Coronene-Transition Metal Complex: View from Quantum Chemistry and Statistical Mechanics

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Abstract. Coronene consists of seven peri-fused benzene rings, regarded as a small fragment of graphene. In the present contribution, the electronic structure as well as solvation structure of coronene and its transition metal complex were studied using density functional theory combined with a statistical mechanics for molecular liquid.

Keywords: coronene, transition metal, RISM-SCF, electronic structure, solvation structure
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INTRODUCTION

Carbon-derived materials such as graphene have been attracting increased interest due to their extraordinary electrical properties as well as huge potential in electronic applications. In the connection to their functionalization, numerous synthetic studies were carried out on a novel class of compounds of polycyclic aromatic hydrocarbons (PAHs) with transition metal complex. In the interest of physical chemistry, there are several outstanding issues on the interaction between the carbon atoms and the metal. For example, it is known that the metal is always bonded with two carbon atoms (η^2) shared between two six membered rings in fullerene (C_{60}) but η^6-type coordination, in which the metal is located above the center of the benzene ring, has never been observed yet. Coronene ($C_{24}H_{12}$) is flat polyaromatic hydrocarbons consisting of seven peri-fused benzene rings and comes to the front as a fragments of graphene. In the present study, several transition metal complexes are examined, especially focused on the binding and ligand-migration.

Another aim of the present study is to establish a realistic consideration of such complex system. In the real situation, these compounds are usually treated in solvent. When the molecule is dissolved into solvent, the electronic structure is affected by the surrounding solvent molecules. It means electronic structure, which is described by quantum chemistry, and solvation structure, which is governed by statistical mechanics, are coupled with each other. In this regard, development of new theories that can bridge between these two methodologies is very important. We have been developing RISM-SCF [1, 2], which compiles two ab initio methods in theoretical chemistry: one is the reference interaction site model (RISM) [3, 4], and the other is ab initio molecular orbital (MO) theory. The method determines the electronic structure and the solvent distribution around the solute in self-consistent manner. It is a remarkable advantage that the RISM-SCF method provides information on the microscopic solvation structure based on the statistical mechanics. The method has been successfully applied to numerous molecular phenomena including chemical reactions, chemical equilibria, charge electron processes and so on [5]. The three-dimensional version of the method (3D-RISM-SCF) is also developed [6].

In this application, the electronic structures of coronene and its transition-metal complex are considered together with solvation effect.

η^6-CORONENE COMPLEXES OF TRANSITION METAL

Three different transition metals were considered, namely, $[CpIr]^{2+}$, $[CpRh]^{+}$ and $[CpRu]^{2+}$. Density functional theory (B3PW91) was employed with 6-31G(d) basis set for C and H atoms. The ECPs and basis set parameters of [7] were used for the metals.

In the complex, two binding sites were found (see Figure 1). One is $\boldsymbol{\eta}^6_{\mathrm{A}}$, in which the metal unit binds to a benzene ring of the edge site, and the other is $\boldsymbol{\eta}^6_{\mathrm{B}}$, in which the metal unit is located at the center of the coronene. Their binding energies are summarized in Table 1. Among the three metals, ruthenium is experimentally reported to be η^6-bounded

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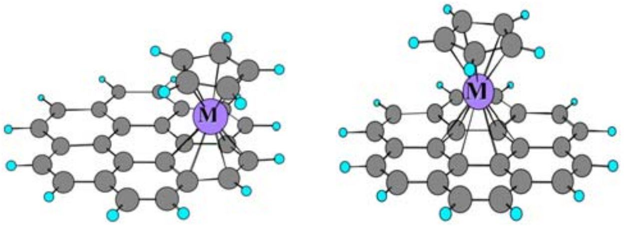

FIGURE 1. Two structure of the transition metal complexes. $\boldsymbol{\eta}^6_\mathrm{A}$ (left-hand side) and $\boldsymbol{\eta}^6_\mathrm{B}$ (right-hand side).

TABLE 1. Computed binding energies of $[\mathrm{CpIr}]^{2+}$, $[\mathrm{CpRh}]^{2+}$ and $[\mathrm{CpRu}]^{+}$ complexes (kcal/mol).

	$[\mathrm{CpIr}]^{2+}$	$[\mathrm{CpRh}]^{2+}$	$[\mathrm{CpRu}]^{+}$
$\boldsymbol{\eta}^6_\mathrm{A}$	171.7	148.9	80.2
$\boldsymbol{\eta}^6_\mathrm{B}$	156.3	133.7	67.3

to coronene in the edge position [8], and our result is consistent with the report. The binding energies for $[\mathrm{CpIr}]^{2+}$ and $[\mathrm{CpRh}]^{2+}$ are also sufficiently great, suggesting that the possibility to obtain stable complex in real experimental condition.

The edge-preference may be simply explained by the charge distribution of π-system since the negative charge assigned to the edge-carbon atoms is than those of the central carbon atoms. Another important view is charge transfer (CT) interaction. The electron population on the metal always increases by the complex formation. In general, CT interaction is classified into donation and back-donation. The former corresponds to the CT from HOMO of the $\pi-$conjugating PAH to the metal d-orbital, and the latter to the metal to LUMO of PAH. Hence the donation is dominative in the present series of complexes. Actually, HOMO of the π-system and LUMO of d-orbital are in the same phase.

Recently, Alvarez *et al.* reported an interesting phenomenon in a corannulene ($C_{20}H_{10}$) derivative [9]. They observed that η^6-Cp*Ir complex of 1,2,5,6-tetramethylcorannulene exhibits migration of the Cp*Ir^{2+} unit on the surface. Corannulene is regarded as a curved-surface fragment of C_{60}, hence it would be interesting to compare the planarity with the curved surface by seeing whether the migration occurs on the planar surface of coronene or not.

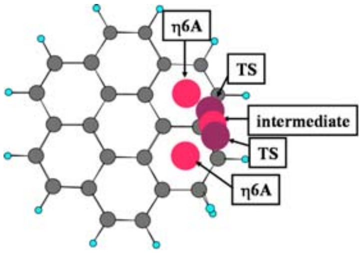

FIGURE 2. The migration path on the coronene.

Figure 2 indicates the computed migration path. It does not stride across the C–C bond corresponding to η^2-coordination, but comes over the edge carbon atom. An intermediate is located just above the carbon, and two transition states (TS) are found between the two stable η^6-coordination structures. The computed activation barriers are higher than those in the corannulene complex; Even the lowest barrier found in the Rh-complex is more than 36 kcal/mol, indicating that the metal unit does not readily migrate on the planar surface. The Ru-complex, which was experimentally observed on the curved surface of the corannulene complex, is the highest among the three metals (more than 50 kcal/mol). The population analysis shows that the donation to the metal is relatively weak near the TS compared to the corannulene, which may be a reason of the high barrier.

RISM-SCF THEORY

The RISM-SCF method compiles *ab initio* electronic structure theory and statistical mechanical theory of molecular liquid. Total energy of the solvation system is defined as the sum of quantum chemical energy of the solute (E_{solute}) and solvation free energy ($\Delta\mu$) [2].

$$\mathscr{A} = E_{\mathrm{solute}} + \Delta\mu = \langle\Psi|H_0|\Psi\rangle + \Delta\mu, \tag{1}$$

Since the electronic structure of the solute molecule and the solvation structure around it are determined in a self-consistent manner, the wave function of the solute molecule is distorted from that in isolated state. The energy difference between the solute in isolated state (E_{isolated}) and that in solution phase (E_{solute}) is a quantity to measure the contribution of “solvation effects" to the electronic structure.

$$\begin{aligned} E_{\mathrm{reorg}} &= E_{\mathrm{solute}} - E_{\mathrm{isolated}} \\ &= \langle\Psi|H|\Psi\rangle - \langle\Psi_0|H|\Psi_0\rangle, \end{aligned} \tag{2}$$

where $|\Psi\rangle$ and $|\Psi_0\rangle$ are wave functions in solution and in gas phase, respectively. Solvation free energy in the present framework of the theory (excess chemical potential derived with hyper-netted chain approximation) is given by,

$$\Delta\mu = -\frac{\rho}{\beta}\sum_{\alpha s}\int d\mathbf{r}\left[c_{\alpha s}(r) - \frac{1}{2}h_{\alpha s}^2(r) + \frac{1}{2}h_{\alpha s}(r)c_{\alpha s}(r)\right], \tag{3}$$

h and c are the total and direct correlation functions, respectively. $\beta = 1/k_{\mathrm{B}}T$, where k_{B} and T are the Boltzmann constant and temperature, respectively.

Applying variational principle to Eq. (1), the Fock operator of the RISM-SCF theory (F^{solv}) including a solute-solvent interaction, V, is naturally derived.

$$F^{\mathrm{solv}} = F^{\mathrm{gas}} + V. \tag{4}$$

The interaction energy between the solute and solvent reaction field is given by,

$$\langle\Psi|V|\Psi\rangle = \sum_{\alpha} V_\alpha \langle\Psi|b_\alpha|\Psi\rangle = \sum_{\alpha} V_\alpha q_\alpha, \tag{5}$$

where b_α is the proper population operator for atom α in the solute molecule and V_α is the electrostatic potential acting on this atom.

$$V_\alpha = \rho\sum_s q_s \int \frac{g_{\alpha s}(r)}{r} d\mathbf{r}. \tag{6}$$

Here $g_{\alpha s}(r)(\equiv h_{\alpha s}(r) - 1)$ is pair correlation function around the solute molecule, namely radial distribution function (RDF). Note that V_α in the present theory is computed from the microscopic information on the solvation structure. Since the Fock operator is modified, this is an extension of standard ab initio MO theory that can handle the solvent effect. And if we replace E_{solute} in Eq. (1) with MM energy or a constant value, it is equivalent to the original RISM equation. From this standpoint, the RISM-SCF theory can be regarded as an extension of a statistical mechanics for liquid (RISM theory) as well as that of ab initio molecular orbital theory.

Recently, we developed the new-generation of RISM-SCF called RISM-SCF-SEDD [10]. In this method, the auxiliary basis sets (ABSs) on each atom are prepared to divide electron density into the components assigned on each atom. Gill, Johnson, Pople, and Taylor proposed a procedure to determine ABSs which reproduce the electrostatic potential (ESP) provided by MO calculation. The great advantage of the procedure is that it treats directly spatial electron density distribution (SEDD) and does not require the set of grid points that was necessary to fit ESP; it is free from these artificial parameters. Furthermore the RISM-SCF-SEDD is much more robust in the connection between RISM and MO calculation than the original version of RISM-SCF. The numerical stability of the new method significantly expands the versatility of the RISM-SCF family, for example, molecules with buried atoms and transition metals.[11, 12]

Figure 3 shows selected RDFs of coronene in dichloromethane solvent (CH_2Cl_2) computed by RISM-SCF-SEDD method. By the solvation electronic structure of the coronene is slightly polarized. Mulliken charge on the edge- carbon sites is changed from -0.225 to -0.2313 $|e|$ and that on the central carbon is from 0.015 to 0.012. As seen in the figure, solvation is relatively weak and the height of the peak is not so deviated from one corresponding to the bulk solvation structure.

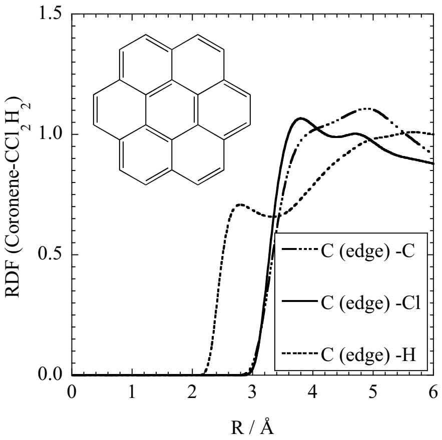

FIGURE 3. RDFs between the edge carbon of coronene and dichloromethane solvent.

SUMMARY

The solvation effect must modify the character of a chemical bond in the solute molecule, and, at the same time, this modification in the electronic structure affects the structure of the solvent molecules surrounding the solute. In this contribution, we show that the coronene - transition metal complex is truly depicted using density functional theory, statistical mechanics for molecular liquid (RISM), as well as their combination.

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