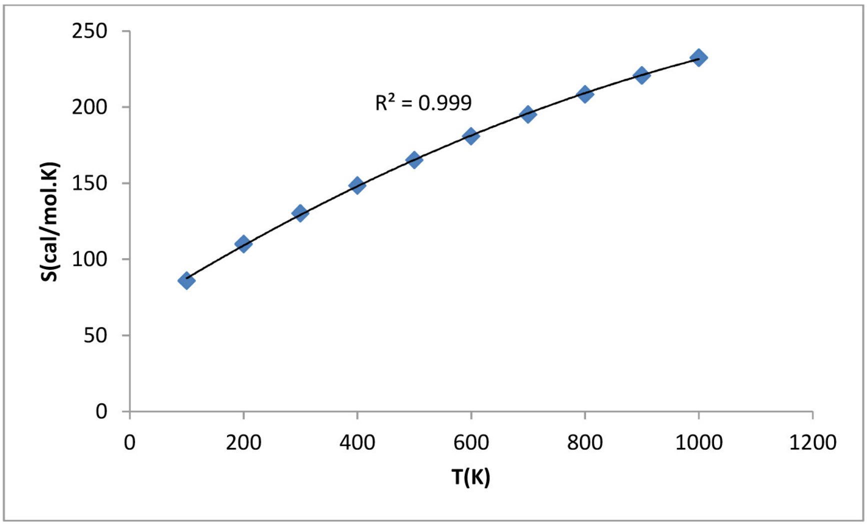
$H = 7\times 10^{-8}\,T^2 + 5\times 10^{-5}\;T - 1366.$

$S = -7\times 10^{-5}\,T^2 + 0.235\,T + 64.65$

$C_v = -7\times 10^{-5}\,T^2 + 0.173\,T + 9.677$







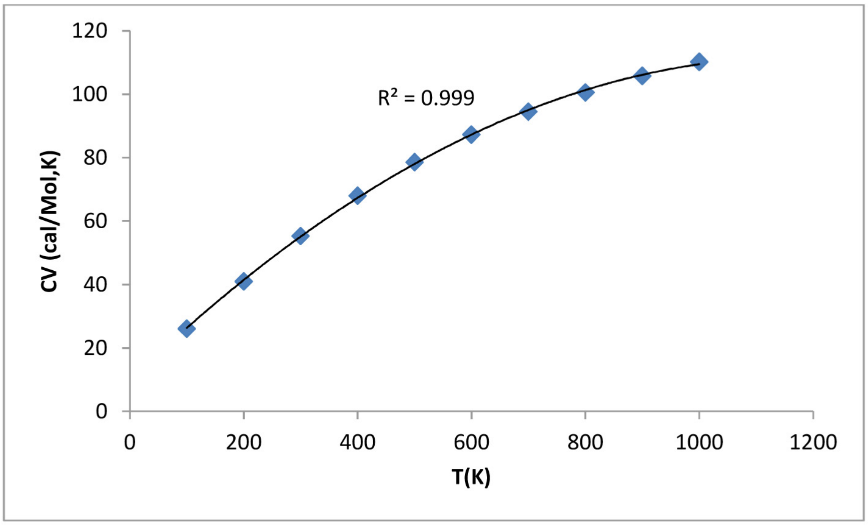


Figure 3. The correlation of heat capacity at constant pressure (Cp), entropy (S) and enthalpy change with temperature.

Table 4. The temperature dependence of thermodynamic parameters of iridatropylium cation.

T	G	H	S Cal/Mol-K	C_V Cal/Mol-Kelvin
100	-1366.106487	-1366.092781	86.003	26.145
200	-1366.122198	-1366.087102	110.118	41.033
300	-1366.141386	-1366.079095	130.294	55.320
400	-1366.163628	-1366.068923	148.570	68.017
500	-1366.188659	-1366.056898	165.362	78.573
600	-1366.216261	-1366.043346	180.843	87.261
700	-1366.246236	-1366.028530	195.161	94.500
800	-1366.278408	-1366.012654	208.454	100.604
900	-1366.312626	-1365.995881	220.845	105.789
1000	-1366.348754	-1365.978344	232.436	110.210

NBO analysis

The Natural Bond Orbital (NBO) analysis of iridatropylium cation has provided the detailed insight into the nature of electronic conjugation between the bonds in this molecule. Figure 4 collects the natural charges on atoms. The largest negative charges (-0.415 e) are located on two carbon atoms, C1 and C6. According to the NBO results, the electron configuration of Ir is: [core]6S(0.47)5d(8.34)6d(0.02)7p(0.02). Thus, 68 core electrons, 8.81 valence electrons (on 5d, and 6s atomic orbitals) and 0.04 Rydberg electrons (mainly on 6d and 7p orbitals) give the total of 76.85 electrons. This is consistent with the calculated natural charge on Ir atom in iridatropylium +0.16 e, which corresponds to the difference between 76.85e and the total number of electrons in the isolated Ir atom (77e).

Natural population analysis

The natural population analysis (NPA) was estimated in terms of natural atomic orbital occupancies. Figure 4indicate the molecular charge distribution on the skeletal atoms for iridatropylium cation. These partial charges distribution on the skeletal atoms reveals that the electrostatic repulsion or attraction between atoms can provide an important role to the intramolecular interaction. Of the carbon atoms in ring, the C2 and C3 atoms coordinated to iridium have larger negative charge (-0.410 e).

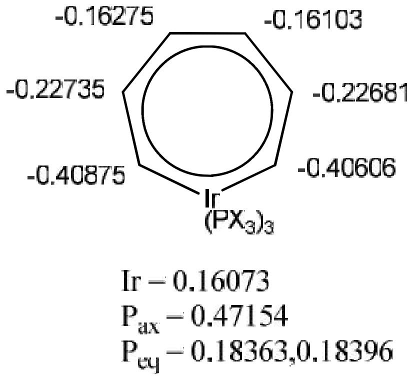


Figure 4. Distribution of NBO charges on the tile molecule.

According to calculations, the iridium atom forms single bonds with three phosphine ligands. NBO calculation show that σ(Ir–P) bonds are formed from $sp^{3.34}d^{0.02}$ and $sp^{3.12}d^{0.04}$ hybrids on equatorial and axial phosphine, respectively. The more contribution of p orbital in hybridation is compatible with lengthen of Ir-P_{eq} bond rather than Ir-P_{ax} bond.

QTAIM analysis

It has been proved, that the AIM-based analysis of electron density can provide valuable information on many physical and chemical properties of the molecular systems

[30-34]. It has been found for instance that the value of electron density (ρ) and its laplacian ($\nabla^2\rho$) estimated at bond critical point (BCP) of a given bond correlate very well with the strength of this bond, as well as with its length, since, as it is well known, both the strength and the length of a given bond are mutually dependent [35-39].

Table 5. Electron densities ρ (e/a_0^3), Laplacians $\nabla^2\rho$ (e/a_0^5), total electron energy density, H(ρ), kinetic energy density, G(ρ), and potential energy density, V(ρ) .

bond	ρ	$\nabla^2\rho$	G	H	V
Ir-C	0.1491	0.2017	0.1211	-0.0706	-0.1917
Ir-P_{ax}	0.1229	0.0673	0.0778	-0.0610	-0.1387
Ir-P_{eq}	0.0839	0.1643	0.0697	-0.0286	-0.0983

Additional valuable information on chemical bond properties is available from the total electron energy density, H(ρ), and its components; kinetic electron energy density, G(ρ), positive by definition, and potential electron energy density, V(ρ), negative by definition. The following relation is known for H(q) and its components [40, 41]:

$$H(\rho)= V(\rho)+ G(\rho)$$

It is known that in the region of the bond CP of weak closed-shell interatomic interactions the kinetic energy density dominates, with G(ρ) magnitude being slightly greater than the potential energy density |V(ρ)| which implies the total energy density H(ρ) > 0 and close to zero, whereas for strong covalent interactions V(ρ) dominates over the kinetic energy density and H(ρ) < 0. This is usually accompanied by $\nabla^2\rho> 0$ for the proper case and $\nabla^2\rho< 0$ for the latter one (there is one exception mentioned in the further part of the discussion). Both G(ρ) and |V(ρ)| values of Ir-C bond are more than Ir-P bonds. However, H(ρ) is invariably positive and very close to zero (Table 5).

$\nabla^2\rho$ values at corresponding BCPs are positive for Ir-P and Ir-C bonds, as it was found for closed-shell interactions. On the other hand, the H(ρ) values are negative, as found for shared interactions. This is in agreement with observations made for the Ti–C bonds in titanium complexes [41], in the case when the metal–ligand bonding has a characteristic that represents a mix of the closed-shell and shared parameters. The more ρ value of Ir-P_{ax} rather than Ir-P_{eq} explains lengthen of Ir-P_{eq} bond rather than Ir-P_{ax} bond.

Hyperpolarizability

Theoretical investigation plays a significant role in understanding the structure-property relationship, which is able to assist in designing novel NLO chormophores. The electrostatic first hyperpolarizability (β) and dipole moment (μ) of the iridatropylium cation have been calculated. From Table 6, it is found that iridatropylium cation show moderate μ.β value.

Table 6. β components and β_{tot} values (10^{-30} esu) for iridatropylium cation.

X	
β_{XXX}	447.7907299
β_{XXY}	-89.1221121
β_{XYY}	252.6907834
β_{YYY}	-71.5387583
β_{XXZ}	43.122429
β_{XYZ}	16.8760843
β_{YYZ}	-95.3657083
β_{XZZ}	303.9209604
β_{YZZ}	-99.2902049
β_{ZZZ}	91.0625307
β_{tot}	8.97003E-30
$\beta_{tot}\times10^{-30}$	8.97
$\mu.\ \beta_{tot}\times10^{-30}$	37.02

Conclusion

Attempts have been made in the present study for investigation of structure, molecular orbitals, thermodynamic parameters, and NBO analysis of iridatropylium cation. After thermodynamic parameters calculation, these calculated in various temperatures. Then relations of the thermodynamic functions vs. temperature were fitted by quadratic formulas. The Natural Bond Orbital (NBO) analysis provided the detailed insight into the type of hybridization and the nature of bonding in iridatropylium cation. NBO and QTAIM analyses have been used for explanation of the Lengthen of Ir-P_{eq} bond rather than Ir-P_{ax} bond. Hyperpolarizability value show a moderate NLO charter for title molecule. The QTAIM analysis indicates the mix of the closed-shell and shared parameters for Ir-C and Ir-P bonds.

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