Molecular simulation study of 1,5-diphenylcarbazide self-assembled monolayers on a copper surface

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Abstract: In this study, the adsorption process of 1,5- diphenylcarbazide (DPC) self-assembled monolayers on a copper surface was investigated by using molecular mechanics. The results indicated that the interaction of the α-electrons in the –NH–NH– group and the π-electrons in the phenyl ring could lead to strong adsorption of the highly symmetric DPC molecules on a copper surface. The synergy efect of the phenyl ring and the –NH–NH– group made the whole DPC molecule lay in parallel orientation on a copper surface when the coverage was low. However, at high coverage, the phenyl ring was sligtly tilted because of the repulsion of the DPC molecules, while the –NH–NH– groups remained parallel to the copper surface.

Keywords: self-assembled monolayers (SAMs) 1,5-diphenylcarbazide, copper, molecular mechanics.

INTRODUCTION

Self-assembled monolayers (SAMs) can be forme on metal surfaces by spontaneous chemisorptions of organic molecules, and have been intensively studied for decades because of their important applications.[1–4] SAMs also offers unique opportunities to further the fundamental understanding of self-orgaization, structure-property relationships and interfacial phenomena.[5] Copper is one of the most important metals in industrial applications. Some organic SAMs have been used to protect copper from corrosion in solution.[6–9]

Molecular simulation has been used to investigate the formation of SAMs on metals and to provide some valuable information about micro structures.[10–11] Jung *et al.*[12] reported the theoretical results of the SAMs of both benzenethiolate (BT) and benzyl mercaptide (BZM) on an Au (111) surface, and found that neither BT nor BZM formed well-ordered structures, except that BZM showed some degree of local ordering with a herringbone structure. Kondoh *et al.*[13] investigated alkanethiolate monolayers on Cu

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(100) and found that the sulfur atom in the thiolate occupied the 4-fold hollow site of the unreconstructed Cu (100) surface.

There are two –NH–NH– groups and two phenyl rings in the 1,5-diphenyl-carbazide (DPC) molecule, the α-electrons and π-electrons of which make it possible that DPC would be well adsorbed on transition metals. It was reported that the DPC molecule had inhibitive effects on both C-steel and 304-steel in acidic solution.[14,15] However, the inhibition effect of DPC on copper has not been reported.

This paper focuses on the application of molecular simulation to study the formation mechanism of the DPC SAMs on a copper surface. The molecular simulation method gives a better understanding of how DPC molecules adsorb on a copper surface and finally form ordered SAMs. It is also expected to be helpful in finding potential orgainic molecules which could be well adsorbed on metals and inhibit their corrosion.

MOLECULAR SIMULATION METHOD

The adsorption progress of DPC molecules on a copper surface was investigated by performing molecular mechanics (MM) in Cerius[2] sofware.[16] The Cu (111) surface used for the simulation consists of four atomic layers, the pre-optimized DPC molecules were attached to the Cu (111 surface. The first layer of copper atoms and the DPC molecules were not fixed, other copper atoms were fixed during the simulations to save substantial amounts of CPU time.[17]

A method named QEq[18] in the molecular simulation program in Cerius[2] software provides for the calculation of the approximate atomic point charges of organic molecules before being adsorbed on the copper surface. The QEq method exploits the notion of electronegativity. In this study, Mulliken's definition was employed:

$$\chi = (I + E)/2 \tag{1}$$

here, I and E are the ionization potential and electron affinity, respectively.

Periodic boundary conditions (PBC) were applied to the simulation cell, which was extended periodically in the x and y directions, periodic in the plane parallel to the copper surface and nonperiodic in the plane normal to the surface. The size of the simulation box was $3.07 \times 1.53 \times 2.50$ nm^3 and the cutoff distance was 0.760 nm. The forcefield used in the current MM was the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) forcefield,[19] which is the first *ab initio* forcefield enabling accurate and simultaneous prediction of gas-phase properties (structural, conformational, vibrational, *etc.*) and condensed-phase properties (equation of state, cohesive energies, *etc.*) for a broad range of molecules and polymers. The employed method of MM was "smart minimization", which began with the steepest descent method, followed by the conjugate gradient method and ended with a Newton method.[20–22]

For the system of DPC molecules and the copper surface, the potential energy can be expressed as a sum of valence or bonded interactions and non-bonded interactions.[19,23] The expression is as follows:

$$E_{\text{total}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{inversion}} + E_{\text{vdW}} + E_{\text{electrostatic}} \tag{2}$$

The bonded interactions consist of bond stretching (E_{bond}), valence angle bending (E_{angle}), dihedral angle torsion (E_{torsion}) and out-of-plane interactions terms (also called inversion, $E_{\text{inversion}}$). The non-bonded interactions consist of van der Waals (E_{vdW}) and electrostatic ($E_{\text{electrostatic}}$) terms. The hydrogen bond interaction term was not taken into account in this system.

The interaction energy can be calculated using the following equation:

$$E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{DPC}}) \tag{3}$$

where E_{total} is the energy of the surface and DPC, E_{surface} is the energy of the surface without DPC and E_{DPC} is the energy of DPC without the surface. These calculations are all single point energies after the system becomes stable.

RESULTS AND DISCUSSION

Electronegativity is expressed by the atomic point charges of the atoms in an organic molecule. Figure 1 shows the molecular structure of DPC molecule, and Table I shows the approximate atomic point charges of each atom in the DPC molecule calculated by the QEq method. The atomic point charges of N13 and N18 are –0.380, that of N14 and N17 are –0.388, and that of O16 is –0.458. In a DPC molecule, the oxygen atom and nitrogen atoms with high electronegativity and the phenyl groups with large electron clouds could become active adsorption centers, as it was reported that good inhibitors usually contain an electron cloud on the aromatic ring or electronegative atoms such as nitrogen and oxygen.[24]

TABLE I. Atomic charges in the DPC molecule

Atom and number	C1 C7	C2 C8	C3 C9	C4 C10	C5 C11	C6 C12	N13 N18	N14 N17	C15	O16
Atomic charge	–0.093	–0.108	0.189	–0.095	–0.115	–0.056	–0.380	–0.388	0.604	–0.458

[*]The number 1, 13 and 16 in C1, N13 and O16 are the sequence number of atoms, respectively. These can be found in Fig. 1.

In this simulation, two different models were considered to explain the adsorption process of DPC molecules on a copper surface. On is the situation of low
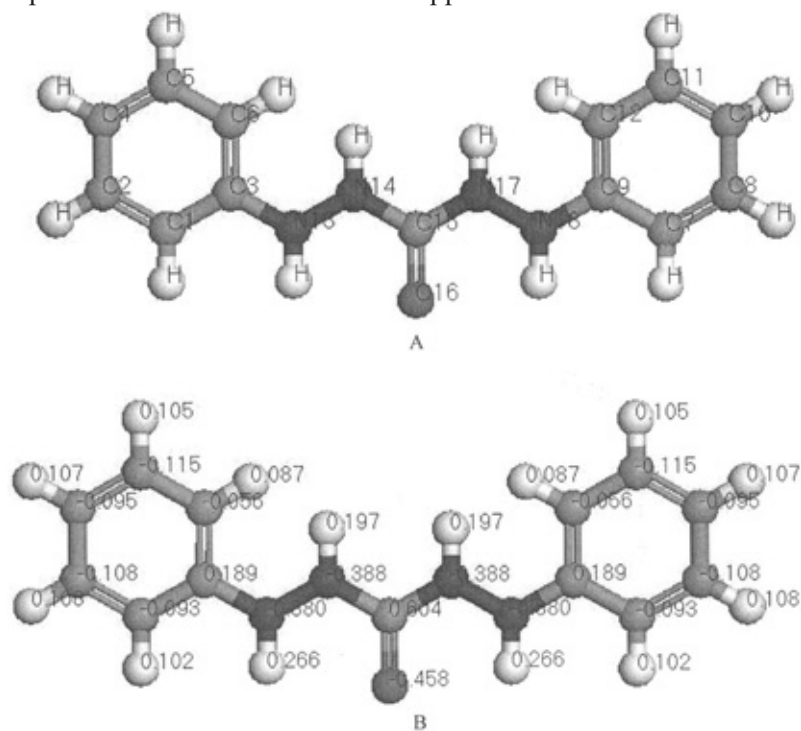

Fig. 1. DPC Molecular structure and atomic charges (detailed data can be found in Table I) A: DPC molecular structure, B: atomic charges in the DPC molecule.

coverage of a single DPC molecules on the copper surface, the other one is the high coverage situation.

Low coverage situation

    In the low coverage situation, only one DPC molecule was adsorbed on the Cu (111) surface. Two initial adsorption states for the DPC molecule were constructed in this model; one was that the DPC molecule was adsorbed in the parallel orientation to Cu (111) surface for a certain distance, the other one was that it was adsorbed in the vertical orientation to the Cu (111) surface. Picture A and B in Fig. 2 show these two different orientations.
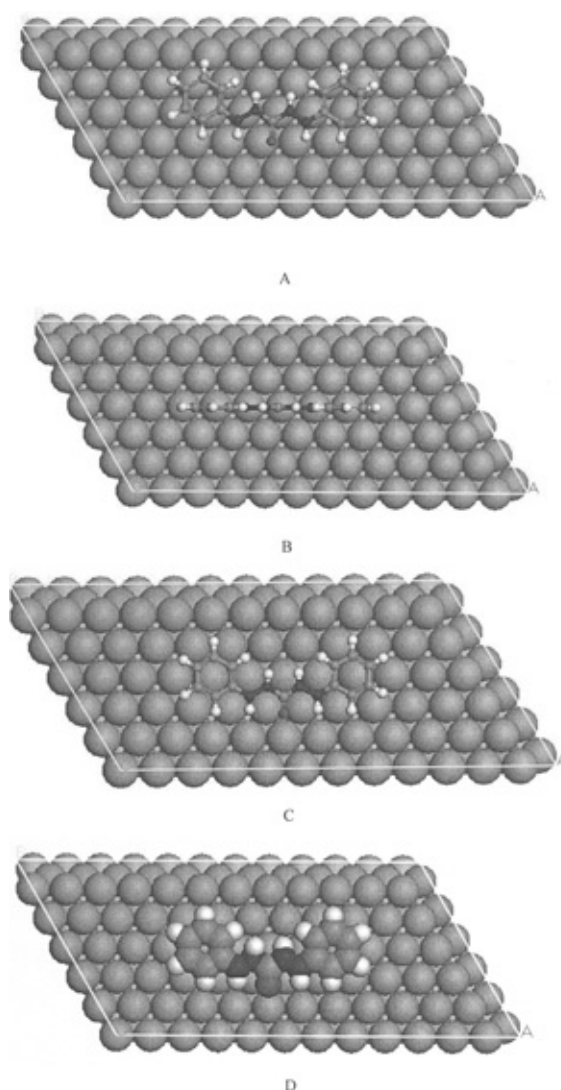

Fig. 2. Adsorption structure of a single DPC molecule on the Cu (111) surface. A: Top view of the original structure of a DPC molecule parallel to the Cu (111) surface; B: Top view of the original structure of a DPC molecule vertical to the Cu (111) surface; C: Top view of the final adsorption structure of a DPC molecule on the Cu (111) surface; D: The same case as C, but in a different display style. All copper atoms are shown in the CPK display style, the DPC molecules in A, B and C are displayed in the ball and stick style, that in D is in the CPK style.

After applying MM to these two initial adsorption states, it was found that as the DPC molecule became close to Cu (111) surface, it was finaly adsorbed in the parallel orientation on the surface, regardless of which initial adsorption state was initially assumed. The final stage is shown in Fig. 2C and Fig. 2D, in which the DPC molecule lies in parallel to the Cu (111) surface and most atoms in the DPC molecule, such as nitrogen, oxygen and carbon atoms, were adsorbed on the 3-fold sites, of the Cu (111) surface. Since the 3-fold sites are the most stable adsorption sites for a Cu (111) surface, the adsorption of DPC molecule on the Cu (111) surface should be stable; this was also verified by the stabilization of the latter part of the energy curve, which is shown in Fig. 3.
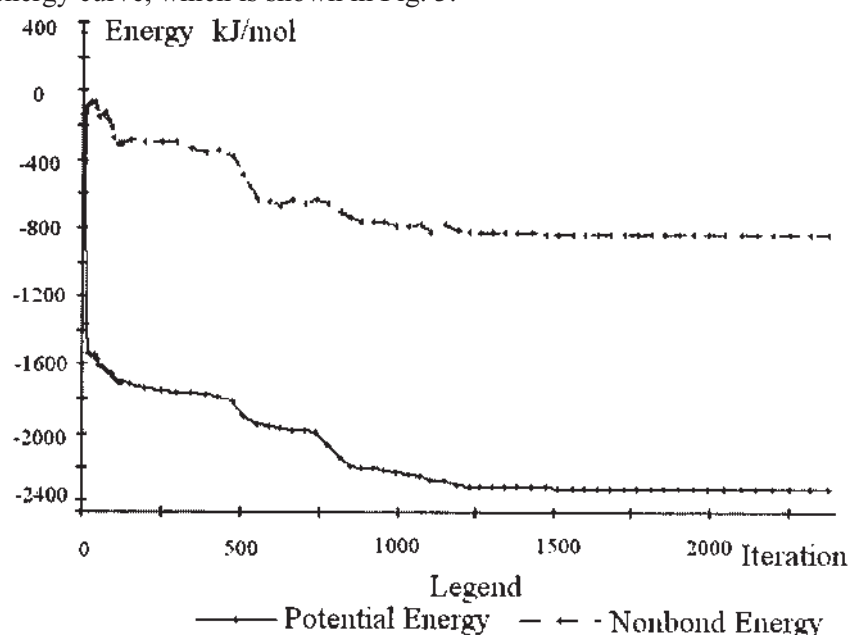

Fig. 3. Energy curve of the adsorption process of a single DPC molecule on the Cu (111) surface.

It was also found that the distances between atoms in the DPC molecule varied after simulation, detailed information is given in Table II. The reason for the change of these distances could be that the DPC molecule changes its form a little so that the most atoms could be adsorbed on the 3-fold sites of the Cu (111) surface, and the adsorption of the DPC molecule on the Cu (111) surface could become stabilized.

High coverage situation

In the high coverage situation, four DPC molecules were adsorbed on a Cu (111) surface which had the same size as that in the low coverage situation. The two initial adsorption states of the DPC molecules were similar to the case in the low coverage situation, either in parallel or in vertical orientation to the Cu (111) surface (top view in Fig. 4A and Fig. 4B).

TABLE II. Change of atomic distances (nm) in the DPC molecule

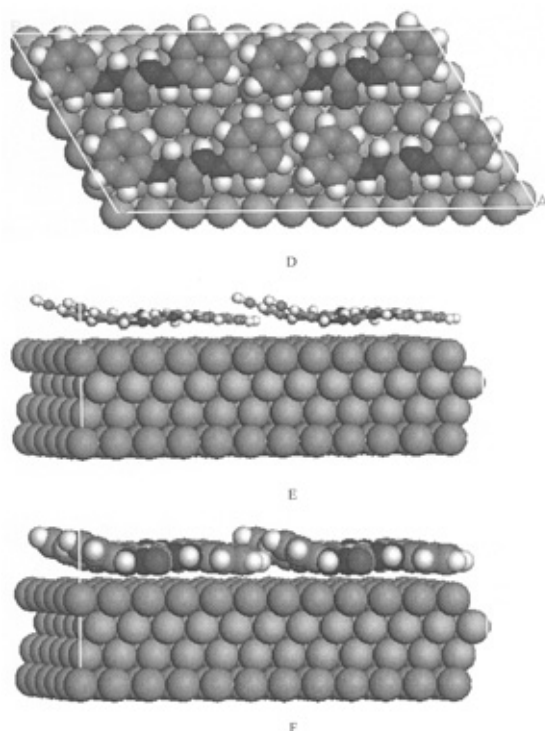| Atomic distance	C4–C10	C3–C9	C2–C8
Before simulation	1.312	0.779	0.313
After simulation	1.219	0.723	1.211

Fig. 4. Adsorption structure of four DPC molecules on the Cu (111) surface. A: Top view of the original structure of DPC molecules parallel to the Cu (111) surface; B: Top view of the original structure of DPC molecules vertical to the Cu (111) surface; C: Top view of the final structure of DPC molecules on the Cu (111) surface; D: The same case as C, but in a different display style; E: Side view of the final structure of DPC molecules on the Cu (111) surface; F: The same case as E, but in a different display style.

After completion of the MM, the DPC molecules became close to the Cu (111) surface and were also adsorbed in the parallel orientation to the Cu (111) surface. Similarly, it was found that the two different initial adsorption states in the high coverage situation also led to the same adsorption structure. However, compared to the low coverage situation, a different results was found from the top view of the simulation images (top view in Fig. 4C and Fig. 4D), in which the nitrogen atoms and the oxygen atoms were almost adsorbed on the 3-fold sites of the Cu (111) surface, but the adsorption sites of some carbon atoms in the phenyl rings were a little away from the 3-fold sites. In fact, some phenyl rings became slightly tilted (side view in Fig. 4E and Fig. 4F).

The reason for these differences in the simulation results between the two situations is considered to be that, in the high coverage situation, the crowed space between the DPC molecules makes adjacent phenyl rings from different DPC molecules repulse each other and become tilted. All the nitrogen atoms and the oxygen atoms were still adsorbed on the 3-fold sites of the Cu (111) surface, which indi-

cates that the interactions between the –NH–NH– group and the copper atoms is much stronger than that between the phenyl rings and the copper atoms.
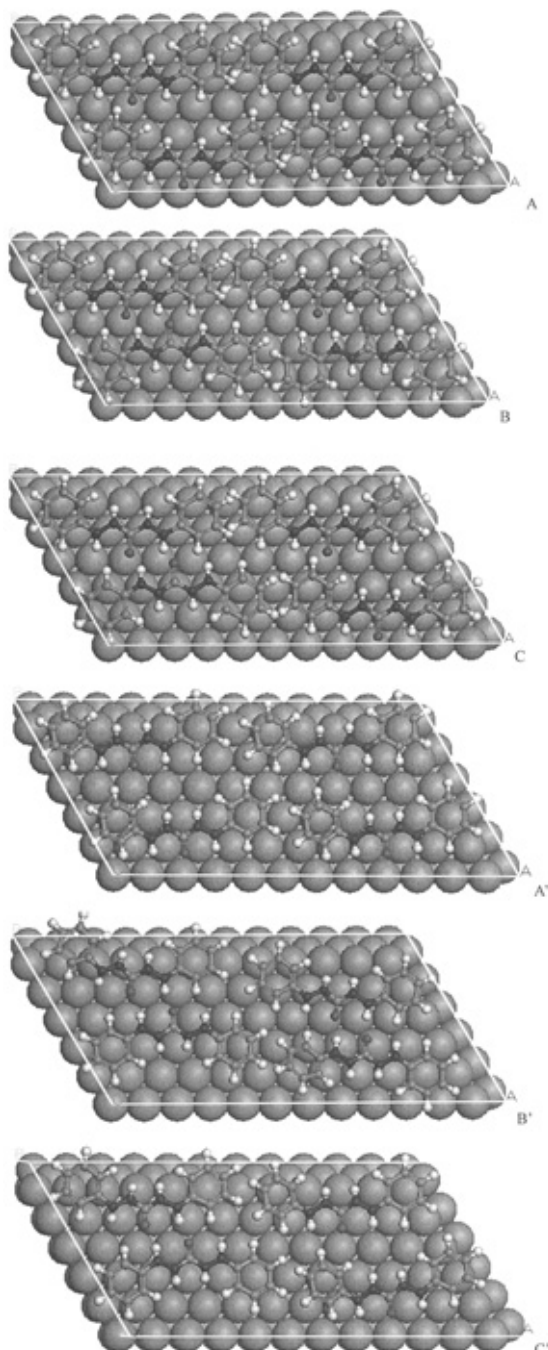

Fig. 5. Three different situations of the adsorption structure of four DPC molecules on the Cu (111) surface. A, B and C are the original structures; A', B' and C' are the adsorption structures by optimized MM.

In fact, there are several conformations for the high coverage situation since four DPC molecules were adsorbed on the copper surface. Three different conformations are discussed, as shown in Fig. 5. The original structures were optimized by MM and different final conformations were obtained. For these conformations, the nitrogen atoms and the oxygen atoms were all almost adsorbed on the 3-fold sites of the Cu (111) surface, but the adsorption sites of some carbon atoms in the phenyl rings were a little away from the 3-fold sites.

TABLE III. Energy of systems of three different states after performing molecular mechanics (MJ/mol)

System/Energy	Low coverage situation (one DPC molecule)	High coverage situation (four DPC molecules)
E_{total}	–11.6545	–12.8233
$E_{surface}$	–11.2512	–11.2449
E_{DPC}	–0.1018	–0.46607
$E_{interaction}$	–0.3015	–1.1124
$E_{interaction}$ for single DPC and surface	–0.3015	–0.2781

The potential energy and its components calculated by MM are list in Table III. The interaction energy was calculated using Eq. (3) and the corresponding data are also listed in Table III. For the low coverage and high coverage situation, the interaction energy between one DPC molecules and the copper surface are –301.5 and –278.1 kJ/mol, respectively. It is known that the energy of intermolecular interaction is about a few kJ/mol and that of a covalent bond is about several dozen kJ/mol. The value of the interaction energy is sufficient to form chemical bonds between the DPC molecule and the copper atoms.

The DPC molecule with two phenyl groups and four nitrogen atoms has a high summetry. The adsorption of organic inhibitor molecules on metals seems to arise mainly from the formation of strong chemical bonds between the nitrogen atoms and the metal atoms, which deplete the charge density of the *d*-orbital required for the metal atoms to bind with other species. In addition to the prominent metal–nitrogen bonds, a phenyl group can also interact with the *d*-orbital of a metal substrate through its π-electrons. The α-electrons of the –NH–NH– group and the π-electrons of the phenyl ring led to strong adsorption of DPC molecules on the copper surface. Finally, DPC can lie in the parallel orientation on the copper substrate, since this molecular configuration is thermodynamically more stable.

CONCLUSION

Oxygen atom and nitrogen atoms with high electronegativity and phenyl groups with large electron clouds in the DPC molecule could become active adsorption centers. The simulation results of MM showed that the α-electrons of the –NH–NH– groups and the π-electrons of the phenyl rings in DPC with a highly

symmetrical structure led to strong adsorption of DPC molecules on copper, while the results at different coverage indicated that the –NH–NH– group had much stronger interaction with the copper atoms than the phenyl rings.

The molecular simulation method could provide some information at the atomic level and might become a new theoretical prediction tool in the search for potential inhibitive organic SAMs on metals.

И З В О Д

МОЛЕКУЛАРНА СИМУЛАЦИЈА САМОУРЕЂУЈУЋИХ МОНОСЛОЈЕВА 1,5-ДИФЕНИЛКАРБАЗИДА НА ПОВРШИНИ БАКРА

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У раду је испитивана адсорпција самоуређеног слоја 1,5-дифеникарбазида (DPC) на површини бакра коришћењем молекуларне механике. Резултати показују да интеракције између α-електрона из –NH–NH– групе и π-електрона из фенилног прстена могу да доведу до јаке адсорпције високо симетричног молекула DPC на површини бакра. Синергетски ефекат фенилног прстена и –NH–NH– групе чини да цео молекул DPC лежи паралелно оријентисан на површини бакра при ниском степену покривености. Међутим, при високом степену покривености фенилни прстен је благо нагнут услед одбојних сила између молекула DPC, док –NH–NH– групе остају паралелне површини бакра.

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