Solvent Effect on the Stability and Properties of Platinum-Substituted Borirene and Boryl Isomers: the Polarizable Continuum Model

Reza Ghiasi,* and Ali Peikari

aDepartment of Chemistry, East Tehran Branch, Islamic Azad University, Qiam Dasht, Tehran, Iran
bYoung Researchers and Elite Club, Pharmaceutical Science Branch, Islamic Azad University, Tehran–Iran (IAUPS)
*e-mail: rezaghiasi1353@yahoo.com, rghiasi@iauet.ac.ir

Received June 23, 2015

Abstract—The structure and properties of platinum borirene complex trans-[Cl(PMe₃)₂Pt(μ-BN(SiMe₃)₂C≡CPh)] and its isomer the platinum boryl complex trans-[Cl(PMe₃)₂PtBN(SiMe₃)₂C≡CPh] were investigated theoretically. The solvent effect on the stability, structural parameters, frontier orbital energies, HOMO–LUMO gaps, and hardness of isomers was investigated using the polarizable continuum model (PCM). It was found that borirene isomer is the most stable isomer in the gas phase and solvent. The calculated results show that the presence of solvent reduces the frontier orbital energy of the studied molecules. Geometries obtained from calculations were used to perform NBO analysis.

Keywords: borirenes, polarizable continuum model (PCM) method, solvent effect, dipole moments, molecular orbital analysis, natural bond analysis (NBO)

DOI: 10.1134/S0036024416110212

INTRODUCTION

Borylated molecular and polymeric species are valuable owing to their extensive application in organic and inorganic synthesis [1–6]. Borirenes are the smallest boron heterocycles. They are isoelectronic with cyclopropenium cations and thus exhibit 2π stabilization [7–9]. A limited number of synthetic routes to borirenes have been reported [10–13]. The first borireny compound reported in 1987, and characterized structurally [12]. On the other hand, the possibility of synthetic approaches to borirenes is powerfully restricted with respect to the offered substituents at the boron atom. Reactivity of these three-membered rings is still very limited and restricted to ring-opening with cleavage of one endocyclic B–C bond, initiated either from protic reagents, for instance, water, methanol, ethanol [12, 13] or hydroboration with 9-borabicyclo-[3.3.1]nonane (9-BBN) [14] reported.

The synthesis of platinum–substituted borirenes via borylene transfer has been reported [15]. The reactivity of platinum borirene complex trans-[Cl(PMe₃)₂Pt(μ-BN(SiMe₃)₂C≡CPh)] which underwent a photochemical rearrangement reaction to afford the platinum boryl complex trans-[Cl(PMe₃)₂PtBN(SiMe₃)₂C≡CPh] has been investigated [16].

The aim of this work is to theoretically study, the stability, geometries, and molecular orbital analysis of platinum borirene complex trans-[Cl(PMe₃)₂Pt(μ-BN(SiMe₃)₂C≡CPh)] and the platinum boryl complex trans-[Cl(PMe₃)₂PtBN(SiMe₃)₂C≡CPh]. The solvent effect on the structure, dipole moment, the frontier orbital energies, and hardness has been investigated. Also, natural bond orbital analysis (NBO) provides the detailed insight into the electronic structure of molecules. We believe that this study facilitates the understanding of the structure and properties of studied isomers.

COMPUTATIONAL METHOD

All calculations were carried out with the Gaussian 09 suite of programs [17]. The systems containing main group elements were described by the standard 6–31G(d,p) basis set [18–21]. Platinum was described by effective core potential (ECP) of Wadt and Hay pseudopotential [22] with a double-ξ valence using the LANL2DZ basis set [22–24]. Geometry optimization was performed using the PBE0PBE method of density functional theory (DFT) [25]. A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum.
REZA GHIASI, ALI PEIKARI

For the solvation effects study we have used a self-consistent reaction field (SCRF) approach, in particular using the polarizable continuum model (PCM) [26]. The population analysis has also been performed by the natural bond orbital method [27] using NBO program [28] of the Gaussian 2009 program package. The information on the MOs was evaluated by total, partial and overlap population density of states (DOS) using the GaussSum 3.0 [29].

RESULTS AND DISCUSSION

Energetic Aspects

Figure 1 presents the structures and numbering schemes of atoms in studied platinum borirene complex \(\text{trans}-[\text{Cl}(\text{PMe}_3)_2\text{Pt}(\mu-\text{BN(SiMe}_3)_2\text{C=})\text{Ph}]\) and platinum boryl complex \(\text{trans}-[\text{Cl}(\text{PMe}_3)_2\text{PtBN(SiMe}_3)_2\text{C}≡\text{CPh}]\). The absolute energies, relative energies, solvation energies of open- and closed-ring isomers have been listed in Table 1. As shown in Table 1, the closed-ring isomer is more stable than that of open-ring isomers. Different solvents prominently affect relative energies (\(\Delta E\)) between closed-ring and open-ring isomers. The vacuum phase has the smallest relative energy which is merely 2.79 kJ/mol. In different solvent will support the \(\Delta E\) to decrease dominantly, it is found that the \(\Delta E\) decrease with polarity of solvents. Figure 2 presents dependence of relative energies of open isomer on dielectric constant of solvents.

Dipole Moments

The dipole moments of open- and closed-ring isomers have been listed in Table 2. As seen in Table 2, closed–ring isomers always have less dipole moment than that of open-ring isomers. In the solution phase, dipole moments are higher than in vacuum. According to Onsager’s solvation model, the compound with greater dipole moment will be more stable in polar solvents. Figure 3 indicates the dependence of \(\Delta \mu = \mu_{\text{closed isomer}} - \mu_{\text{open isomer}}\) on dielectric constant of the solvents.

Bond Distances

The selected bond distances of closed and open isomers and experimental data for closed isomer have been collected in Table 3. As seen from Table 3, theoretical results are approximately close to the experimental values 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

---

Table 1. Dielectric constants of solvents (\(\varepsilon\)), absolute energy (\(E\), Hartree), relative energy (\(\Delta E = E(\text{closed isomer}) - E(\text{open isomers})\), kcal/mol), solvation energy (\(E_{\text{solv}}\), kcal/mol), for closed and open isomers of \(\text{trans}-[\text{Cl}(\text{PMe}_3)_2\text{Pt}(\mu-\text{BN(SiMe}_3)_2\text{C=})\text{Ph}]\) in vacuum and various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\varepsilon)</th>
<th>(E) (Open)</th>
<th>(E_{\text{solv}})</th>
<th>(E) (Closed)</th>
<th>(E_{\text{solv}})</th>
<th>(\Delta E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>–</td>
<td>–2706.0231</td>
<td>–</td>
<td>–2706.0275</td>
<td>–</td>
<td>2.79</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>5.70</td>
<td>–2706.0370</td>
<td>–8.72</td>
<td>–2706.0400</td>
<td>–7.88</td>
<td>1.94</td>
</tr>
<tr>
<td>THF</td>
<td>7.43</td>
<td>–2706.0383</td>
<td>–9.54</td>
<td>–2706.0412</td>
<td>–8.58</td>
<td>1.83</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>8.93</td>
<td>–2706.0390</td>
<td>–10.03</td>
<td>–2706.0418</td>
<td>–8.99</td>
<td>1.75</td>
</tr>
<tr>
<td>Quinoline</td>
<td>9.16</td>
<td>–2706.0391</td>
<td>–10.09</td>
<td>–2706.0419</td>
<td>–9.04</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Fig. 1. The structures of a platinum-substituted I, borirene complex; closed isomer, II, boryl complex; open isomer.