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COMPUTATIONAL STUDY OF MOLECULAR STRUCTURE, ^{1}H NMR, ELECTRONIC SPECTRA, SOLVENT EFFECT AND PROPERTIES OF PLATINABENZENE

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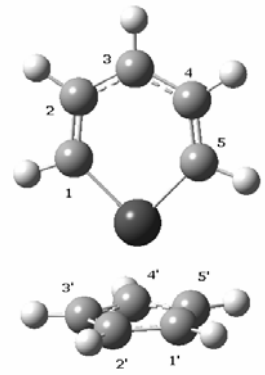
The structure and properties of platinabenzene were investigated by density functional theory method (mpw1pw91). The density of states (DOS) was beneficially used to analyze the main features of electronic structure. The influence of solvent on the structural parameters, frontier orbital energies and wavelength absorption maximum (λ_{max}) of this structure has been studied. Chemical shift values of protons have been calculated and compared with similar synthesized platinabenzene. The thermodynamic properties of the title compound at different temperatures were calculated. The results of atoms in molecules theory (AIM) and natural bond orbital (NBO) analysis have provided new insights into Pt–ligand bonding, the hybridization of atoms and the electronic structure of the title molecule.



INTRODUCTION

Metallabenzenes are six-membered metallacycles analogous to benzene that each CH unit has been replaced by an isolobal transition-metal fragment $\{ML_n\}$.[1-3] Many synthesis of metallabenzenes have been reported.[4] For example, when platinum incorporated into benzene the stable platinabenzene complexes formed. The first platinabenzene, $(C_5H_3Ph_2)Pt(\eta^5\text{-}C_5H_3Ph_2)$ was reported in 2002.[5] The formation of this complex as a stable product related to mutual stabilization of the η^5-bonded cyclopentadienyl ligand and the platinabenzene moiety.[3] The structure and properties of platinabenzenes have been studied experimentally and theoretically.[6-12]

From experimental and theoretical examinations one sees that the actual experimental knowledge concerning platinabenzenes compounds is still relatively limited due to the subtle nature of such compounds.

In the present study, we report the quantum chemical studies of the structure and properties of model platinabenzene, $Pt(C_5H_5)(\eta^5\text{-}C_5H_5)$. To have a superior rationalization on the title compound, we study the geometrical structure, aromaticity, and significant electronic properties like charges on the molecule, HOMO–LUMO energies and second order perturbation energies calculated by NBO/NLMO analysis. Also, the relations of thermodynamic functions vs. temperatures have been determined by quadratic formulas.

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COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian 03 suite of program.[13] The calculations of systems contain C, and H described by the standard 6-311G(d,p) basis set.[14-17] For Pt element standard LANL2DZ basis set[18-20] is used and Pt described by effective core potential (ECP) of Wadt and Hay pseudopotential[18] with a doublet-ξ valance using the LANL2DZ. Geometry optimization was performed utilizing with Modified Perdew-Wang Exchange and Correlation (mpw1pw91).[21] A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum.

For study of solvation effects, we have used a self-consistent reaction field (SCRF) approach, in particular using the polarizable continuum model (PCM).[22] By using this method, the geometry of the studied complex was re-optimized and the UV/Vis spectrum was calculated by DFT/TD-DFT with the same functionals and basis sets.

GaussSum 2.2.6.1 was used to prepare total density of state (TDOS) or density of state.[23] The population analysis has also been performed by the natural bond orbital method[24] using NBO program[25] under Gaussian 2003 program package.

Natural bond orbital analysis stresses on the role of intermolecular orbital interaction in the complex, particularly charge transfer. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic importance by second-order perturbation theory. For each donor NBO (i) and acceptor NBO (j), the stabilization energy $E^{(2)}$ associated with electron delocalization between donor and acceptor is estimated as:

$$E^{(2)}=-q_i\frac{(F_{i,j})^2}{\varepsilon_j-\varepsilon_i}$$

where q_i is the orbital occupancy, ε_i, ε_j are diagonal elements and $F_{i,j}$ is the off-diagonal NBO Fock matrix element.

The nucleus-independent chemical shift (NICS) index, based on the magnetic criterion of aromaticity, is probably the most widely used probe for examination of chemical compounds aromatic properties.[26] It is defined as the negative value of the absolute magnetic shielding. NICS values are calculated using the Gauge independent atomic orbital (GIAO) [27] method at the same method and basis sets for optimization.

The AIM2000 program[28] was used for topological analysis of electron density. The following characteristics of ring critical points (RCPs) are taken into account: density at RCP ($\rho(rc)$), its Laplacian ($\nabla^2\rho(r_c)$).

RESULT AND DISCUSSION

1. Energy

Fig. 1 shows the molecular structure and atomic numbering of platinabenzene molecule. The energies of platinabenzene in gas phase and in different media by using the PCM model are listed in Table 1. E_T is the total energy and ΔE_{solv} is the stabilization energy by solvents, the relative energy of the title compound in a solvent to that in the gas phase.

From Table 1, we can see that the calculated energy depends on the size of the dielectric constant of solvents. In the PCM model, the energies E_T decrease with increasing dielectric constants of solvents. On the other hand, ΔE_{solv} values indicate to increasing of stability in more polar solvents. This is because of a dipole in the molecule will induce a dipole in the medium, and the electric field applied to the solute by the solvent (reaction) dipole will in turn interact with the molecular dipole that leads to net stabilization. This suggests that the platinabenzene molecule has more stability in polar solvent rather than gas phase.

Table 1

Dielectric constants of solvents, Absolute energy (E, Hartree), solvent stabilization energies (ΔE_{solv}, kcal/mol), and dipole moment (μ, Debye) values for platinabenzene in different media by using the PCM model

	ε	E_T	ΔE_{solv}	μ
gas	-	-506.2135	-	1.062
n-pentane	1.84	-506.2192	-3.560	1.360
Cyclohexane	2.02	-506.2195	-3.793	1.428
Diethylamine	3.58	-506.2215	-5.055	1.673
Chloroform	4.90	-506.2223	-5.549	1.773
ChloroBenzene	5.62	-506.2228	-5.847	1.829
THF	7.58	-506.2234	-6.204	1.902
Iodoethane	7.62	-506.2234	-6.235	1.907
Dichloromethane	8.93	-506.2237	-6.417	1.941

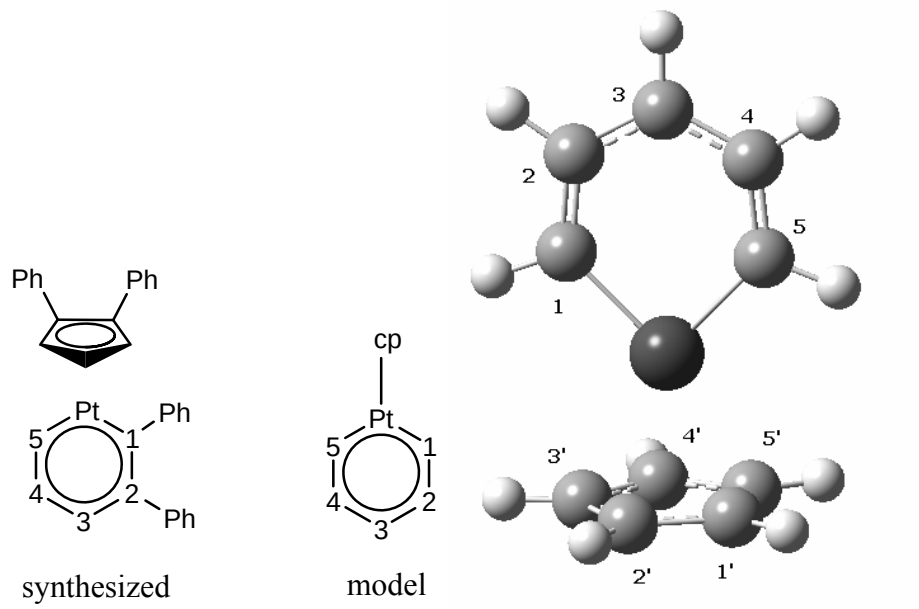


Fig. 1 – Structures synthesized and model platinabenzenes.

2. Dipole moment

Dipole moment values of platinabenzene molecule in gas phase and in different media by using the PCM model are listed in Table 1. These values show the solvent effect on the stabilization energy is in parallel with that on the dipole moment of the solute. A good linear relationship between the solvent stabilization energies and the dipole moments of platinabenzene molecule in the set of solvents is shown in Fig. 2. As a result, there is a larger dipole moment of solute, and the higher stabilization energy in the stronger solvent polarity.

3. Geometrical structure

The optimized structure of platinabenzene with numbering of the atoms is shown in Fig. 1. Table 2 compares the calculated bond lengths and angles for platinabenzene with those of experimentally available from X-ray data for synthesized platinabenzene. From the theoretical values we can find that most of the optimized bond lengths that are slightly larger than the experimental values at the calculated values using mpw1pw91 level, due to that the theoretical calculations belong to platinabenzene and isolated molecule in gaseous phase and the experimental results belong to molecule in solid state.

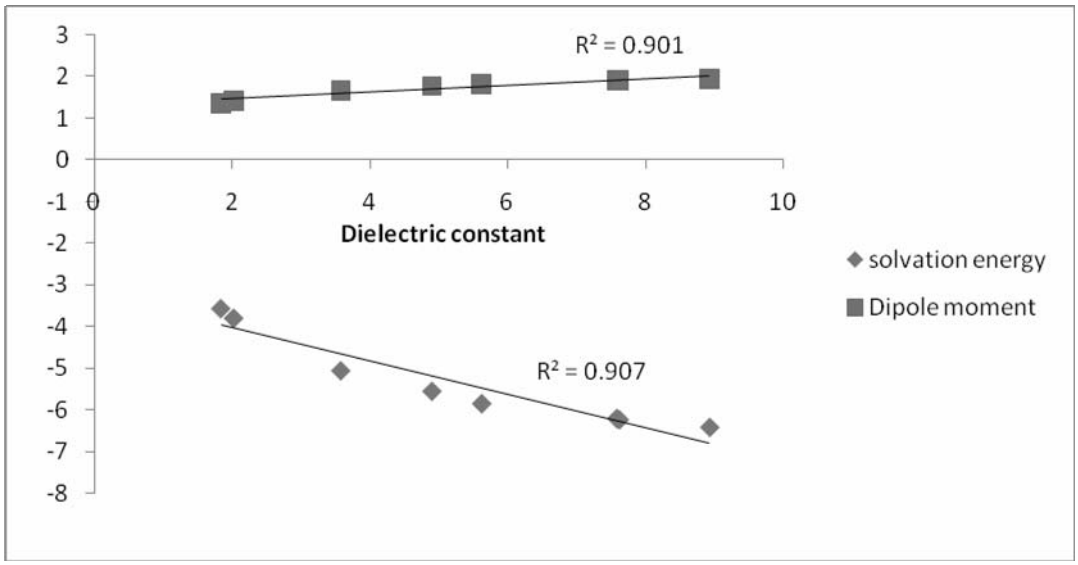


Fig. 2 – Linear correlation of dielectric constant and salvation energy and dipole moment in platinabenzene.

Table 2

Structure parameters for synthesized and model platinabenzene (in angstrom and degree)

bond	exp	gas	n-pentane	Cyclohexane	Diethylamine	Chloroform	ChloroBenzene	THF	Iodoethane	Dichloromethane
Pt-C1	1.959	1.930	1.931	1.932	1.933	1.933	1.933	1.934	1.934	1.934
C1-C2	1.387	1.376	1.377	1.377	1.377	1.377	1.378	1.378	1.378	1.378
C2-C3	1.395	1.393	1.393	1.393	1.394	1.394	1.394	1.394	1.394	1.394
C3-C4	1.381	1.393	1.393	1.393	1.394	1.394	1.394	1.394	1.394	1.394
C4-C5	1.364	1.376	1.377	1.377	1.377	1.377	1.378	1.378	1.378	1.378
C5-Pt	1.929	1.929	1.930	1.931	1.932	1.932	1.933	1.933	1.933	1.933
∠C5-Pt-C1	89.0	88.6	88.7	88.7	88.7	88.7	88.8	88.8	88.8	88.8
∠Pt-C1-C2	129.0	130.5	130.5	130.4	130.4	130.3	130.3	130.3	130.3	130.3
∠C1-C2-C3	122.6	123.6	123.6	123.7	123.7	123.7	123.7	123.7	123.8	123.7
∠C2-C3-C4	124.0	123.1	123.1	123.1	123.1	123.1	123.1	123.1	123.1	123.1
∠C3-C4-C5	124.1	123.5	123.6	123.6	123.7	123.7	123.7	123.7	123.7	123.7
∠C4-C5-Pt	130.0	130.6	130.5	130.5	130.4	130.4	130.4	130.4	130.4	130.4

The solvent polarity influences is well-known in both the structure and properties of conjugated organic molecules and metal complexes.[5, 29-31] The structural data for the optimized structures of platinabenzene in the eight studied solvents are gathered in Table 2. The results show that structural parameters are changed by polarity of surrounding media. These values indicate lengthening of Pt-C and CC bonds in the set of solvents rather than gas phase. Also, these values show that PtC and CC bond lengths increases with increasing of dielectric constant of solvent. On the other hand, CPtC, CCC, PtCC angles increase with increasing of dielectric constant of solvent.

4. Frontier orbital analysis

In addition, 3D plots of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of platinabenzene are shown in Fig. 3. The region of HOMO and LUMO levels spread over the entire molecule and calculated energy gap of HOMO–LUMO's explains the ultimate charge transfer interface within the molecule. According to calculation, the band gap energy (ΔE) (transition from HOMO to LUMO) of the molecule is about 3.738 eV, while for benzene is 7.18 eV. The highest occupied and the lowest unoccupied molecular orbitals are localized mainly on the both rings. On the other hand, the HOMO-1 molecular orbitals are localized mainly on six-membered ring.

Also, the inclusion of solvation effects leads to changes on the molecular orbital energies (Table 3). In solution, HOMO and LUMO are stabilized, with respect of corresponding values in vacuum. As seen from Table 3, gap of the HOMO-LUMO decreases in solution phase rather than vacuum. This gap decreases with increasing of dielectric constant of solvent.

To understand the central features of bonding interactions of compounds, we have performed the total density of states of (TDOS), partial (PDOS), and crystal orbital overlap population (COOP). The DOS, PDOS, and COOP of platinabenzene are sketched in Fig. 4.

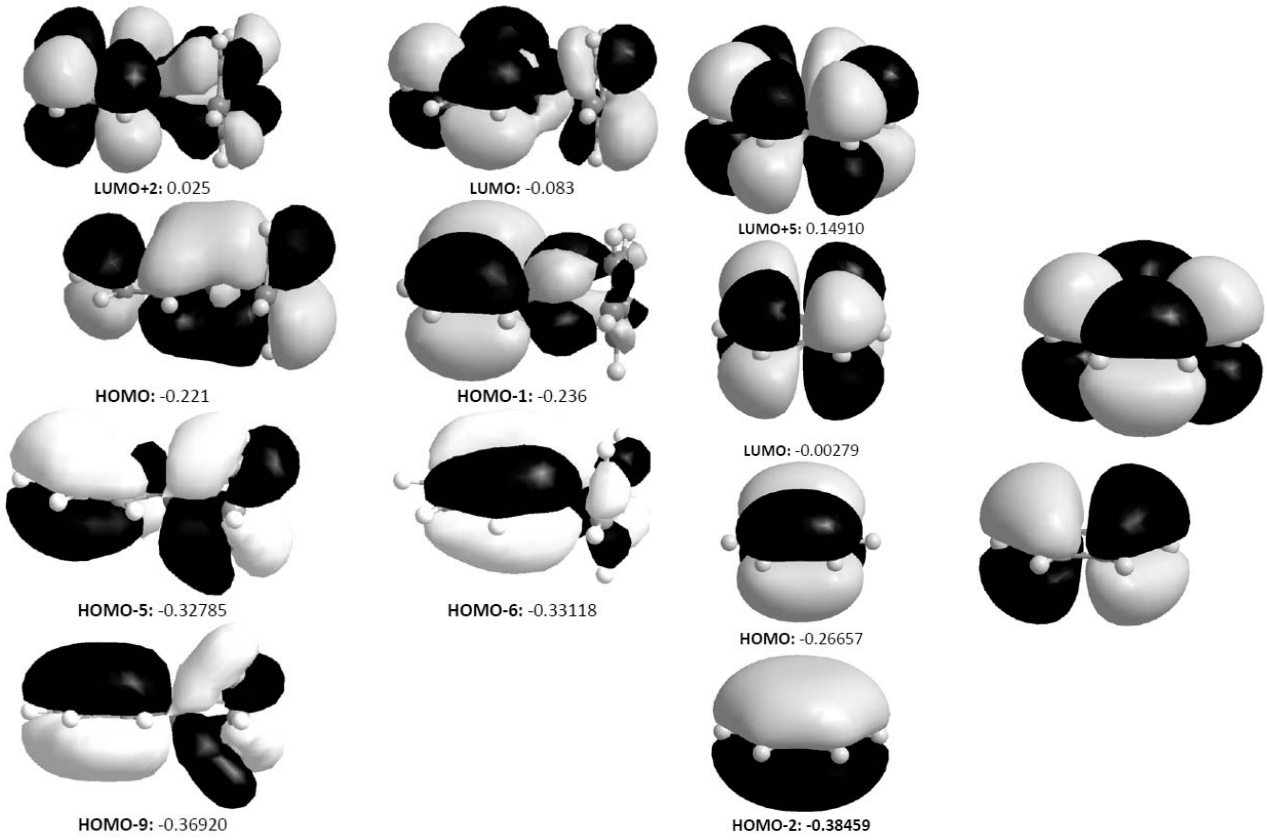


Fig. 3 – Molecular orbital plots of platinabenzene complexe and benzene.

Table 3

Frontier orbital energies (Hartree), HOMO-LUMO gap (ΔE, eV), Hardness (η, eV), chemical potential (μ, eV) and electrophilicity (ω, eV) of platinabenzene in different media by using the PCM model

	E(HOMO)	E(LUMO)	ΔE	η	μ	ω
gas	-0.2210	-0.0837	3.74	1.87	-4.15	4.60
n-pentane	-0.2227	-0.0859	3.72	1.86	-4.20	4.74
Cyclohexane	-0.2229	-0.0861	3.72	1.86	-4.20	4.75
Diethylamine	-0.2248	-0.0882	3.72	1.86	-4.26	4.88
Chloroform	-0.2256	-0.0891	3.72	1.86	-4.28	4.93
ChloroBenzene	-0.2261	-0.0896	3.71	1.86	-4.30	4.97
THF	-0.2268	-0.0903	3.71	1.86	-4.31	5.01
Iodoethane	-0.2268	-0.0904	3.71	1.86	-4.32	5.01
Dichloromethane	-0.2272	-0.0907	3.71	1.86	-4.32	5.04

The PDOS essentially indicates that composition of the fragment orbitals contribute to the molecular orbitals. As clearly shown in this figure, the PDOS reveals that the HOMO and LUMO are fairly localized on $(C_5H_5)Pt$ and with fewer contributions from Cp fragments.

The OPDOS illustrates nonbonding, bonding and antibonding nature of interaction between two atoms, orbitals or groups. Zero value of the OPDOS indicates that nonbonding interactions. The positive and negative values indicate that bonding and anti-bonding interaction. In addition, the OPDOS diagrams permit us to resolve and comparison of donor–acceptor features of the ligand and determine bonding, non-bonding.

5. IPs and EAs

The ionization potential (IP) and electron affinity (EA) are well defined properties that can be calculated by DFT to estimate electrons of the compounds. These values aim to get in detail rationalization of relationship between structure and electronic behavior of the molecule, in particular the response of molecule to formation of a hole, or to the addition of an electron, additional information is derived.

The calculations show that, the IP_a in molecule are 7.354 eV, and IP_v is from 7.463 eV. On the other hand, the EA_a and EA_v are 0.852 and 1.058 eV, respectively.

6. Electronic spectra

The most intensity electronic transition (λ_{max}) of platinebenzene calculated. The wavelength, oscillator strength and the composition of transitions obtained by TD-DFT calculations are gathered in Table 4. As seen from this table, the most intense electronic transition of molecules is attributed to HOMO→LUMO transition. Fig. 3 presents these transitions occur between molecular orbitals with the π-characteristics.

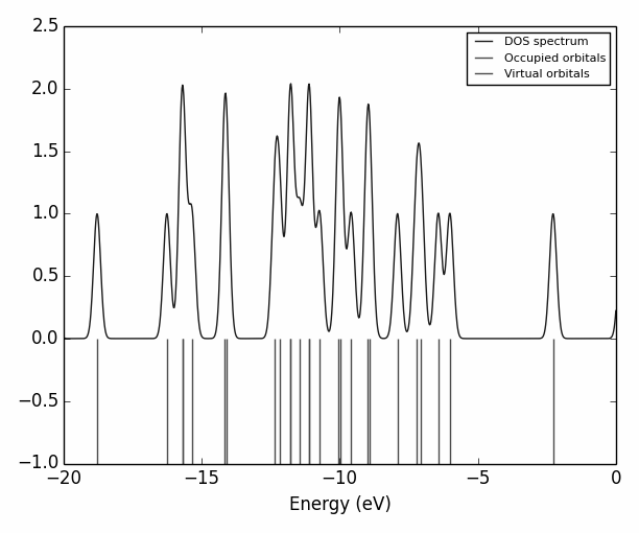
Inclusion of solvation effects leads also to changing on λ_{max} (Table 4). In solution, the λ_{max} is red-shifted with respect to corresponding values in vacuum.

7. ^{1}H NMR spectrum

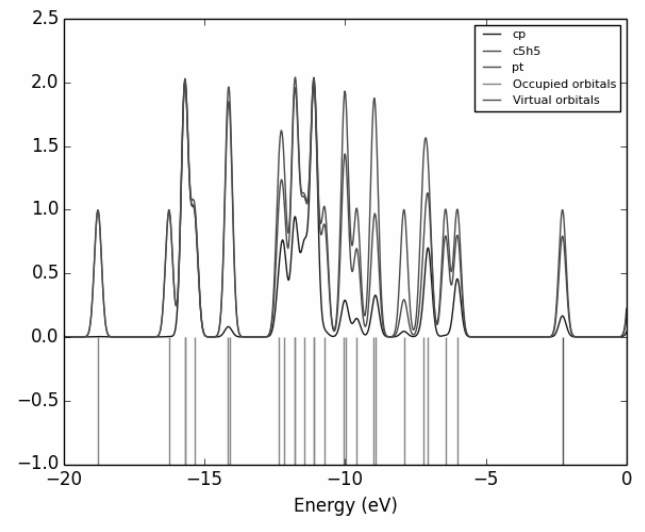
The chemical shift values of protons of platinabenzene obtained by GIAO methods. These values indicate that δ= 12.1, 7.4, and 7.1 ppm (respect to TMS). The value at δ=12.1 ppm is assignable to the proton in *ortho* position to Pt. the *para*-proton signal is at δ=7.1 ppm, while the meta-proton gives rise to a signal at δ=7.4 ppm. There is good compatibility between these values and experimental values in synthesized platinabenzene. The chemical shift values of synthesized platinabenzene are: δ= 12.8 (*ortho*), 8.2 (*para*), 7.4 (*meta*) ppm.

8. Nucleus independent chemical shift

NICS values of platinabenzene have been calculated in center and 0.5, 1.0, 1.5, and 2.0 Å above of the center of rings. These values are -3.31, -5.24, -6.69, -5.56, and -3.86 ppm, respectively. Therefore, platinabenznee exhibits the most negative NICS values above of the rings center. This is compatibles with π-aromaticity in these rings.



(a)



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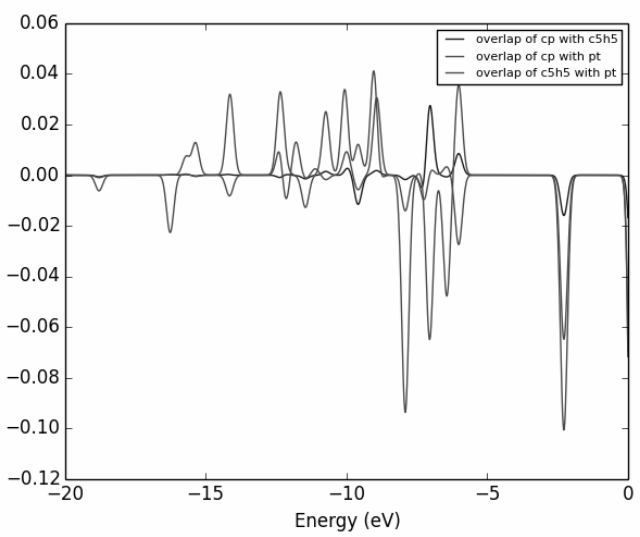

(c)

Fig. 4 – (a) The calculated total electronic density of states(DOS) diagrams, (b) the calculated partial electronic density of states diagrams (PDOS), and (c) crystal orbital overlap population (COOP) for the platinabenzene.

9. Thermodynamic properties

The energies and thermodynamic parameters of the compound have also been computed and are presented in Table 5. The frequency calculations compute the zero point energies, thermal correction to internal energy, enthalpy, Gibbs free energy and entropy as well as the heat capacity for a molecular system were listed in Table 5.

The temperature dependence of the thermodynamic properties heat capacity at constant pressure (Cp) and entropy (S) for platinabenzene were also determined and listed in Table 6. Fig. 5 depicts the correlation of heat capacity at constant pressure (Cp), entropy (S) and enthalpy change with temperature along with the correlation equations. From Table 6, 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. The corresponding fitting equations for platinabenzene are:

$$G = -1E\text{-}07\ T^2 - 0.0001T - 506.05;\ R^2 = 1$$

$$H = 7E\text{-}08T^2 + 3E\text{-}05T - 506.05;\ R^2 = 0.9994$$

$$S = -3E\text{-}05T^2 + 0.1598T + 58.528;\ R^2 = 1$$

$$Cv = -7E\text{-}05T^2 + 0.1598T - 1.4549;\ R^2 = 0.9988$$

10. Natural bond orbital analysis (NBO)

The Natural Bond Orbital (NBO) analysis of platinabenzene has provided the detailed insight into the nature of electronic conjugation between the bonds in this molecule. Table 7 collects the natural charges on atoms. The largest negative charges are located on two carbon atoms, C3' (-0.333) in Cp and C2, C4 (-0.326) in C_5H_5Pt ring.

According to the NBO results, the electron configuration of Pt is: [core] 6S(0.50) 5d(8.73) 6p(0.01) 6d(0.02) 7p(0.01). Thus, 68 core electrons, 9.23 valence electrons (on 5d and 6s atomic orbitals) and 0.04 Rydberg electrons (mainly on 6p, 6d and 7p orbitals) give the total of 77.27 electrons. This is consistent with the calculated natural charge on Pt atom in platinabenzene +0.73 e, which corresponds to the difference between 77.27e and the total number of electrons in the isolated Pt atom (78 e).

Table 4

Maximum Absorption wavelength (λ_{max},nm),
and Oscillator strength (f) for platinebenzene in different media by using the PCM model

	attributed	λ_{max}	f
gas	HOMO→LUMO	374.74	0.2472
n-pentane	HOMO→LUMO	385.46	0.3299
Cyclohexane	HOMO→LUMO	386.65	0.3425
Diethylamine	HOMO→LUMO	386.42	0.3362
Chloroform	HOMO→LUMO	387.67	0.3470
ChloroBenzene	HOMO→LUMO	389.25	0.3602
THF	HOMO→LUMO	386.96	0.3402
Iodoethane	HOMO→LUMO	389.13	0.3587
Dichloromethane	HOMO→LUMO	387.38	0.3438

Table 5

SCF energy, total energy, the zero point energies, vibrational energy,
thermal correction to internal energy, enthalpy, Gibbs free energy and entropy as well as the heat capacity for platinabenzene

SCF energy (a.u.)	-506.213
Total energy (thermal), E_{total} (kcal mol^{-1})	110.954
Zero-point vibrational energy, E0 (kcal mol^{-1})	104.670
Vibrational energy, E_{vib} (kcal mol^{-1})	109.176

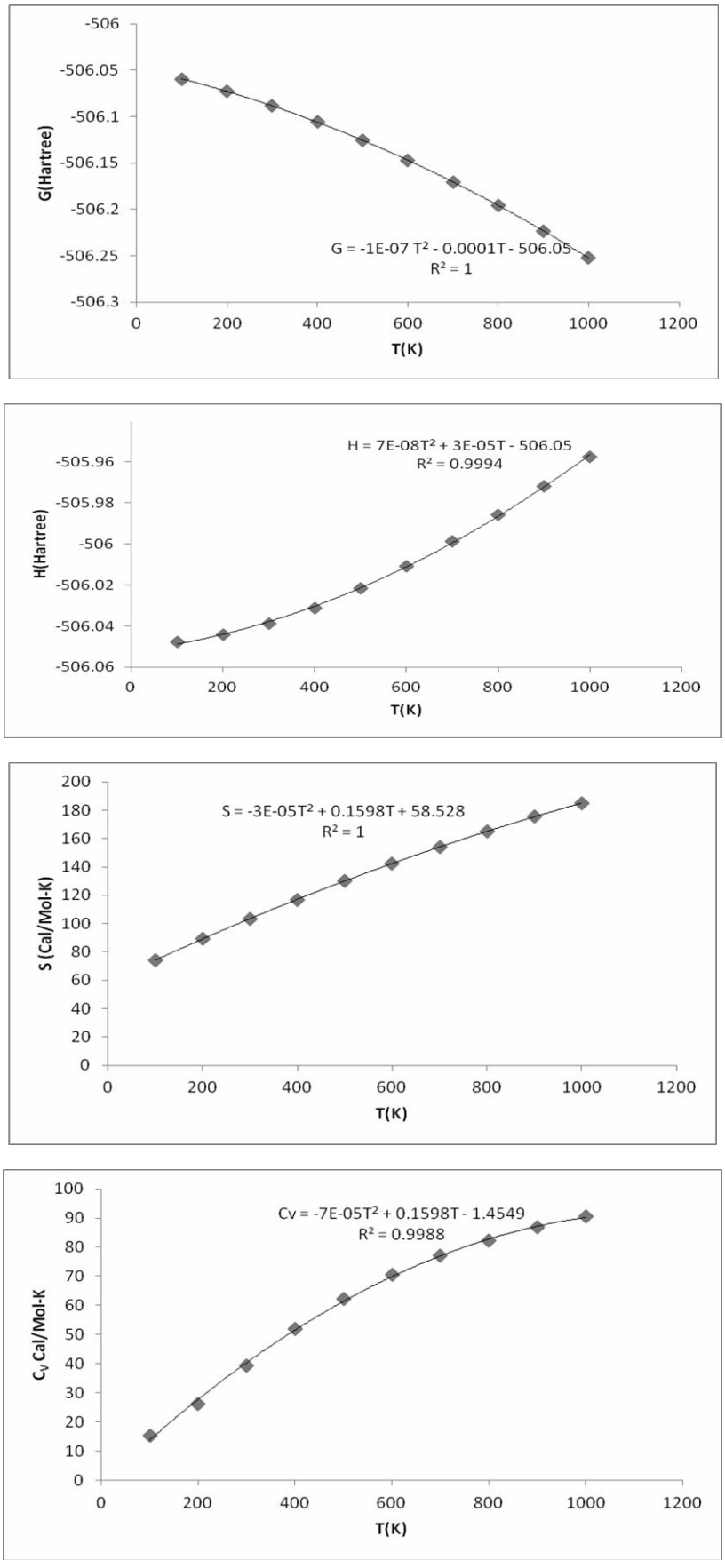

Fig. 5 – Variations of thermodynamic parameters and temperature for platinabenzene.

Table 6

Thermodynamic parameters in different temperature for platinabenzene

T(K)	G	H	S Cal/Mol-K	C_V Cal/Mol-Kelvin
100	-506.060	-506.048	74.226	15.255
200	-506.073	-506.044	89.360	26.102
300	-506.088	-506.039	103.207	39.295
400	-506.106	-506.031	116.856	51.918
500	-506.125	-506.022	130.046	62.313
600	-506.147	-506.011	142.523	70.514
700	-506.171	-505.999	154.207	77.034
800	-506.196	-505.986	165.117	82.338
900	-506.223	-505.972	175.311	86.746
1000	-506.252	-505.957	184.858	90.468

Table 7

The NBO atomic charges of platinabenzene

Atom	Pt	C1'	C2'	C3'	C4'	C5'	C1	C2	C3	C4	C5
q	0.745	-0.287	-0.319	-0.333	-0.287	-0.319	-0.2920	-0.326	-0.097	-0.326	-0.301

Table 8

Occupancy of natural orbitals (NBOs) and hybrids of platinabenzene

NBO	occupancy	Hybride
σ(Pt-C5)	1.889	0.6219 Pt sd 1.07+ 0.7831 C 5 sp 2.36
σ(Pt-C1)	1.888	0.6222Pt sd 1.06+ 0.7829 C1 sp 2.36
π(Pt-C1)	1.809	0.9012Pt p 1.00 d99.99(99.95%) + 0.4334 C 1 p 1.00
σ(C1 – C2)	1.984	0.6925 C 1 sp 1.44+ 0.7215 C 2 sp1.68
σ (C2 – C3)	1.979	0.7079 C 2 sp 1.80 + 0.7063 C 3 sp1.72
π (C2 – C3)	1.620	0.7542 C 2 p 1.00+ 0.6567 C 3 p 1.00
σ(C3 – C4)	1.979	0.7061 C 3 sp 1.73+ 0.7082 C 4 sp 1.80
σ (C 4 - C 5)	1.984	0.6929 C 4 sp 1.44+ 0.7210 C 5 sp1.69
π (C 4 - C 5)	1.688	0.6547 C 4 p 1.00 + 0.7559* C 5p 1.00

Table 9

The theoretical bond lengths (Å) 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) at critical points for platinabenzene

	r	ρ	$\nabla^2\rho$	G	-H	-V
Pt-C1	1.930	0.168	0.219	0.140	0.085	0.224
C1-C2	1.376	0.318	-0.913	0.109	0.337	0.447
C2-C3	1.393	0.309	-0.880	0.099	0.319	0.418
C3-C4	1.393	0.309	-0.880	0.099	0.319	0.418
C4-C5	1.376	0.318	-0.914	0.109	0.338	0.447
C5-Pt	1.929	0.168	0.219	0.140	0.085	0.225
Pt-C3'	2.360	0.065	0.195	0.064	0.015	0.079
Pt-C4'	2.362	0.066	0.186	0.063	0.016	0.079
Pt-C5'	2.357	0.066	0.191	0.064	0.016	0.079
Pt-C1'	2.357	0.066	0.191	0.064	0.016	0.079
Pt-C2'	2.362	0.066	0.186	0.063	0.016	0.079

Table 8 lists the calculated occupancies of natural orbitals. Three classes of NBOs are included, the Lewis-type (σ and π bonding or lone pair) orbitals, the valence non-Lewis (acceptors, formally unfilled) orbitals and the Rydberg NBOs, which originate from orbitals outside the atomic

valence shell. The calculated natural hybrids on atoms are also given in this table.

In the NBO method, delocalization of electron density (ED) between occupied Lewis-type orbitals and formally unoccupied (antibonding or Rydberg) non-Lewis NBOs corresponds to a stabilizing donor–acceptor interaction. The strength of this interaction can be estimated by the second order perturbation theory. Thus, the results obtained from NBO analysis provide convenient basis for investigating conjugative interactions in molecular systems.

According to calculations, the Pt atom forms a single bond (sigma bond) and a double bond (σ and π bonds) with two carbon atoms C5 and C1 atoms, respectively. As follows from Table 8, the σ(Pt–C5) bond is formed from an $sd^{1.07}$ hybrid on Pt (which is the mixture of 48.51% s, 0.05% p and 51.44% d atomic orbitals). On the other hand, σ(Pt–C1) bond is formed from an $sd^{1.06}$ hybrid on Pt (which is the mixture of 48.35% s, 0.04% p and 51.61% d atomic orbitals). The π(Pt–C1) bond is formed from a $pd^{99.99}$ hybrid on Pt (which is the mixture of 0.05% p and 99.95% d atomic orbitals).

11. AIM Analysis

The molecular graph of platinabenzene showed that there was a bond critical point (BCP) located at the midpoint between Pt and C1, C2 atoms, and two bonds paths linked the BCP to the two Pt atoms; the topology structures confirmed the presence of the Pt-C bond. Table 9 gives the topological data for platinabenzene (taken from the BCP calculations for the Pt-C bond), including the electron density ρ(r) values, the Laplacian of the electron density $\nabla^2\rho(r)$, and the total energy density H_c (the sum of the Lagrangian kinetic density G_c and the virial energy density V_c). The ρ(r) and $\nabla^2\rho(r)$ values for the Pt-C bonds at the BCP were 0.168 and 0.219 au, respectively; the G_c, $-V_c$, and $-H_c$ values for the Pt-C bonds were 0.140, 0.085, and 0.224 au, respectively. The positive $\nabla^2\rho(r)$, negative H_c, and the G_c/V_c ratio all revealed that the Pt-C bond belonged to partially covalent interactions.

CONCLUSIONS

The structure and properties of platinabenzene have been investigated theoretically. The molecular orbital analysis and solvent effects, thermodynamic properties of the title compound were performed on the basis of DFT calculations. The consistency between the calculated and structural data indicates that the used level can generates reliable geometry and related properties of the title compound. NICS calculation shows that platinabenzene has π-aromaticity. Thermodynamic properties in the range from 100 to 1000 K are obtained. The gradients of C_V, H and S to the temperature increases. But, that of G decreases, as the temperature increases. The molecular structure of platinabenzene calculated by the mpw1pw91 density functional method shows Pt-C(Cp) bond lengths are larger than Pt-C_{ring}. The atoms in molecules analysis indicate the metal–ligand bonding has a characteristic that represents a mix of the closed-shell and shared parameters. The Natural Bond Orbital (NBO) analysis has provided the detailed insight into the type of hybridization and the nature of bonding in platinabenzene.

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