

# The Rhodathiabenzene and Rhodaoxabenzene: Structure and Bonding and Density Functional Calculations

Reza Ghiasi,<sup>1,\*</sup> and Mozhddeh Abdoli<sup>2</sup>

<sup>1</sup> Department of Chemistry, East Tehran Branch, Islamic Azad University, Qiam Dasht, Tehran, Iran.

rezaghiasi1353@yahoo.com

<sup>2</sup> Department of Chemistry, Saveh Branch, Islamic Azad University, Saveh, Iran.

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**Abstract.** The electronic structure and properties of the rhodathiabenzene and rhodaoxabenzene isomers have been investigated using the hybrid density functional mpw1pw91 theory. The energetic aspect shows that I-isomer is the most stable isomer. Molecular orbital analysis shows linear correlation between hardness and anisotropic polarizability values of rhodaoxabenzene isomers. These calculations indicate a linear relation between  $\Sigma BO_R$  (sum of Wiberg indices in ring) and relative energy for rhodathiabenzene. The atoms in molecule analysis indicates a correlation between  $r(\text{Rh-X}; \text{X}=\text{C}, \text{S}, \text{P}, \text{O})$  bonds and the electron density of bond critical point in all species.

**Key words:** Metallabenzenes, Rhodaoxabenzene, Rhodathiabenzene, Quantum theory atoms in molecules (QTAIM), Wiberg bond index.

**Resumen.** Se han investigado la estructura electrónica y propiedades de isómeros del rodatiabenceno y del rodaoxabenceno usando el funcional híbrido mPW1PW91. El aspecto energético muestra que el isómero-I es el más estable. El análisis de orbitales moleculares muestra una correlación lineal entre la dureza y la anisotropía de la polarizabilidad de los isómeros del rodaoxabenceno. Estos cálculos indican una relación lineal entre  $\Sigma BO_R$  (la suma de los índices de Wiberg en el anillo) y la energía relativa para el rodatiabenceno. El análisis de átomos en moléculas indica una correlación entre las distancias de enlace  $r(\text{Rh-X}; \text{X}=\text{C}, \text{S}, \text{P}, \text{O})$  y la densidad electrónica en el punto crítico de enlace de todas las especies.

**Palabras clave:** Metalbencenos, rodaoxabenceno, rodatiabenceno, teoría cuántica de átomos en moléculas (QTAIM), índice de enlace de Wiberg.

## Introduction

Metallabenzenes are organic/transition-metal “hybrids” which own aromatic properties. They have been shown to reveal many similarities to heterobenzenes: downfield chemical shifts for ring protons, planarity of the six membered metallacycle, no alternation of bond lengths, and even electrophilic aromatic substitution [1-11]. There is now an extensive amount of relevant synthetic, structural, spectral, computational, and reactivity data for metallabenzenes. Chen *et al.* [12] and Bianchini *et al.* [13, 14] have independently synthesized iridathiabenzene via insertion of iridium into C-S bonds of thiophene. The rhodium analogue has been similarly generated in a thiophene ring-opening reaction [15]. As with other 4d transition metals, uncoordinated rhodabenzene is probably unstable. The inability to isolate a rhodabenzene is congruent with the DFT calculations reported by van der Boom, Martin, and co-workers [16].

In the present study, the stability, geometries and properties of Rhodaoxabenzene, and Rhodathiabenzene isomers are investigated theoretically. The analysis of quantum theory atoms in molecules has been used for providing valuable information on bonding characters.

## Computational Method

All calculations were carried out with the Gaussian 2003 suite of program [17] using the standard 6-31G(d,p) basis set calculations of systems contain C, H, O, S and P (Method 1) [18, 19]. Also, for calculation of polarizability and hyperpolariz-

ability values 6-311+G(d,p) basis has been used (Method 2) [20].

For Rh element standard LANL2DZ basis set [21-23] are used and Rh described by effective core potential (ECP) of Wadt and Hay pseudopotential [24] with a doublet- $\xi$  valence using the LANL2DZ. Geometry optimization was performed utilizing one parameter hybrid functional with modified Perdew-Wang exchange and correlation (mpw1pw91) [25]. A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum.

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  $\beta$  was obtained from the relation (equation 1):

$$\beta_{\text{tot}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (1)$$

upon calculating the individual static components (equation 2)

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (2)$$

Due to the Kleinman symmetry (equation 3) [26]:

$$\beta_{xyy} = \beta_{yxy} = \beta_{yyx}; \beta_{yyz} = \beta_{zyy} = \beta_{zyz}, \dots \quad (3)$$

one finally obtains the equation that has been employed (equation 4):

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (4)$$

The isotropic polarizability  $\langle\alpha\rangle$  is calculated as the mean value as given in the following equation [27]:

$$\langle\alpha\rangle = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (5)$$

and the polarizability anisotropy invariant is:

$$\Delta\alpha = \left[ \frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{2} \right]^{\frac{1}{2}} \quad (6)$$

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

## Result and Discussion

### Energetic criteria

Absolute energy and relative energy values of the heterocyclic rhodabenzene (Fig. 1) are presented in Table 1. The relative energies values show that stability of the possible isomers decrease in the following trend:

$$\text{I} > \text{V} > \text{III} > \text{IV} > \text{II}$$

This trend shows that I- isomers are more stable than other isomers.

### Polarizability

Polarizabilities describe the response of a system in an applied electric field [30]. They determine not only the strength of molecular interactions (such as the long range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the non-linear optical properties of the system [31].

The calculated isotropic and anisotropy polarizability values indicate these values decrease when heteroatom is X=O

**Table 1.** Absolute energy (Hartree), relative energy (kcal/mol), electron densities  $\rho(\text{e}/\text{a}_0^3)$  and Laplacians  $\nabla^2\rho$  ( $\text{e}/\text{a}_0^3$ ) values at the ring critical point for Rhodaoxabenzene and Rhodathiabenzene isomers.

	E	$\Delta E$	$\rho(3,+1)$	$\nabla^2\rho$
			X=O	
I	-1424.638	0.00	0.014465	0.081791
II	-1424.582	35.55	0.017816	0.110183
III	-1424.604	21.50	0.016930	0.101254
IV	-1424.582	35.51	0.017885	0.110644
V	-1424.631	4.67	0.014844	0.085764
			X=S	
I	-1747.652	0.00	0.012521	0.066212
II	-1747.582	43.64	0.013485	0.076203
III	-1747.598	33.72	0.012399	0.064717
IV	-1747.581	44.33	0.013602	0.076994
V	-1747.645	4.27	0.012777	0.069383

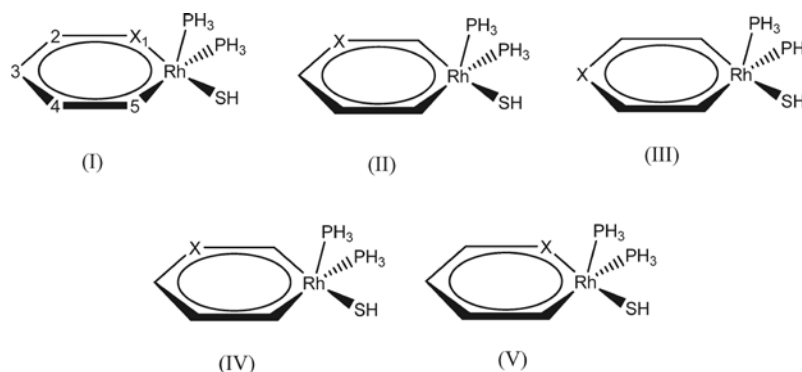
(Table 2). Thus, the larger isotropic polarizability of X=S rings resulting in the stronger response of external field.

It is well known that a general characteristic required for basis sets to perform well for polarizability calculations is that they should contain diffuse functions (Method 2) [32, 33]. These values are more than method 1. Again, the calculated isotropic and anisotropy polarizability values are more in X=S rings (Table 2).

### Molecular structural parameters

The selected structural parameters have been gathered for rhodaoxabenzene and rhodathiabenzene isomers in Table 3. These values show that Rh-C, RhS,  $\text{RhP}_{\text{apical}}$ , and  $\text{RhP}_{\text{basal}}$  bond lengths are compatible with experimental data for similar compounds [15, 16]. These bond lengths are indicative of structural aromaticity. The structural analysis in I-isomer (most stable isomer) shows that:

*Rh-P distances:* Rh-P<sub>basal</sub> bonds are larger than Rh-P<sub>apical</sub> bonds.



**Fig. 1.** The geometric structure of rhodathiabenzene and rhodaoxabenzene isomers.

**Table 2.** Anisotropic and isotropic polarizability values (in Debye. Å) for Rhodaoxabenzene and Rhodathiabenzene isomers.

Method 1					
X	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{isotropic}$	$\alpha_{anisotropic}$
X=O					
I	203.583	150.291	106.023	153.30	84.61
II	209.769	150.452	118.120	159.45	80.51
III	195.924	150.798	108.182	151.63	76.00
IV	207.454	149.636	119.538	158.88	77.39
V	230.250	153.956	110.545	164.92	104.96
X=S					
I	226.241	169.426	112.655	169.44	98.37
II	237.990	166.114	121.091	175.07	102.12
III	230.496	162.415	110.817	167.91	103.97
IV	234.260	167.803	122.234	174.77	97.58
V	238.970	170.007	115.426	174.80	107.23
Method 2					
X	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{isotropic}$	$\alpha_{anisotropic}$
X=O					
I	224.274	167.054	126.189	172.51	85.34
II	232.315	170.761	136.477	179.85	84.11
III	214.232	167.619	126.113	169.32	76.36
IV	229.435	170.056	137.459	178.98	80.77
V	251.161	172.287	130.537	184.66	106.10
X=S					
I	246.054	188.183	133.529	189.26	97.46
II	261.723	186.528	140.417	196.22	106.06
III	251.363	180.353	131.951	187.89	104.03
IV	257.249	189.351	141.621	196.07	100.64
V	258.057	188.832	136.044	194.31	105.99

*Rh-S distances:* The Rh-S bond (2.31 Å) is shorter than Rh-SH (2.41 Å). These trends reveal important  $\pi$ -bonding between these ring atoms.

*CC distances:* the CC bond distances analysis presents the C2-C3 bond is shorter than C3-C4 bond. This shows that resonance structure (II) has a greater contribution to the bonding picture (Fig. 2).

### Wiberg bond index matrix in the NAO basis

Wiberg indices are electronic parameters related to the electron density between atoms. They can be obtained from a natural population analysis and provide an indication of the bond strength [34]. These values have been computed for rings atoms (Table 4). The bond delocalization can also be found from the calculated bond indices. The C-C bond indices are comparable to the calculated those for benzene (1.462).

The bond indices of Rh-C single, and double bond are got from the results of calculated model complexes *trans*-[Rh(SH)<sub>2</sub>(CH<sub>3</sub>)(PH<sub>3</sub>)<sub>2</sub>] and *trans*-[Rh(SH)<sub>2</sub>(=CH<sub>2</sub>)(PH<sub>3</sub>)<sub>2</sub>]<sup>-</sup>

which are optimized at mpw1pw91 level and using the same basis sets as the context. The Rh-C5 bond indexes are intermediate between calculated Rh-C single and double bond indices (X=O: 0.595 and 1.194; X=S: 0.5689 and 1.174, respectively).

These values indicated good linear relation between  $\Sigma B O_R$  with relative energy for rhodathiabenzene (Fig. 3).

### Frontier orbital energies and chemical hardness

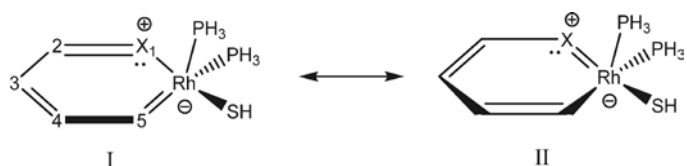
The frontier orbital energies, HOMO-LUMO gap energy, hardness, chemical potential, and electrophilicity of all complexes computed are given in the Table 5. To evaluate the hardness and chemical potential of these complexes, these values can be calculated from the HOMO and LUMO orbital energies using the following approximate expressions:

$$\mu = -\frac{E_{HOMO} + E_{LUMO}}{2} \quad (7)$$

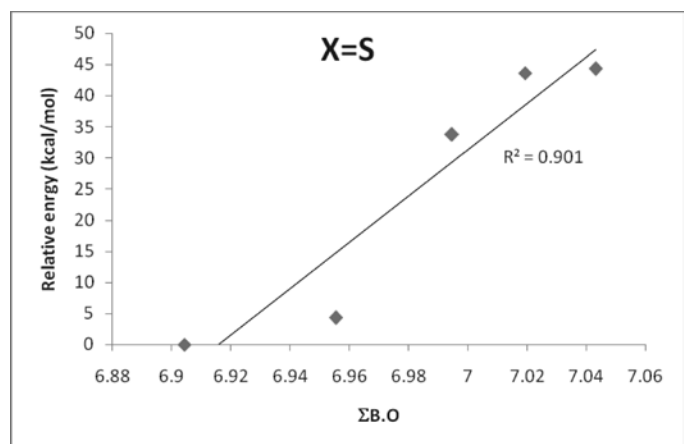
$$\eta = -\frac{E_{LUMO} - E_{HOMO}}{2} \quad (8)$$

Where  $\mu$  is the chemical potential (the negative of the electronegativity), and  $\eta$  is the hardness [35, 36]. To evaluate the electrophilicity of these complexes, we have calculated the electrophilicity index,  $\omega$ , for each complex measured according to Parr, Szentpaly, and Liu [37] using the expression:

$$\omega = \frac{\mu^2}{2\eta} \quad (9)$$



**Fig. 2.** The resonance structures for *ortho* isomers of rhodathiabenzene and rhodaoxabenzene.



**Fig. 3.** A linear correlation between relative energies and  $\Sigma B.O$  values for rhodaxabenzene isomers.

**Table 3.** Selected bond lengths (Å) values for Rhodaoxabenzene and Rhodathiabenzene Isomers.

X	Rh-1	1-2	2-3	3-4	4-5	5-Rh	Rh-P <sub>axial</sub>	Rh-P <sub>basal</sub>	Rh-SH
X=O									
I	2.045	1.288	1.376	1.420	1.367	1.993	2.172	2.422	2.369
II	1.914	1.341	1.331	1.370	1.398	1.932	2.253	2.394	2.523
III	2.009	1.340	1.360	1.348	1.342	1.993	2.164	2.394	2.470
IV	1.935	1.405	1.366	1.337	1.334	1.907	2.257	2.387	2.527
V	1.960	1.379	1.410	1.381	1.282	2.027	2.211	2.263	2.524
X=S									
I	2.314	1.711	1.363	1.429	1.362	1.995	2.174	2.410	2.417
II	1.943	1.683	1.692	1.383	1.391	1.951	2.222	2.396	2.508
III	2.028	1.343	1.747	1.738	1.345	2.006	2.159	2.404	2.428
IV	1.950	1.399	1.379	1.697	1.681	1.930	2.229	2.375	2.533
V	1.988	1.368	1.423	1.365	1.705	2.282	2.195	2.321	2.512

**Table 4.** Wiberg bond index for ring atoms in rhodaoxabenzene and rhodathiabenzene isomers.

	Rh-1	1-2	2-3	3-4	4-5	5-Rh	ΣB.O
X=O							
I	0.3434	1.2794	1.5078	1.2593	1.6468	0.6343	6.671
II	0.8191	1.0821	1.0726	1.5251	1.4049	0.7640	6.6678
III	0.5751	1.8265	0.9757	1.0078	1.7997	0.5943	6.7791
IV	0.7849	1.3743	1.5554	1.0504	1.1017	0.8116	6.6783
V	0.7363	1.5770	1.3129	1.4562	1.3103	0.3546	6.7473
X=S							
I	0.5136	1.2390	1.6171	1.2221	1.6947	0.6178	6.9043
II	0.7305	1.3757	1.2579	1.4613	1.4700	0.7239	7.0193
III	0.5528	1.8277	1.1030	1.1284	1.7984	0.5845	6.9948
IV	0.7505	1.4320	1.4950	1.2398	1.3875	0.7383	7.0431
V	0.6493	1.6603	1.2494	1.5883	1.2542	0.5540	6.9555

**Table 5.** Frontier orbital energies (Hartree), HOMO-LUMO gap energy (eV), hardness (eV), chemical potential (eV) and electrophilicity (eV) for Rhodaoxabenzene and Rhodathiabenzene Isomers.

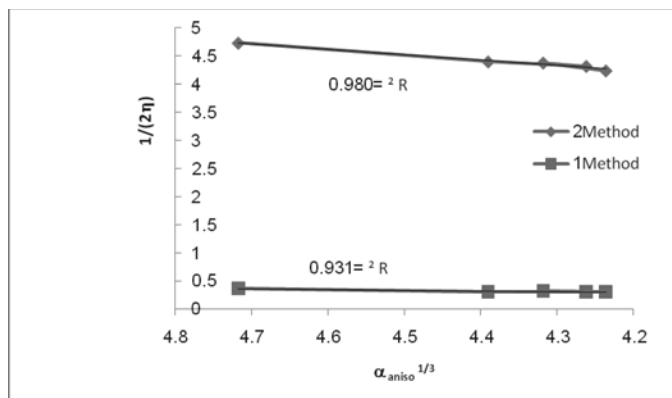
X	E(HOMO)	E(LUMO)	ΔE	η	μ	ω
X=O						
I	-0.192	-0.075	3.161	1.580	3.634	4.179
II	-0.191	-0.078	3.089	1.544	3.660	4.336
III	-0.200	-0.082	3.215	1.608	3.833	4.569
IV	-0.195	-0.078	3.186	1.593	3.722	4.348
V	-0.190	-0.091	2.700	1.350	3.816	5.393
X=S						
I	-0.199	-0.086	3.080	1.540	3.887	4.907
II	-0.190	-0.081	2.983	1.491	3.688	4.559
III	-0.196	-0.084	3.049	1.524	3.803	4.744
IV	-0.195	-0.083	3.040	1.520	3.775	4.688
V	-0.198	-0.096	2.776	1.388	3.990	5.736

These values show that most stable isomer has maximum hardness in rhodathiabenzene complex, as expected from the principles of minimum energy and minimum polarizability in most cases. Furthermore, the hardness and chemical potential values of rhodathiabenzene complexes are higher than rhodaoxabenzene complexes (except in V-isomer). The values of electrophilicity index in Table 5 indicate a higher electrophilicity in rhodathiabenzene.

Fig. 4 confirms the linear behavior between  $\alpha_{\text{anisotropic}}^{1/3}$  and  $1/(2\eta)$ , as expected for rhodaoxabenzene isomers [38].

### Hyperpolarizability

Since even a small absorption at the operating wavelength of optic devices can be detrimental, it is important to make NLO chromophores as transparent as possible without compromising the molecule's non-linearity. The first static hyperpolarizability ( $\beta_{\text{tot}}$ ) values for the molecules are shown in Table 6. The results show that the magnitude of the first hyperpolarizability tensor of all molecules is rather small. The V- isomer has the most



**Fig. 4.** A linear correlation between  $\alpha_{\text{anisotropic}}^{1/3}$  and  $1/(2\eta)$  values for rhodaoxabenzene isomers.

$\beta_{\text{tot}}$  values. On the other hand, we calculated hyperpolarizability values with diffuse functions for nonmetal elements (Method 2). These values are more than method 1. Again, the most  $\beta_{\text{tot}}$  value has been shown for V- isomer.

**Table 6.** The  $\beta$  components and  $\beta_{\text{tot}}$  values ( $10^{-30}$  esu) for rhodaoxabenzene and rhodathiabenzene Isomers.

	Method 1				
	X=O				
	I	II	III	IV	V
$\beta_{XXX}$	-449.559	462.261	-126.882	376.820	-257.384
$\beta_{XXY}$	-97.116	-156.492	-20.035	-102.552	-265.183
$\beta_{XYY}$	-139.959	-164.289	-29.505	-151.766	-187.258
$\beta_{YYY}$	-41.915	-176.278	31.728	-176.473	-120.595
$\beta_{XXZ}$	-125.261	-66.619	-223.685	-327.416	-348.012
$\beta_{XYZ}$	104.990	112.145	99.888	71.796	86.328
$\beta_{YYZ}$	-9.198	-35.445	-52.752	-19.492	-33.600
$\beta_{XZZ}$	-0.049	32.089	-38.803	46.810	35.520
$\beta_{YZZ}$	0.339	63.299	4.472	53.186	-7.707
$\beta_{ZZZ}$	-73.597	-246.429	-145.454	-283.169	-236.014
$\beta_{\text{tot}}$	5.533E-30	4.76E-30	4.02E-30	6.2417E-30	7.24751E-30
$\beta_{\text{tot}} \times 10^{-30}$	5.53	4.76	4.02	6.24	7.25
	X=S				
	I	II	III	IV	V
$\beta_{XXX}$	-306.094	359.214	-121.385	359.326	-144.322
$\beta_{XXY}$	-118.565	-178.593	-48.471	-156.692	-207.442
$\beta_{XYY}$	-121.836	-174.596	-85.234	-166.716	-151.662
$\beta_{YYY}$	-8.154	-114.737	64.565	-128.023	-68.065
$\beta_{XXZ}$	-142.233	-168.860	-365.851	-300.132	-325.024
$\beta_{XYZ}$	110.495	121.049	141.091	75.141	63.327
$\beta_{YYZ}$	17.243	-14.309	-55.857	-26.771	-52.148
$\beta_{XZZ}$	26.214	37.728	66.704	49.975	-7.482
$\beta_{YZZ}$	-27.464	42.790	-39.567	52.733	12.655
$\beta_{ZZZ}$	-128.447	-223.635	-217.822	-225.844	-177.993

Table 6. Continue.

$\beta_{\text{tot}}$	4.31453E-30	4.55E-30	5.66E-30	5.59E-30	5.92E-30
$\beta_{\text{tot}} \times 10^{-30}$	4.31	4.55	5.66	5.59	5.92
Method 2					
X=O					
	I	II	III	IV	V
$\beta_{XXX}$	700.255	313.796	-338.963	177.996	-573.308
$\beta_{XXY}$	-95.471	-175.345	-9.256	-86.908	-300.482
$\beta_{XYY}$	-168.109	-340.487	-103.745	-315.873	-256.248
$\beta_{YYY}$	-188.572	-415.700	-6.554	-411.727	-244.498
$\beta_{XXZ}$	-82.934	-22.911	-200.084	-367.867	-297.549
$\beta_{XYZ}$	164.943	156.348	131.182	99.455	151.979
$\beta_{YYZ}$	34.676	-30.637	-3.569	-54.438	3.080
$\beta_{XZZ}$	-99.313	-125.888	-172.690	-84.887	-111.377
$\beta_{YZZ}$	15.766	97.793	27.404	87.210	11.103
$\beta_{ZZZ}$	-80.196	-259.862	-143.814	-238.839	-221.986
$\beta_{\text{tot}}$	4.5375E-30	5.22E-30	6.11E-30	6.99774E-30	1.03573E-29
$\beta_{\text{tot}} \times 10^{-30}$	4.54	5.22	6.11	7.00	10.36
X=S					
	I	II	III	IV	V
$\beta_{XXX}$	-524.752	196.023	-264.855	198.061	-396.389
$\beta_{XXY}$	-80.309	-185.191	-47.045	-162.064	-180.842
$\beta_{XYY}$	-167.976	-279.407	-93.416	-286.346	-205.947
$\beta_{YYY}$	-87.789	-270.318	-8.217	-320.739	-132.948
$\beta_{XXZ}$	-74.428	-172.730	-328.020	-310.551	-345.173
$\beta_{XYZ}$	126.304	162.475	180.360	119.957	116.577
$\beta_{YYZ}$	45.936	0.704	-13.365	-22.547	-8.881
$\beta_{XZZ}$	-99.581	-74.830	-97.131	-51.222	-128.329
$\beta_{YZZ}$	-10.004	64.464	-23.720	73.710	42.297
$\beta_{ZZZ}$	-190.668	-239.559	-219.275	-189.778	-174.916
$\beta_{\text{tot}}$	7.26723E-30	5.09199E-30	6.27781E-30	5.86118E-30	8.13881E-30
$\beta_{\text{tot}} \times 10^{-30}$	7.27	5.09	6.28	5.86	8.14

### AIM analysis

It has been proved that the AIM-based analysis of electron density can provide valuable information on many physical and chemical properties of molecular systems [39-43].

Table 7 indicates  $\nabla^2\rho$  values of Rh-C, Rh-O, Rh-S, and Rh-PH<sub>3</sub> bonds at corresponding BCPs are positive, as it was found for closed-shell interactions. On the other hand, the  $H(\rho)$  values are negative, as found for shared interactions. This is in agreement with observations made for the Ti-C bonds in titanium complexes [44] and transition metal carbonyl clusters [45], in the case when the metal-ligand bonding has a characteristic that represents a mix of the closed-shell and shared parameters. The strong polar character is also revealed by the large  $G(\text{rb})/\rho(\text{rb})$  ratio and atomic charges, while the covalence is manifested by large and negative  $H(\text{rb})/\rho(\text{rb})$  (Table 7).

Moreover, the  $H(\rho)$  values are more negative for Rh-C1 and Rh-C5 bonds in rhodaoxabenzene, which is directly connected with relative greater predominance of  $|V(\rho)|$  magnitude over the  $G(\rho)$  magnitude. This suggests a more covalent character of the Rh-C1 and Rh-C5 bonds of rhodaoxabenzene as compared with the rhodathiabenzene. Furthermore, Rh-C bonds have more negative  $H(\rho)$  values rather than Rh-S, Rh-O and Rh-P bonds. Generally, when the value of  $|H(\rho)|$  are greater (with negative sign), there is more covalent character of the bond.

The  $\rho(3,+1)$  and  $\nabla^2\rho(3,+1)$  values have been gathered in Table 1. There is a good linear relationship between  $\rho(3,+1)$  and relative energies in rhodaoxabenzene isomers ( $R^2 = 0.985$ ). The most stable isomers has minimum  $\rho(3,+1)$  and  $\nabla^2\rho(3,+1)$  values.

The results from QTAIM calculations may also explain the fact that the calculated Rh-P<sub>basal</sub> bonds are slightly longer than

**Table 7.** Electron densities  $\rho$  ( $e/a_0^3$ ), Laplacians  $\nabla^2\rho$  ( $e/a_0^5$ ), total electron energy density,  $H(\rho)$ , kinetic energy density,  $G(\rho)$ , and potential energy density,  $V(\rho)$  at the Rh-C critical points for rhodaoxabenzene and rhodathiabenzene Isomers.

Rh-1						
X	$\rho$	$\nabla^2\rho$	G	H	V	
						X=O
I	0.091761	0.533518	0.138910	-0.005531	-0.144441	
II	0.156336	0.375987	0.164849	-0.070852	-0.235701	
III	0.130690	0.233199	0.112690	-0.054391	-0.167081	
IV	0.151911	0.303088	0.145369	-0.069597	-0.214967	
V	0.146262	0.231797	0.124982	-0.067033	-0.192016	
						X=S
I	0.090780	0.211931	0.081240	-0.028257	-0.109498	
II	0.144754	0.334566	0.146174	-0.062533	-0.208707	
III	0.126419	0.224890	0.107768	-0.051546	-0.159314	
IV	0.147235	0.283781	0.136919	-0.065974	-0.202893	
V	0.137999	0.228480	0.117375	-0.060255	-0.177630	
Rh-5						
X	$\rho$	$\nabla^2\rho$	G	H	V	
						X=O
I	0.136943	0.181292	0.107051	-0.061728	-0.168779	
II	0.153614	0.286527	0.142989	-0.071357	-0.214346	
III	0.135741	0.206882	0.111000	-0.059279	-0.170279	
IV	0.159298	0.373367	0.166659	-0.073317	-0.239976	
V	0.095311	0.566721	0.147593	-0.005912	-0.153505	
						X=S
I	0.136120	0.191546	0.108331	-0.060444	-0.168775	
II	0.147672	0.259462	0.131936	-0.067070	-0.199006	
III	0.132522	0.203864	0.107934	-0.056968	-0.164903	
IV	0.149053	0.332836	0.149230	-0.066021	-0.215252	
V	0.096413	0.220096	0.086272	-0.031248	-0.117520	
Rh-PH <sub>3</sub> (axial)						
X	$\rho$	$\nabla^2\rho$	G	H	V	
						X=O
I	0.122641	0.085532	0.084205	-0.062822	-0.147026	
II	0.103285	0.144448	0.079065	-0.042952	-0.122017	
III	0.124337	0.089253	0.084973	-0.062659	-0.147632	
IV	0.102352	0.146700	0.078857	-0.042182	-0.121038	
V	0.113809	0.114025	0.080669	-0.052162	-0.132831	
						X=S
I	0.121912	0.092439	0.084400	-0.061290	-0.145690	
II	0.110221	0.131682	0.081790	-0.048869	-0.130659	
III	0.125612	0.086202	0.086105	-0.064555	-0.150661	
IV	0.108443	0.135719	0.081107	-0.047177	-0.128284	
V	0.117511	0.100986	0.081242	-0.055996	-0.137238	

Table 7. Continue.

Rh-PH <sub>3</sub> (basal)						
X	$\rho$	$\nabla^2\rho$	G	H	V	
X=O						
I	0.072333	0.180423	0.066587	-0.021481	-0.088068	
II	0.076781	0.175615	0.068158	-0.024254	-0.092412	
III	0.076340	0.185599	0.070060	-0.023661	-0.093721	
IV	0.077958	0.174870	0.068609	-0.024892	-0.093501	
V	0.099955	0.190133	0.085821	-0.038288	-0.124109	
X=S						
I	0.074866	0.174476	0.066850	-0.023231	-0.090081	
II	0.076538	0.177088	0.068318	-0.024046	-0.092364	
III	0.075420	0.178011	0.067785	-0.023282	-0.091066	
IV	0.079890	0.176768	0.070140	-0.025948	-0.096088	
V	0.089451	0.179528	0.076669	-0.031787	-0.108457	
Rh-SH						
X	$\rho$	$\nabla^2\rho$	G	H	V	
X=O						
I	0.083288	0.167555	0.066947	-0.025058	-0.092005	
II	0.062728	0.132379	0.049623	-0.016528	-0.066152	
III	0.068466	0.157024	0.058006	-0.018750	-0.076757	
IV	0.062520	0.132440	0.049562	-0.016452	-0.066014	
V	0.062350	0.135098	0.050243	-0.016469	-0.066712	
X=S						
I	0.076282	0.152060	0.060255	-0.022240	-0.082495	
II	0.064650	0.136254	0.051421	-0.017357	-0.068778	
III	0.073884	0.173774	0.064313	-0.020870	-0.085183	
IV	0.061952	0.132234	0.049329	-0.016271	-0.065600	
V	0.064056	0.139428	0.052053	-0.017196	-0.069250	

the remaining Rh-P<sub>axial</sub> bonds (Table 7). The QTAIM calculations show that the electron density on RCP of Rh-P<sub>axial</sub> bond is larger, in comparison to Rh-P<sub>basal</sub>.

## Conclusion

In this paper, an attempt has been made to examine the structure, bonding and stabilization of rhodathiabenzene and rhodaoxabenzene isomers with the hybrid density functional mpw1pw91 theory. Calculations illustrate:

1. Energetic criteria suggest that I- isomer enjoys conspicuous stabilization in rhodathiabenzene and rhodaoxabenzene isomers.
2. Bond lengths and Wiberg index values the six membered metallacycles indicate to some amount aromatic properties.
3. The frontier orbitals investigation exhibited that most stable isomer has maximum hardness in rhodathiabenzene complex, as expected from the principles of

minimum energy and minimum polarizability in most cases.

4. Quantum theory atoms in molecules (QTAIM) exemplify Rh-C, Rh-S, Rh-P, and Rh-O bonding. This analysis showed that metal-ligand bonding has a characteristic that signifies a mix of the closed-shell and shared parameters.

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