Supporting Information

Interaction of the $(2\sqrt{3} \times 3)$rect. Adsorption-Site Basis and Alkyl-Chain Close Packing in Alkanethiol Self-Assembled Monolayers on Au(111): A Molecular Dynamics Study of Alkyl-Chain Conformation

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Figure S1. The eye-cross stereo image pair of the molecular geometry. In this alkyl-chain centric model the molecular axis passes through the origin where it intersects the surface. The tilt angle ($\theta$) is defined by the angle between the surface normal and the axis of the molecule (molecular axis). The twist of the molecular backbone ($\phi$) is defined by the angle between the tilt plane (green plane) containing the surface normal and the molecular axis and the plane of the carbon atoms (blue plane, the molecular plane). Zero twist angle is defined where these two planes coincide and the bond between the head group and alpha methylene makes the largest angle with respect to the surface normal ($\alpha$-CH$_2$ is closer to the substrate). The twist angle increases positively in the counterclockwise direction while looking down the molecular axis (right-handed coordinate system). The direction of the tilt ($\chi$) is the angle between the positive x-axis and the projection of the molecular axis on the plane of the substrate (xy-plane).
A. Discussion of alkyl chain twist angles measurements by infrared reflection absorption spectroscopy (IRRAS)

The principle experimental measurements of the twist of the alkyl-chain plane (φ) in SAMs come from IRRAS. Nuzzo et al.\textsuperscript{1-2} use a single-chain per unit-cell model and report a twist angle of 55°. The most recent study of Laibinis et al.\textsuperscript{3} followed up the previous work using a two-chain per unit-cell model and report twist angles of $-48^\circ$ and $+50^\circ$. We use this latter work for comparison to our simulations. Because a clear and consistent definition of the molecular twist angle is critical for comparison of simulation and experiment, and because the definition of φ (and its zero) in ref. 3 is muddied by the introduction of positive and negative tilt angles, we will discuss the definition in detail for further clarification.\textsuperscript{4} We also justify our interpretation of the reported twist angles as $\phi = +132^\circ$ and $+50^\circ$, based on the inherent symmetries and the discussion in ref. 3.

The molecular geometry of an all-trans alkane chain can be visualized by applying three rotations to the molecule. We begin with the molecule standing straight up on the surface (xy-plane) with the alkyl-chain axis (molecular axis) aligned with the surface normal (z-axis). The alkyl plane aligned with the xz-plane, with the projection of the S to $\alpha$-CH$_2$ bond vector pointing in the $+x$-direction. This standing up conformation of the molecule corresponds to zero tilt ($\theta = 0^\circ$) and zero twist ($\phi = 0^\circ$). Now, rotation of the standing up alkane chain about its molecular axis (z-axis) in the counterclockwise direction (while looking down the molecular axis toward the surface) introduces positive twist. The tilt of a molecule is achieved by rotation of the molecular axis about the y-axis where tilting towards the $+x$-axis is described as a positive tilt. For tilt direction ($\chi$), the tilted molecule is again rotated around the z-axis (rotation from $+x$-axis to $+y$-axis is defined as the positive $\chi$). Stated another way, the angles are defined using the right-handed coordinate convention.
Figure S2 shows two views of the molecular twist looking along the physical rotation axis (Figure 2, Left) and the molecular axis (Figure 2, Right). The twist of a chain is defined by the relative orientation of the carbon plane and the tilt plane, as shown in Figure S1. For an all-trans chain in this projection, the twist angle is defined by the angle between the tilt direction and the first bond (S-αCH₂). With the sulfur fixed on the surface, changing the twist angle causes the molecular axis to precess around the sulfur. Changing the twist also changes the Au-S-CH₂ bond angle. Twisting a single chain within a SAM would also change its distance to neighboring chains. We depict two twist angles, φ = +132° and +50° (see the discussion below).
For a full understanding of the reported φ values in ref. 3, we need to discuss the basics of the IRRAS measurement and how φ is determined. IRRAS is sensitive to the orientation of the transition dipole of the mode in the monolayer. The component of the transition dipole normal to the metallic substrate (Au(111) in our case) contributes to the IRRAS absorption, while the parallel component to the substrate is strongly suppressed. Consequently, the observed intensity varies with the cosine square of the angle of the mode with the surface normal. The angle of the mode to the surface normal can be obtained by comparing the intensity in the film to that of a suitable reference phase. Typically, a polycrystalline solid phase alkanethiol or disulfide has been used, which has alkyl chain conformations and molecular environment closely related to that found in SAMs. This approach also relies on the assumption that the transition dipole strength in the SAM is the same as that in the reference phase. This assumption has been shown to work well for the methylene stretching modes, but not so well for the methyl stretching modes,1-3 as we will discuss.

The infrared modes used to measure the chain twist are those of the d+ and d− methylene stretching. These two modes and the molecular axis are mutually orthogonal. The d+ involves the CH2 symmetric stretching, where the stretching vibration of the odd and even CH2s are 180° out of phase—antisymmetric in the plane of the chain. The d− involves the CH2 antisymmetric stretching, where the stretching vibration of the odd and even CH2s are in phase—antisymmetric out of the plane of the chain. For a given tilt angle, the d+ intensity will be maximum at φ = 0° and 180° and zero at 90° and 270°. The d− intensity is offset by 90°, with maximum at φ = 90° and 270° and zero at 0° and 180°. These properties give the mode intensities C2 symmetry about the molecular axis (φ = φ + 180°) as well as two mirror planes—the tilt plane (φ = −φ) and the plane perpendicular to the tilt plane containing the molecular axis (φ = 180° − φ). As a result,
methylene modes alone cannot distinguish between symmetry equivalent twists, i.e. $\phi = -50^\circ$, $+50^\circ$, $+130^\circ$, and $-130^\circ$ will have the same $d^+$ and $d^-$ intensities.

The three methyl stretching modes have different symmetry with respect to the twist angle and should in principle further constrain the twist angle. The $r^+$ symmetric stretch is oriented along the CH$_2$-CH$_3$ bond. The $r_a^-$ antisymmetric stretch is perpendicular to the CH$_2$-CH$_3$ bond and in the plane of the alkyl chain. The $r_b^-$ antisymmetric stretch is perpendicular to the CH$_2$-CH$_3$ bond and perpendicular to the plane of the alkyl chain. Unlike the symmetry of the methylene modes, the methyl $r^+$ and $r_a^-$ modes possess only mirror plane symmetry—the tilt plane ($\phi = -\phi$). The $r_b^-$ mode has the same symmetry as the methylene $d^-$ mode. The lower symmetry of the methyl modes could further constrain the twist angle within the tilt-plane mirror symmetry. Twist angles in the range 90° to 270° (through 180°) orient the CH$_2$-CH$_3$ bond more normal to the surface—increasing the intensity of $r^+$ mode and decreasing the intensity of $r_a^-$ mode. Whereas twist angles in the range $-90^\circ$ to $+90^\circ$ (through 0°) orient the CH$_2$-CH$_3$ bond more parallel to the surface—increasing the intensity of $r_b^-$ mode and decreasing the intensity of $r^+$ mode. Therefore, these two modes can be used to distinguish twists related by C$_2$ symmetry about the molecular axis and mirror symmetry about the plane perpendicular to the tilt plane containing the molecular axis. However, the methyl modes are complicated by Fermi resonances and the intensities in the SAM do not correspond as well with the reference phase as do the methylene modes. Since the methyl mode intensities do not correspond well to the reference phase, good fits for CH$_2$ and CH$_3$ modes could not be achieved by twisting the molecule alone. In addition, the $r_b^-$ is weaker in the SAM and appears as a shoulder on the stronger $r_a^-$, thus not as useful for molecular orientation. Therefore, more interpretation was required.

Given these symmetries, it is perplexing why Laibinis et al. report $\phi = -48^\circ$ and $+50^\circ$, which should be practically indistinguishable from the methylene and methyl modes. They use two
arguments to guide their interpretation. First, the observed odd-even methyl-mode intensity oscillation. Second, the hypothesis that the surface-S-CH₂ bond orientation and/or torsion angles should be the same for all the molecules. The latter is quite reasonable from the prevailing view at the time, that all the molecules had the same adsorption site, but is not generally the case for the models we consider in our work presented here. Below, we discuss the former line of reasoning.

The intensity of the \( r^+ \) mode is observed to be strongest for even-length chains and lower for odd-length chains. The \( r^- \) mode displays the opposite odd-even dependence. The conclusion is that the CH₂-CH₃ bond is more normal to the surface for even than for odd.\(^5\) This supports the hypothesis that the twist angle is in the range \(-90^\circ\) to \(+90^\circ\). However, their models over predict the magnitude of the oscillation by factor of 2–3 (ref. 3, Figure 5). Nevertheless, they say the two twist angles were restricted to the range of \(-90^\circ\) to \(+90^\circ\) for their fitting. This was argued as satisfying the “methyl surface corrugation” (ref. 3 footnote 43), which we presume to mean the orientation of the methyl groups. This choice of twist angles has the effect of increasing \( r^+ \) at the expense of \( r^- \). Reasonable fits of the methyl modes required assuming 45% gauche fraction of the C-C-C-CH₃ bond. That equally good fits could have been obtained choosing instead \( \phi = +132^\circ \) and \(+50^\circ\) seems likely given the data shown in (ref. 3, Figures 8 and 9). Although that choice would make the surface-S-CH₂ bond orientation and/or torsion angles different for the two twist classes. There is also a logical inconsistency in the discussion of the angular difference between the two twist angles. The discussion concludes the difference should be \( 82^\circ \), but the difference between the reported angles is \( 98^\circ \). The choice of \( \phi = +132^\circ \) and \(+50^\circ\) would satisfy the \( 82^\circ \) difference.
B. Gauche fraction definition

In the all-trans configuration of the alkyl chain, all the carbon atoms lie on a plane—the molecular plane (Figure S1, blue plane). Thermal motion causes the carbon atoms to deviate from the all-trans molecular plane. Excursions of each C–C–C–C bond dihedral angle ($\Psi$) from the trans energy well into the adjacent gauche wells can be quantified by the gauche fraction.

Figure S3. The C–C–C–C dihedral potential energy ($E_\Psi$) term is plotted against the dihedral angle ($\Psi$) on the left y-axis. The trans and two gauche conformations are noted. On the right y-axis, we plotted the probability density function of the dihedral angle ($PDF_\Psi$) for model A at 200 K. We use semi-log axis for $PDF_\Psi$ to better illustrate the gauche population as gauche population is significantly smaller than the trans population.

The torsion around the $C_{i-1}C_iC_{i+1}$ bond is characterized by the $C_{i-1}C_iC_{i+1}C_{i+2}$ dihedral angle, defined by the angle between the planes containing $C_{i-1}, C_i, C_{i+1}$ and $C_i, C_{i+1}, C_{i+2}$ where the anticlockwise rotation of the $C_{i+1}C_{i+2}$ bond about the $C_{i-1}C_i$ bond defines the positive increment.
of $\Psi$ keeping the $C_{i-1}--C_i$ bond unchanged. For a C10 molecule the index $i$ runs from 1 to 8, where $C_1$ is the alpha carbon and $C_0$ is the sulfur.

The C-C-C-C dihedral potential ($E_\Psi$) is shown in Figure S3 (left vertical axis), with the parameters given in Table S3. There is a global energy minimum at $180^\circ$ (trans, antiperiplanar) and two local minima at $65^\circ$ and $295^\circ$ (gauche, synclinal). The C-C-C-C bond conformation is termed trans (all four carbon atoms lie on a plane) when $150^\circ \leq \Psi \leq 210^\circ$ corresponding to the minimum energy configuration of $\Psi$. Deviation from the trans conformation could result in one of the two gauche conformations namely positive gauche (+gauche) and negative gauche (−gauche) and they are defined as follows: for +gauche, $30^\circ \leq \Psi \leq 90^\circ$ and for −gauche, $270^\circ \leq \Psi \leq 330^\circ$.

The $\Psi$ probability density function ($PDF_\Psi$) for model A at 200 K is overlaid in Figure S3 (right vertical axis) showing the distribution of dihedral angles. The semi-log $PDF_\Psi$ plot shows most of the dihedral angles lie in the trans well (99.33 %) with a very small population in the gauche wells (0.67 %), i.e. molecules are predominantly trans in the monolayer. Consistent with previous studies, most of the gauche conformations reside at the surface. The terminal dihedral bonds have a 4.5% gauche fraction, which is 85% of the gauche population in the monolayer. Note the local maxima of the $PDF_\Psi$ for the gauche conformations does not occur at the gauche potential energy minima, but is biased towards the trans conformation side of the wells. This is because the molecules are also subject to C-C-C-H and H-C-C-H dihedral potentials—$PDF_\Psi$ is a system property.

For the purpose of characterizing the gauche fraction, dihedral angles $0–120^\circ$ are counted as +gauche and $240–360^\circ$, as −gauche, corresponding to the potential energy wells, shown as two green regions in Figure S3. The gauche fraction presented in the paper (Figure 3) is calculated as follows:
Here \( N_{+\text{gauche}} \), \( N_{-\text{gauche}} \), and \( N_{\text{total}} \) are the population of the dihedral angle in the positive and negative gauche regions and the total population of the C-C-C-C dihedral angle respectively. Such that \( N_{\text{total}} = N_{+\text{gauche}} + N_{-\text{gauche}} + N_{\text{trans}} \).

C. Force field parameters

Bond stretching: \( K_r (r - r_0)^2 \)

Table S1. Force Field Parameters for Bond Stretching

| Bond       | \( r_0 \) (Å) | \( K_r \) (kcal/ mol Å\(^2\)) |
|------------|---------------|-------------------------------|
| S-C\(^9\)  | 1.81          | 222                           |
| C-H\(^{10}\)| 1.09          | 340                           |
| C-C\(^{10}\)| 1.529         | 268                           |

Bond bending: \( K_\theta (\theta - \theta_0)^2 \)

Table S2. Force Field Parameters for Bond Bending

| Bond Angle | \( \theta_0 \) (°) | \( K_\theta \) (kcal/ mol rad\(^2\)) |
|------------|-------------------|-------------------------------------|
| ∠S-C-C\(^9\)| 114.7             | 50.0                                |
| ∠C-C-C\(^{10}\)| 112.7             | 58.35                               |
| ∠C-C-H\(^{10}\)| 110.7             | 37.5                                |
| ∠H-C-H\(^{10}\)| 107.8             | 33.0                                |

Dihedral angle vibration: \( \frac{1}{2} K_\phi^1 (1 + \cos \phi) + \frac{1}{2} K_\phi^2 (1 - \cos 2\phi) + \frac{1}{2} K_\phi^3 (1 + \cos 3\phi) \)
Table S3. Fourier Components of the Dihedral Angles

| Dihedral Angle | $K^1_\phi$ (kcal/mol) | $K^2_\phi$ (kcal/mol) | $K^3_\phi$ (kcal/mol) |
|----------------|------------------------|------------------------|------------------------|
| C-C-C-C$^{11}$ | 0.528                  | -0.186                 | 0.900                  |
| C-C-C-H$^{12}$ | 0                      | 0                      | 0.366                  |
| H-C-C-H$^{11}$ | 0                      | 0                      | 0.150                  |

Non-bonded interaction: $4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) + C \frac{q_i q_j}{\varepsilon_0 r}$, where $r < r_c = 12$ Å.

Table S4. Force Field Parameters for Non-Bonded Interactions

| Interaction Site | $\sigma$ (Å) | $\varepsilon$ (kcal/mol) | $q_i$ (e) |
|------------------|--------------|--------------------------|----------|
| Au$_{adatom}^{13}$ | 2.934        | 0.039                    | 0        |
| S$^{12}$         | 3.550        | 0.250                    | 0        |
| C (in CH$_2$)$^{11}$ | 3.5          | 0.066                    | -0.12    |
| C (in CH$_3$)$^{11}$ | 3.5          | 0.066                    | -0.18    |
| H (in CH$_2$)$^{11}$ | 2.5          | 0.030                    | 0.06     |
| H (in CH$_3$)$^{11}$ | 2.5          | 0.030                    | 0.06     |

The cutoff distance for both the vdW interaction and the Coulombic potential is the same, 12 Å. The mixing rule used is $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$. The Coulombic interaction is treated via PPPM method.
D. Structure of different models of Au-S interface

Initially, the coordinates for the sulfur and Au adatoms are taken from the references mentioned cited in (Table 1). However, due to the inconsistent (2\sqrt{3} \times 3) rect. unitcell dimensions, we have rescaled all the coordinates using the Au-Au distance of 2.88376 Å.\textsuperscript{14} The corresponding size of the unitcell is (8.65127 Å \times 9.98963 Å). All the Au/S interface models are simulated with and without the top layer of Au atoms (nominal Au(111) surface atoms). Inclusion of these Au atoms did not affect the simulation results for the SAMs, but does increase the computational expense. Thus we conclude the top-layer gold atoms are not a critical component for our MD modeling of the SAM structure, therefore not reported in Table S5. The coordinates (Å) of the sulfur atoms and the gold adatoms for each model are reported in Table S5. We have used 6 significant figures to reduce round-off errors.
Table S5. Sulfur and Gold Adatom Coordinates

| Model | Adatoms | Vacancies | Coordinate of S atoms [x, y, z] | Coordinate of Au Adatoms |
|-------|---------|-----------|-------------------------------|-------------------------|
| A     | 1       | 1         | [-8.32380, 3.31830, 13.32000];  | [-3.52380, 9.77170, 13.32000]. |
|       |         |           | [-4.69710, 5.39830, 13.32000];  |                         |
|       |         |           | [-9.65710, 8.81170, 13.92000];  |                         |
|       |         |           | [-5.17710, 10.89170, 13.92000]. |                         |
| B     | 4       | 0         | [6.47838, 3.77866, 1.36841];    | [7.05530, 2.32384, -0.42612]; |
|       |         |           | [2.17786, 6.35487, 1.44976];    | [2.94827, 4.95950, -0.33068]; |
|       |         |           | [6.74862, 8.15539, -0.05977];   | [6.19585, 5.82202, 0.14563];  |
|       |         |           | [2.34536, 10.70081, -0.07553].  | [1.85646, 8.34482, 0.12379].  |
| C     | 0       | 0         | [-6.09580, -0.95400, 14.43490]; | N/A                     |
|       |         |           | [-2.38030, 1.95350, 14.09960];  |                         |
|       |         |           | [-6.51550, 5.19760, 14.89380];  |                         |
|       |         |           | [-1.43590, 7.87580, 14.94380].  |                         |
| D     | 2       | 0         | [-2.79830, 0.22660, 5.03000];   | [-2.88570, 2.49908, 5.47000]; |
|       |         |           | [-7.60550, 2.58650, 5.03000];   | [-7.16840, 4.85900, 5.47000]. |
|       |         |           | [-3.32270, 4.68420, 5.03000];   |                         |
|       |         |           | [-7.16840, 7.04400, 5.03000].   |                         |
| E     | 1.2     | 2.8       | [6.97806, 1.12880, 16.00281];   | [3.40381, 6.76089, 16.38680]; |
|       |         |           | [2.65246, 3.62619, 16.00281];   | [-0.92179, 6.76089, 16.38680].|
|       |         |           | [5.29453, 5.22251, 16.70918];   |                         |
|       |         |           | [0.96893, 7.71989, 16.70918].   |                         |
|  |  |  |  |  |
|---|---|---|---|---|
| **F** | 4 | 0 | [-10.09329, 5.82739, 4.80000]; [-5.76760, 8.32483, 4.80000]; [-10.09329, 9.15733, 4.80000]; [-5.76760, 11.65478, 4.80000]. | [-10.09329, 5.82739, 2.40000]; [-5.76760, 8.32483, 2.40000]; [-10.09329, 9.15733, 2.40000]; [-5.76760, 11.65478, 2.40000]. |
| **G** | 2 | 0 | [7.52002, 2.91155, 9.87941]; [3.49748, 5.52212, 9.93266]; [8.03580, 7.56142, 9.83508]; [3.38609, 10.17833, 9.73591]. | [7.65434, 5.24762, 9.72556]; [3.24224, 7.84172, 9.69442]. |
| **H** | 2 | 1 | [7.40589, 2.86455, 9.78721]; [3.48157, 5.51290, 9.83151]; [8.04538, 7.50390, 9.84549]; [3.32828, 10.18725, 9.67556]. | [7.60367, 5.20053, 9.69969]; [3.20234, 7.84312, 9.64630]. |
| **I** | 2 | 1 | [7.59130, 2.70457, 9.74405]; [3.48331, 5.20823, 9.80910]; [7.86329, 7.37781, 9.80354]; [3.22494, 9.88605, 9.80267]. | [7.55506, 5.05234, 9.64422]; [3.22828, 7.53903, 9.67939]. |
| **J** | 2 | 1 | [7.62810, 2.73302, 9.80484]; | [7.52526, 5.07040, 9.64368]; [3.17018, 7.53873, 9.59298]. |
|  |  |  |  |  |
E. Spatial distribution of molecular height at 250 K

Figure S4. The spatial distribution of the height difference at the methyl interface at 250 K for models A-J. The numbering scheme for the basis types is same as that shown in Table 1 in the main paper. For better visualization, the $(2\sqrt{3} \times 3)$ rect. unit cell (blue box) is tiled $3 \times 3$ for easy visualization of the patterns. The position of the circles is the average position of the methyl groups and the color of the circle represent the average height of the molecule. The gray scale is kept the same for all the models for better comparison, the higher molecules are represented by the lighter shades.
F. Average height of the basis molecules for the models at 250 K

Figure S5. The average height of the four basis-type methyl-group C atoms at 250 K from the Au(111) substrate for each model separated by contribution. The darker segments (Au-S) represent the z-height of the S head groups from the Au(111) substrate, the contribution to the z-height from the S atom adsorption site. The lighter segments (S-CH₃) represent the z-height of the methyl group C atoms from the corresponding S atoms, the contribution to the z-height from the molecular conformation.
G. Comparison of basis molecule average height, SD, and SDoM at 200 and 250 K

Figure S6. The standard deviation (SD) and the standard deviation of the mean (SDoM) for molecular heights are shown for each basis type for ten models. The black vertical error bars represent the SD of height, whereas the small (~50 time smaller than the SD) magenta bars shows the corresponding SDoM. Notice the height difference between 200 K and 250 K and the larger SD error bars for 250 K.
G. Spatial distribution of the folded twist at 250 K

Figure S7. The spatial distribution of the molecular twist is shown for ten Au-S interfacial models at 250 K for models A-J. The position of the circles is the average position of the methyl groups, and the color of the circle represents the average value of the folded twist; Blue: $0^\circ \leq \phi < 90^\circ$ and Red: $90^\circ \leq \phi < 180^\circ$. The corresponding tilt direction (black arrow) and the $(2\sqrt{3} \times 3)$rect. unit cell (gray rectangle) are shown for comparison. The numbering scheme for the basis molecules is the same as in Table 1 in the main paper. The $(2\sqrt{3} \times 3)$rect. unit cell is tiled $3 \times 3$ for easy visualization of the patterns.
Figure S8. The alkyl chain geometry of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reference structure in the reduced close-packed coordinate system (see main paper). The S head group positions are at the vertex of the arrow and the magenta lines. The chain axis is located at the end of the arrow. The magenta lines for each arrow indicated the chain tilt direction. The twist is the angle between the magenta line and the arrow. The dotted ellipses show the possible positions of the idealized all-trans alkyl chain axis as the twist is swept in a full circle around the S headgroup. The basis types are indicated by the color of the arrows (red = 1, green = 2, blue = 3, and black = 4).
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(4) The molecular symmetry relates the twist at positive tilt angle with the twist at negative tilt angle: $\theta = -\theta$ and $\varphi = 180^\circ + \varphi$.

(5) The discussion in Ref. 3 sometimes uses odd and even to refer to the number of methylenes HS(CH$_2$)$_n$CH$_3$ and sometimes odd-even with respect to the total number of carbon atoms HSC$_n$H(2$n$+1).

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(7) The definition of +gauche and −gauche is more obvious when the conformation is described in terms of the torsion angle. These describe the same angle, but the dihedral angle is
defined between 0° and 360° with the zero at the cis conformation. The torison angle is
defines between −180° and +180° with the zero at the trans conformation.

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