Theoretical Investigation of 6-Mercaptopurine Isomers’ Adsorption on the Au(001) Surface: Revealing the Fate of Different Isomers

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ABSTRACT: Density functional theory (DFT) calculations were performed for the adsorption of different isomers of 6-mercaptopurine on the Au(001) surface. All of the configurations of four thione and two thiol isomers were considered. The results show that the thione isomers adsorbed more strongly on the Au(001) surface compared with the thiol ones. In all of the configurations, the calculated binding energy of ma-8 is the largest, in which the S atom of 6-mercaptopurine binds strongly with one Au atom on the monodentate sites and 6-mercaptopurine retains a flat geometry, predominantly with an approximately 30° orientation between the C=S bond and the Au–Au bond of the catalyst. Additionally, the 6-mercaptopurines in ma-2, mb-5, and mc-3 also bind more strongly onto the surface, which show relatively higher stability on the surfaces, indicating a high preference for adsorption. Charge density differences and TDOS analyses for the four configurations also show that the electronic charges are accumulated between Au and S atoms in the Au–S bonds, indicating occurrence of adsorption and chemical-bond formation.

INTRODUCTION

Gold has been used in many technological applications in the field of nanomaterials because of its high chemical stability, interesting optical properties, and good biocompatibility. Therefore, the surfaces of gold materials were extensively employed as a platform in building different devices based on the bottom-up approach either from the gas phase or from liquid media under ambient conditions. Thiol self-assembled monolayers (SAMs) on gold were discovered in the early 80 s and since then have attracted the interest of both the surface science and nanotechnology communities. These monolayers are robust and easy to prepare and represent fundamental building blocks for creating complex structures for a wide variety of nanotechnological applications, as they are simple means to link inorganic, organic, and biological materials to both planar and nanostructured gold surfaces. Specifically, thiol self-assembly becomes the simplest and most efficient route for functionalizing all kinds of substrate topographies including single crystals, polycrystals, and nanoparticles (NPs). This strategy permits us not only to design surfaces with controlled physical and chemical properties but also to perform additional chemical reactions to build complex molecular systems with specific activity. Nowadays, a wide range of thiol-based applications on gold surfaces are found in medicine, biochemistry, catalysis, and electronics. Because of the complexity of nanoparticle surfaces, researchers have been using solid surfaces to study various facets of Au nanoparticle surfaces. Carefully designed experimental studies have been undertaken on the adsorption of thiol species such as 6-mercaptopurine on the Au(100), Au(111), and Au(001) surfaces and hexanethiol on the Au(100) surface.

6-Mercaptopurine (6-MP) is one of the thiol family for which its interaction with Au surfaces has been studied theoretically and experimentally. Maza et al. investigated the self-assembled monolayers (SAMs) of 6-MP on the Au(100) – (1 × 1) and Au(111) – (1 × 1) surfaces to understand the interplay of molecule–substrate interactions for heterocyclic thiols capable of bonding to the surface by two anchors, which spontaneously form a highly disordered film on Au(111). Carro et al. reported a different scenario for 6-MP adsorption. Carro et al. showed that 6-MP lifts the reconstruction upon adsorption and ejects a large excess of gold adatoms. Their results show that 6-MP molecules prefer to arrange in highly ordered adatom-free domains in the bridging configuration, while the ejected adatoms form gold islands. Even though there are many reports to support the experimental results, some fundamental questions remain unanswered including: (1) What are the adsorbed configuration of thione and thiol on the Au surfaces? (2) Which one of the 6-MP isomers can stably adsorb on Au surfaces? (3) What are the corresponding adsorption energies? In this work, we provide answers to some of these questions by...
carrying out detailed density functional theory (DFT) based calculations.

In particular, the present work aims to elucidate the interactions of all different isomers of the thiones and thiols of 6-MP on the Au(001) surface to gain useful information about the most stable configurations of 6-MP on the Au surface. In the following, we give a brief description of our theoretical procedure, which is followed by a discussion of the results.

■ RESULTS AND DISCUSSION

Thione Isomer Adsorption on the Au(001) Surface. 6-MP(1,7) Isomer Adsorption Configurations. Based on whether one hydrogen atom is linked to the S atom, the 6-MP isomers can be categorized into two isomers, thione isomers and thiol isomers. For the thione isomers, according to refs16, 17, there are four predominant isomers of 6-MP(1,7), 6-MP(1,9), 6-MP(3,9), and 6-MP(3,7). For thiol isomers, there are two isomers for consideration: 6-MP(7,10) and 6-MP(9,10). We tried our best to check all of the possible adsorption modes, including monodentate and bridging bidentate, as illustrated in Scheme 1. The monodentate state

Scheme 1. Adsorption Mode of 6-MP Isomer Molecules on the Au Surface

![Scheme 1](image)

can be categorized into two types, thione and thiol isomers. We sampled three types of adsorption modes for thione and thiol isomers on the Au(001) surface according to Figure 1.

Figure 1. Chemical structure of the 6-mercaptopurine (6-MP) molecule.

Since the 6-MP(1,7) isomer is the most stable isomer in the gaseous phase, eight relatively stable configurations for this isomer on the Au(001) surface were first constructed, as shown in Figure 2. They are named ma-1, ma-2, ma-3, ma-4, ma-5, ma-6, ma-7, and ma-8. In Figure 2, the front, side, and top views of adsorption geometries are presented. The selected geometric parameters of the adsorbed 6-MP isomers are listed in Table 1, and the corresponding adsorption energies with inclusion of the vdW correction are also given in Table 2. After optimization, it is found that the most stable geometries of the adsorbed species have the monodentate type except for ma-2 which has the bridging bidentate type. In all cases, 6-MP(1,7) formed S–Au coordination bonds on the surface except for ma-4 and ma-5 cases. In these two cases, the shortest distances are 2.86 Å of H–Au for ma-4 and 3.28 Å of S–Au for ma-5, which shows that 6-MP is physisorbed in these two complexes and the corresponding interactions are very weak. In ma-1, ma-3, ma-6, ma-7, and ma-8 complexes, the S–Au bond distances are 2.62, 2.52, 2.57, 2.58, and 2.52 Å, respectively.

Specifically, in ma-2, a Au–S–Au bridging bidentate bond is formed with a bond angle of 75.3°.
The energy values in parentheses are calculated with the PBE-D3 method.

As shown in configurations from ma-1 to ma-8 in Figure 2, the 6-MP(1,7) isomer can also adsorb onto the Au(001) surface leading to S–Au bond formation. It can be seen from Table 2 that ma-8 has the largest adsorption energy, −21.56 kcal/mol. The second most stable configuration is ma-2, with an adsorption energy of −17.77 kcal/mol. In ma-2, the 6-MP(1,7) isomer is bridged to the Au atom on the surface via two S–Au bonds with lengths of 2.58 and 2.62 Å. The dihedral angle between the purine ring and the Au surface is almost 30°. In configuration ma-7, the dihedral angle is similar to that in ma-6. In configurations ma-4 and ma-5, the 6-MP(1,7) isomer did not link to the Au surface, and the corresponding Au–S distance in ma-5 is 3.28 Å. The adsorption geometries in Figure 2 also show that 6-MP in ma-4 and ma-5 interact with the surface only by long-range weak interactions. S–Au σ-bonds were not found for any of the stably adsorbed geometries. This suggests that they bind very loosely to the Au surface. In other words, on the Au(001) surface, the bridging bidentate is more favorable for the 6-MP(1,7) isomer. In ma-8, the S atom of 6-MP binds strongly with one Au atom on the monodentate sites and 6-MP retains a flat geometry, predominantly with about a 30° orientation between the C–S bond of 6-MP and the Au–Au bond of the surface.

**6-MP(1,9) Isomer Adsorption Configurations.** 6-MP(1,9) is different from 6-MP(1,7) because the hydrogen atom links to the N(9) atom instead of the N(7) atom. Both of these isomers are thione configurations. According to refs 16 and 17, the relative energies of these two isomers are very similar (relative energy is 3.0 kcal/mol at B3LYP/6-31+G**[Ref 16]), so studying the adsorption of the 6-MP(1,9) isomer to the Au(001) surface seems to be necessary. As shown in Figure 3, the adsorbed isomers were named mb-1, mb-2, mb-3, mb-4, and mb-5. The selected geometric parameters of adsorbed 6-MP isomers are also listed in Table 1, and the corresponding adsorption energies with inclusion of the vDW correction are also given in Table 2. As shown in Figure 3, the 6-MP(1,9) isomer can also adsorb onto the Au(001) surface via two potential modes, monodentate for configurations mb-2, mb-3, and mb-4 and bridging bidentate for mb-5. In these five configurations, the most stable one is mb-5, with an adsorption

### Table 1. Selected Geometries of Four Thione Tautomers 6-MP(1,7) and 6-MP(1,9) Adsorbed onto Au(001) Surface with the Method of PW91-D3

| adsorbate | converged geometry | $E_{ab}$ (kcal/mol) |
|-----------|--------------------|---------------------|
| 6-MP(1,7) | ma-1               | −11.53              |
|           | ma-2               | −17.77 (−16.30°)    |
|           | ma-3               | −14.06              |
|           | ma-4               | −2.44               |
|           | ma-5               | −6.09               |
|           | ma-6               | −12.38              |
|           | ma-7               | −8.95               |
|           | ma-8               | −21.56 (−20.40°)    |
|           | mb-1               | −16.23              |
|           | mb-2               | −5.24               |
|           | mb-3               | −6.76               |
|           | mb-4               | −13.92              |
|           | mb-5               | −18.94 (−17.50°)    |

**The energy values in parentheses are calculated with the PBE-D3 method.**

| species | optPBE-D3  | ma-1 | ma-2 | ma-3 | ma-4 | ma-5 | ma-6 | ma-7 | ma-8 | mb-1 | mb-2 | mb-3 | mb-4 | mb-5 |
|---------|------------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| S–Au    | 1.64       | 1.71 | 1.72 | 1.70 | 1.67 | 1.68 | 1.70 | 1.70 | 1.69 | 1.67 | 1.68 | 1.68 | 1.71 | 1.69 |
| H–Au    | 107.4      | 103.2| 107.4| 109.7| 152.4| 138.3| 119.9| 111.8| 119.9| 111.8| 110.1| 107.4| 109.7| 107.4|
| S–C     | 63.5       | 111.0| 94.7 | 49.4 | 94.1 | 89.5 | 87.6 | 78.8 | 115.8| 108.2| 50.9 | 32.3 | 75.3 | 68.2 |
| H–C     | 3.16       | 3.26 | 2.45 | 3.46 | 3.16 | 3.26 | 2.45 | 3.46 | 3.16 | 3.26 | 2.45 | 3.46 | 3.16 | 3.26 |
| S–H     | 1.68       | 1.69 | 1.67 | 1.69 | 1.69 | 1.67 | 1.69 | 1.67 | 1.69 | 1.67 | 1.69 | 1.67 | 1.69 | 1.69 |
| H–C     | 123.8      | 122.1| 122.1| 122.1| 122.1| 122.1| 122.1| 122.1| 122.1| 122.1| 122.1| 122.1| 122.1| 122.1|
| S–C     | 50.9       | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 | 50.9 |
| H–H     | 107.4      | 103.2| 107.4| 109.7| 152.4| 138.3| 119.9| 111.8| 119.9| 111.8| 110.1| 107.4| 109.7| 107.4|

"Au(100) in surface from ref 6. **Au(111) in surface from ref 6."
energy of $-18.94$ kcal/mol. In this configuration, 6-MP forms a $30^\circ$ tilting angle between the plane of the molecule and the Au surface. The isomer 6-MP(1,9) is also bridged to the Au surface atom via two S–Au bonds with distances of 2.58 and 2.62 Å. However, in configurations mb-2 and mb-3, the S–Au distances are 2.89 and 2.83 Å, implying that the bonds are relatively weaker and in mb-4, the S–Au distance is 2.48 Å, indicating that a strong bond is formed between the isomer and Au atom.

Two Isomers’ (6-MP(3,9) and 6-MP(3,7)) Adsorption Configurations. Both 6-MP(3,9) and 6-MP(3,7) are also two thione isomers. As seen from Figures 4 and 5, these adsorption configurations were named mc-1, mc-2, and mc-3 for 6-MP(3,9) configurations and md-1 and md-2 for 6-MP(3,7) configurations. The corresponding geometrical parameters are also listed in Table 1. As seen from Table 1, in mc-2, a weak interaction between the S atom and Au atoms are formed with distances of 3.26 and 3.46 Å. In mc-3, the S–Au bond is formed and the distance is 2.45 Å. The corresponding bond angle for C–S–Au is 122.1°. In mc-1 and mc-2, the optimized geometries retain an approximately vertical configuration with respect to the Au surface. Each of them adopted a 90° orientation with respect to the Au–Au bonds of the Au surface. Of particular interest in this study was the bonding style for certain geometries in the optimized adsorbate-cluster pairs. Table 3 shows that mc-3 is the most stable one with the adsorption energy of $-17.94$ kcal/mol, followed by mc-2 ($-9.95$ kcal/mol) with an energy difference of 7.99 kcal/mol.

In 6-MP(3,7) adsorption configurations, there are two complexes md-1 and md-2. In md-1, the optimized geometries retain an approximately vertical configuration with respect to
The energy values in parentheses are calculated with the PBE-D3 method.

Table 3. Adsorption Energies of Two Thiol Tautomers 6-MP(3,9) and 6-MP(3,7) Adsorbed onto the Au(001) Surface with the Method of PW91-D3

| adsorbate      | converged geometry | $E_\text{a}$ (kcal/mol) |
|----------------|-------------------|-------------------------|
| 6-MP(3,9)      | mc-1              | -2.37                   |
|                | mc-2              | -9.95                   |
|                | mc-3              | -17.94 (-16.60°)        |
| 6-MP(3,7)      | md-1              | -6.92                   |
|                | md-2              | -17.11 (-16.24)         |

Thiol Isomers’ Adsorption on the Au (001) Surface. 6-MP(7,10) Isomer Adsorption Configurations. In the thiol configurations, there are two main predominant isomers for consideration, 6-MP(7, 10) and 6-MP(9, 10). Four configurations were considered for the adsorption of 6-MP(7, 10): me-1, me-2, me-3, and me-4. Similarly, four configurations were considered for the adsorption of isomer 6-MP(9, 10): mf-1, mf-2, mf-3, and mf-4. They are given in Figures 6 and 7. From Figure 6, in the adsorbed complexes me-1, me-2, me-3, and me-4, the S atoms of the group −SH in me-2 and me-4 link directly to the Au surface with distances of 2.99 and 2.62 Å for the S−Au bonds. In this case, the interaction in me-4 is stronger than that in me-2. It is also determined that the angle C−S−Au is 148.3 and 111.0° in me-2 and me-4 configurations, respectively (see Table 5). They belong to classic monodentate bonds. However, in me-1 and me-3, it is the hydrogen atoms that interact weakly with the Au atoms on the surface. Moreover, in me-1, the distance between the hydrogen atom and the Au atom is 3.35 Å, implying relatively weak interaction. In me-3, the distance between the hydrogen atom and Au atom is 2.52 Å, implying relatively stronger interaction. In me-2, me-3 and me-4, the optimized geometries retain approximately vertical configurations on the Au surface, similar to 6-MP(1,9) shown in Figure 3. In me-2, me-3, and me-4, the molecule vertically adsorbed onto the Au surface and the only one exception, in me-1, that the molecule is also reclining. It is also shown from Table 4 that me-4 is the most stable configuration in the thiol isomers with the adsorption energy of −5.09 kcal/mol followed by me-3 with an energy difference of 0.78 kcal/mol with the adsorption energy of −4.31 kcal/mol. Me-1 and me-2 were found to have higher relative energies with adsorption energies of −3.85 and −3.58 kcal/mol, leading to bond breakage of H−Au and S−Au bonds.

6-MP(9,10) Isomer Adsorption Configurations. From Figure 7, in the adsorbed complexes of 6-MP(9,10), the S atoms of the −SH group in mf-2 and mf-4 also adsorbed directly to the Au surface with distances of 2.95 and 2.56 Å, respectively. According to Table 5, it is found that in mf-2, the angle C−S−Au is 128.9°, while it is 113.0° in mf-4. However, in mf-1 and mf-3, it is the hydrogen atom or nitrogen atom that interacts with the Au atom of the Au surface. In mf-1, the shortest distance between 6-MP and the Au atom is 3.65 Å, implying weak interaction only by long-range interactions; however, in mf-3, the shortest distance is 2.47 Å between the H atom and Au atom, and the second shortest distance is 3.10 Å between the N atom and Au atom, implying relatively strong interaction. In mf-2, mf-3, and mf-4, the molecule also adsorbed vertically to the Au surface, while in mf-1, the molecule is slightly tilted. As shown in Table 4, mf-4 is the most stable one with the adsorption energy of −5.06 kcal/mol, followed by mf-3 (−2.98 kcal/mol) with an energy difference of 2.08 kcal/mol. mf-1 and mf-2 were also found to be unstable with smaller adsorption energies of −2.07 and −2.53 kcal/mol, leading to bond breakage of H−Au and S−Au bonds.

Comparison of Two Methods. To evaluate the precision of the method used, we repeated the adsorption energy calculations of 6-MP to the Au surface using the PW91-D3 functional and then performed single-point calculations for the more stable configurations using the vdW corrected functional of optPBE-vdW. The results of ma-2, ma-8, mb-5, and mc-3 are listed in Table 3. When the energies of these two methods (PW91-D3 and optPBE-D3) are compared, it is found that the adsorption energies are slightly different because a stronger binding between 6-MP and the Au surface is suggested. After
Distances are given in angstroms. D3 calculation results show a systematic increase of the adsorption energy by 1.44 kcal/mol. For the energy is increased to 17.11 kcal/mol by 0.87 kcal/mol. For the S atom, the energy is increased to 17.50 kcal/mol from 16.30 kcal/mol.

The charge density difference isosurfaces for the four most stable adsorption configurations are given in Figure 8. As can be seen from Figure 8, charge density difference isosurfaces show that the electronic charge is accumulated between Au and S atoms in the Au–S bonds. This behavior shows the stronger and more covalent character during S–Au bond formation. The isosurfaces also show that the electronic charges on ma-2 and mb-5 are more than those on ma-8 and mc-3. This mainly resulted from the differences between the double and single Au–S chemical bonds. The isosurfaces also reveal that the electronic charges on ma-2 and mb-5 accumulated on the Au surfaces and, moreover, the electronic charges on ma-2 accumulated nearly twice for the S atom at the bridge site than that found on mb-5.

Since the 6-MP geometry with the S atom in the bridge position interacting with the gold substrate is energetically the most favored configuration, one would expect that all of the molecules should adsorb in this configuration similar to ma-2 and mb-5. However, this arrangement implies a large tilting (Figure 3a,b) and therefore a smaller surface coverage than that obtained with less tilted configurations.

The Bader charge analyses for the Au–S–C–N bonds of the 6-MP molecules are also given in Table 6. The results indicate that the S and N atoms in ma-2 and mb-5 are negatively charged, while the S atoms in ma-8 and mc-3 are positively charged, and the N atoms are negatively charged. However, all Au atoms are positively charged except for Au(1) in mb-5 for which the partial charge is zero. This indicates that charge is transferred from Au atoms to the S atoms and the chemical bonds are indeed formed. The charges from the N to S atoms are much larger than that found from the Au to the S atoms. These results are similar to those found for the 6-MP molecules on the Au(111) and Au(100) surfaces. All of the results show that the charge transfer in ma-2 is dramatic in all of the complexes because of double-bond formation. In Table 7, the bond orders of the Au–S bond for four complexes ma-2, ma-8, mb-5, and mc-3 are also given, and from the data, we can conclude that in ma-8 and mc-3, the S–Au bond is relatively stronger because of the larger bond order, and for ma-2 and mb-5, it is relatively weaker. But, it shows that the chemical bonds are formed for these four configurations.

To further obtain information about the interaction of 6-MP isomers adsorbed on the Au(001) surface in detail, the density of states (DOS) has also been investigated for four configurations ma-2, ma-8, mb-5, and mc-3. Total density of states (TDOS) is given in Figure 9, in which the two figures at the bottom are for a clean Au surface and an isolated 6-MP. As seen from the changes of TDOS plots, one can conclude that for the Au(001) surface, 6-MP adsorption configurations exhibit a similar electronic state distribution for the reason that their types of surface atom sites are equivalent. Four Au surfaces are sensitive to 6-MP molecule adsorption. In other words, the adsorbed molecules expose an important influence on the electronic properties of Au(001) clean surfaces. However, for the S atom of the 6-MP molecule, the TDOS peaks have moved to a lower energy and remain slightly far from the Fermi level compared to those of the isolated 6-MP molecule. Turning to the Au(001) surface, the TDOS main peaks have moved to a lower energy for the S atoms. This behavior shows that the electronic charge is accumulated between Au and S atoms in the Au–S bonds.
peaks have moved to a higher energy and remain close to the Fermi level compared to those of the clean surface before adsorption. The intrinsic bonding mechanism for 6-MP molecule adsorption on Au(001) surfaces can be obtained by analyzing the PDOS in the adsorbed systems. Thus, the existence of a covalent bond between 6-MP and Au(001) surfaces is understandable.

## COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were performed using the VASP 5.2.2 program. Two functionals, PW91 and Perdew-Burke-Ernzerhof (PBE), were employed. To correctly account for van der Waals (vdW) interactions, we used the DFT-D3 method with Becke-Johnson (BJ) damping. This combination of the functional and dispersion correction has been shown by Goerigk and Grimme to provide a very robust description of vdW effects in comparison with other GGA-based formulations. The projector augmented plane wave (PAW) method has been used to represent the atomic cores with the PBE potential. The energy cut off was set to be 450 eV. A $5 \times 5 \times 1$ Monkhorst-Pack $k$-point mesh per unit cell was used. The Au(001) substrates were represented by a five atomic layer and a vacuum of about $\sim 17$ Å that separates two successive slabs. Surface relaxation is allowed in the three uppermost Au layers of the slab, and the atomic coordinates of the adsorbed species were allowed to relax without further constraints. To prepare the 6-MP-Au(001) complexes, the adsorbates are placed on just one side of the slab at different initial configurations. Radical 6-MP species were optimized in an asymmetric box of $20 \times 20^\circ \times 40$ Å. The calculated Au lattice constant is 4.16 Å, which is in good agreement with the experimental value (4.078 or 4.080 Å). One 6-MP molecule was placed on the surface of the $3 \times 3$ supercell to eliminate the interaction of neighboring molecules. The average binding energy per adsorbed 6-MP species on Au(001) surfaces, $E_b$, is defined in the following equation:

$$E_b = E_{(6-MP/Au)} - E_{(Au)} - E_{(6-MP)}$$

in which $E_{(6-MP/Au)}$, $E_{(Au)}$, and $E_{(6-MP)}$ are the total electronic energies of the adsorbed 6-MP on a Au(001) surface, a bare
Au(001) surface, and a 6-MP molecule in a vacuum, respectively. If this value is a negative number, the adsorption is exothermic.

A more negative $E_b$ value also indicates stronger (exothermic) adsorption. The most stable complexes were reoptimized using the PBE-D3 method. The geometries and absorption energies were found not to be sensitive to the choice of the functional according to our results (See Table 2 in the next Section).

**CONCLUSIONS**

Density functional theory (DFT) calculations were performed for the adsorption of different isomers for 6-mercaptopurine on the Au(001) surface. Two functionals, PW91 and Perdew–Burke–Ernzerhof (PBE), were employed. To correctly account for van der Waals (vdW) interactions, we used the DFT-D3 method with Becke–Johnson (BJ) damping. All of the configurations of four thione and two thiol isomers were considered. The results show that the adsorption of thione isomers is much stronger than that of thiol isomers. In all of the configurations, the binding energy of ma-8 is the largest, in which the S atom of 6-mercaptopurine binds strongly with one Au atom on the monodentate sites and 6-mercaptopurine retains a flat geometry, predominantly with about a 30° orientation between the C–S bond of 6-mercaptopurine and the Au–Au bond of the catalyst. Additionally, the 6-mercaptopurines in ma-2, mb-5, and mc-3 also bind more strongly to the surface and they show relatively higher stability on the surfaces, indicating a high preference for adsorption of these forms. Charge density difference analysis also shows that the electronic charges are accumulated between Au and S atoms in the Au–S bonds.

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**Notes**

The authors declare no competing financial interest.

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