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Effect of Sulfur Oxidation on the Transmission Mechanism of $^4J_{HH}$ NMR Coupling Constants in 1,3-Dithiane

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Long-range $^4J_{HH}$ couplings in 1,3-dithiane derivatives are rationalized in terms of the effects of hyperconjugative interactions involving the S═O group. Theoretical and experimental studies of $^4J_{HH}$ couplings were carried out in 1,3-dithiane-1-oxide (**2**), *cis*-1,3-dithiane-1,3-dioxide (**3**), 1,3-dithiane-1,1,3-trioxide (**4**), and 1,3-dithiane-1,1,3,3-tetraoxide (**5**) compounds. Hyperconjugative interactions were studied with the natural bond orbital, NBO, method. Hyperconjugative interactions involving the $\mathrm{LP_O}$, oxygen lone pair and $\sigma^*_{\mathrm{C2-S1}}$ and $\sigma^*_{\mathrm{S1-C6}}$ antibonding orbitals yield an increase of $^4J_{H_{eq}-H_{eq}}$ couplings. Long-range $^4J_{H_{ax}-H_{ax}}$ couplings were also observed between hydrogen atoms in axial orientation, which are rationalized as originating in hyperconjugative interactions involving the bonding $\sigma_{\mathrm{C_6-H_{ax}}}$ and antibonding $\sigma^*_{\mathrm{S=O}}$ orbitals. The symmetry for orbital interactions is possible only when the S═O group is in the axial orientation.

Introduction

Stereochemical properties of NMR spin−spin coupling constants (SSCCs) are mostly based on the ability of their Fermi contact (FC) terms for being transmitted through the electronic molecular structure.[1,2] For $^nJ_{XY}$ couplings with $n \leq 3$ as well as for through-space SSCCs, exchange interactions play a key role in their transmission. On the other hand, for $n > 3$, charge-transfer interactions are excellent carriers for the spin information associated to the FC interaction.[3] In this context, the most important sources of stereochemical information were, for many years, $^3J_{HH}$ SSCCs, which are strongly dependent on the torsion angle of the respective vicinal hydrogen atoms, as shown by Karplus.[4,5] During the past few years, there was not only an important increase in the understanding of that transmission but also there was a large increase in the possibility for calculating SSCCs for medium- to large-sized molecules and, therefore, during the past decade other types of SSCCs like, for instance, $^1J_{CH}$,[6−8] and $^2J_{CH}$[9] besides $^3J_{CH}$[10−15] SSCCs were considered for stereochemical purposes. Whereas the $^3J_{HH}$ couplings are widely applied to assign conformational preferences,[16−20] the same attention is not paid to long-range $^4J_{\mathrm{HH}}$ SSCCs, probably due to its usually smaller absolute values than those of $^3J_{HH}$ SSCCs. However, a few interesting $^4J_{HH}$ SSCCs are worth mentioning like those in fused cyclopropanes,[21] which resemble the behavior of those in allylic systems studied by Garbisch et al.[22] It should be mentioned that to get accurate values for $^4J_{HH}$ SSCCs the ^{1}H NMR spectra should be acquired with high digital resolution. In a recent paper, Dias and co-workers[23] discussed the potential of $^4J_{HH}$ SSCCs to determine conformational preferences by studying the conformational equilibrium in alkyl and silyl ethers, which were determined mainly by intramolecular hydrogen-bonds.

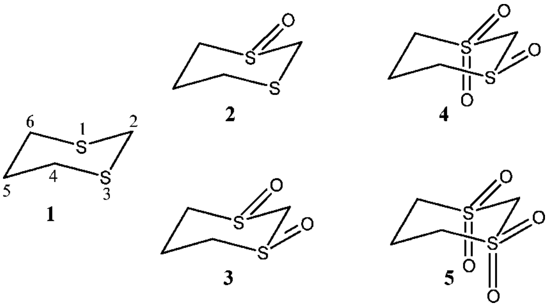

Figure 1. Structures for studied compounds: 1,3-dithiane (**1**), 1,3-dithiane-1-oxide (**2**), *cis*-1,3-dithiane-1,3-dioxide (**3**), 1,3-dithiane-1,1,3-trioxide (**4**), and 1,3-dithiane-1,1,3,3-tetraoxide (**5**).

To get deeper insight into factors affecting the efficiency of $^4J_{HH}$ coupling pathways, the ^{1}H spectra of several 1,3-dithiane compounds (Figure 1) with different degrees of sulfur oxidation are studied in the present work.

Hyperconjugative interactions along the $^4J_{HH}$ coupling pathway involving both bond and antibonding orbitals were analyzed using the NBO[24] approach, to rationalize the influence of electronic delocalization interactions on transmission mechanisms of $^4J_{HH}$ coupling in oxidized 1,3-dithianes (Figure 1). Sulfur-containing six-membered rings and its sulfoxide and sulfone derivatives have been widely studied.[25] The enthalpies of formation and the energy of the S═O bond for several six-membered ring sulfoxides and sulfones were determined[26−30] including also conformational analyses[13−15,31,32] and stereoelectronic effects on nucleophilic addition to alkylidene sulfoxide.[33] In the NMR case, some studies were performed to analyze the stereoelectronic effects on $^1J_{CH}$ coupling constants of sulfur lone pairs[8,34−36] and of S═O bonds corresponding to sulfoxide and sulfone[37] groups. However, there are not analyses about stereoelectronic effects on long-range SSCCs, such as $^4J_{HH}$, which can be used to determine not only molecular structures but also conformational preferences.[23,25]

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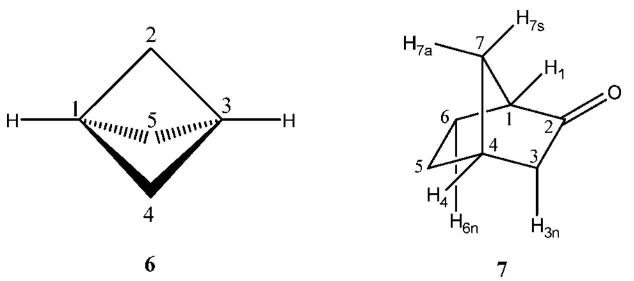

6 **7**

Figure 2. Bicyclo[1.1.1]pentane (**6**) and norbornanone (**7**).

TABLE 1: Experimental and Calculated[a] Long-Range ${}^4J_{HH}$ SSCCs (in Hz) for 1−5

${}^4J$	1	2	3	4	5[b]
$H_{2ax}H_{6ax}$	(0.87)	0 (0.31)	0 (0.36)	1.51 (1.10)	1.07 (0.98)
$H_{2ax}H_{4ax}$	(0.87)	0 (0.24)	0 (0.36)	0 (0.32)	1.07 (0.98)
$H_{2eq}H_{6eq}$	(1.19)	2.60 (2.45)	2.02 (2.23)	2.11 (2.77)	1.07 (2.23)
$H_{2eq}H_{4eq}$	(1.19)	0 (0.80)	2.02 (2.23)	2.11 (2.06)	1.07 (2.23)

[a] Calculated values are in parentheses. [b] Experimental SSCCs are the average value at room temperature.

It is well-known[38] that ${}^4J_{H_1H_5}$ SSCCs are transmitted with enough efficiency that allows their experimental observation when the intermediate bonds $H_1-C_2-C_3-C_4-H_5$ are in a planar W arrangement. In such a case, charge transfer interactions defining its coupling pathway are mainly $\sigma_{C_3-C_4} \rightarrow \sigma^*_{C_2-H_1}$ and $\sigma_{C_2-C_3} \rightarrow \sigma^*_{C_2-H_1}$[39] and their respective back-donation interactions.

A very efficient ${}^4J_{H_1H_3} = 18.2$ Hz SSCC was reported in bicyclo[1.1.1]pentane, **6** (Figure 2).[40] It is noted that the H_1 and H_3 protons are connected by three planar equivalent W coupling pathways, where the corresponding C−C bonds are very strained and, therefore, are very good electron donors by σ-hyperconjugative interactions, facilitating the FC transmission between H_1 to H_3. However, it should also be recalled that a through-space contribution between the C_1 and C_3 bridge-head carbon atoms might be transmitted[41] and that both coupling protons are in a configuration that favors a non-negligible and negative diamagnetic spin orbit, DSO, contribution.[42]

Parella et al.[43] reported in norbornanone (**7**) (Figure 2), ${}^{3,4}J_{C_1,H_4} = +\ 5.2$ Hz and ${}^{3,4}J_{C_4,H_1} = +\ 8.5$ Hz. This unexpected asymmetry was recently rationalized[44] as originating in an additional coupling pathway activated in the four-bond contribution through the $C_1-C_2-C_3-C_4$ bridge containing the carbonyl moiety. This additional coupling pathway takes place through the simultaneous occurrence of these two hyperconjugative interactions, $\sigma_{C_1-C_7} \rightarrow \sigma^*_{C_2=O}$ and $\sigma_{C_3-C_4} \rightarrow \sigma^*_{C_2=O}$, which enhances the ability of the $H_1-C_1-C_2-C_3-C_4$ four-bond coupling pathway for transmitting the FC term of ${}^{3,4}J_{C_4,H_1}$ SSCC. It is highlighted the similitude of this additional coupling pathway to that of homoallylic couplings, which have been known since many years ago,[45,22] the main difference being this, whereas in homoallylic couplings the intermediate antibonding orbital is of π^* symmetry, in ${}^{3,4}J_{C_4,H_1} = +\ 8.5$ Hz, **7**, is of σ^* symmetry. On similar grounds can be rationalized the differences observed in the same compound,[46] (Figure 2) for ${}^4J_{H_{3n}H_{7a}} = 4.2$ Hz and ${}^4J_{H_{6n}H_{7s}} = 2.3$ Hz. For the former SSCC strong interactions of types $\sigma_{C_3-H_n} \rightarrow \pi^*_{C_2=O}$ and $\sigma_{C_1-C_7} \rightarrow \pi^*_{C_2=O}$ should constitute an additional coupling pathway, rendering ${}^4J_{H_{3n}H_{7a}} > {}^4J_{H_{6n}H_{7s}}$. However, it should be highlighted that in this case, the intermediate antibonding orbital defining this coupling pathway is of π^* symmetry, like in homoallylic SSCCs.

Computational Details

All structures were fully optimized at the B3LYP functional[47] and aug-cc-pVDZ basis set[48] level using the *Gaussian 03*[49] program. Electronic structures from **1**−**5** were studied using NBO analysis[50] at the B3LYP/cc-pVDZ level using the geometries optimized.

The ${}^4J_{HH}$ couplings in **1**−**5** were also calculated using the CP-DFT/B3LYP methodology[51] as implemented in the *Gaussian 03* package[49] of programs. All four terms of ${}^4J_{HH}$ spin−spin coupling constant (Fermi contact, FC; spin dipolar, SD; paramagnetic spin orbit, PSO; and diamagnetic spin orbit, DSO) were carried out using the EPR-III basis set,[52] which is a triple-ζ type and includes diffuse and polarization functions. The *s* part of this basis set is enhanced to better reproduce the electronic density in the nuclear regions because this point is particularly important when calculating the FC term.[53] The EPR-III basis set was used for the carbon and hydrogen atoms and cc-pVDZ basis set for other atoms present in the molecules studied.

Experimental Section

NMR Experiments. ^{1}H NMR spectra were recorded on spectrometer operating at 300.25 MHz for ^{1}H. Measurements were carried out at a probe temperature of the 25 °C, using solutions of ca. 10 mg cm^3 in $CDCl_3$ for **2** and in DMF-d_7 for **3**−**5**. The ^{1}H spectra were based on the TMS reference. Typical conditions for ^{1}H spectra were: 16 transients, spectral width 2500 Hz, with 32 k data points, giving an acquisition time of 6.35 s and zero filled to 128 k to give a digital resolution of 0.04 Hz/point.

Compounds. 1,3-dithiane (**1**) and 1,3-dithiane-1,1,3,3-tetraoxide (**5**) are commercially available and were used without further purification, whereas **2**−**4** were prepared according procedure described in the literature.[54]

Results and Discussion

The experimental ${}^4J_{HH}$ coupling constants for studied compounds (Figure 1) were measured directly from the ^{1}H NMR spectra, whereas theoretical values were calculated at the B3LYP/EPR-III level of theory (Table 1).

The experimental trends of ${}^4J_{HH}$ SSCCs are correctly described by theoretical calculations, as observed in Table 1. Long-range ${}^4J_{H_{eq}H_{eq}}$ can only be observed when the sulfur atom in the coupling pathway is oxidized to sulfoxides **2** and **3** with S═O group at equatorial position. For sulfones **4** and **5**, it can also be observed long-range ${}^4J_{H_{ax}H_{ax}}$ SSCCs between hydrogen atoms in the axial position, suggesting that they are observed due to the axial orientation of the S═O group.

The effect of sulfur oxidation and orientation of the S═O bond on the ${}^4J_{HH}$ coupling pathway can be easily observed directly from ^{1}H NMR spectra for **2**−**5**, shown in Figure 3, where for the sake of simplicity only signals for hydrogen atoms (axial and equatorial) at position 2 are displayed.

In **2**, as shown in part a of Figure 3, for both protons (H_{6eq} and H_{4eq}) in the equatorial position, only ${}^4J_{H_{2eq}H_{6eq}}$ is observed, whereas ${}^4J_{H_{2eq}H_{4eq}}$ cannot be detected. It is noted that the main difference between the corresponding coupling pathways is that in the former the sulfur atom is oxidized (sulfoxide), whereas in the latter the corresponding sulfur atom is not oxidized. The relevant role played by the sulfur oxidation along the ${}^4J_{H_{eq}-H_{eq}}$ four-bond coupling pathway is also appreciated when analyzing the ^{1}H NMR spectra for **3** and **4**. It is noted that in **3** the S═O groups are in equatorial position (this is the only stable form[55−57] for this compound) and was observed a doublet of triplets for H_{2eq} signal (part b of Figure 3) due to the geminal coupling

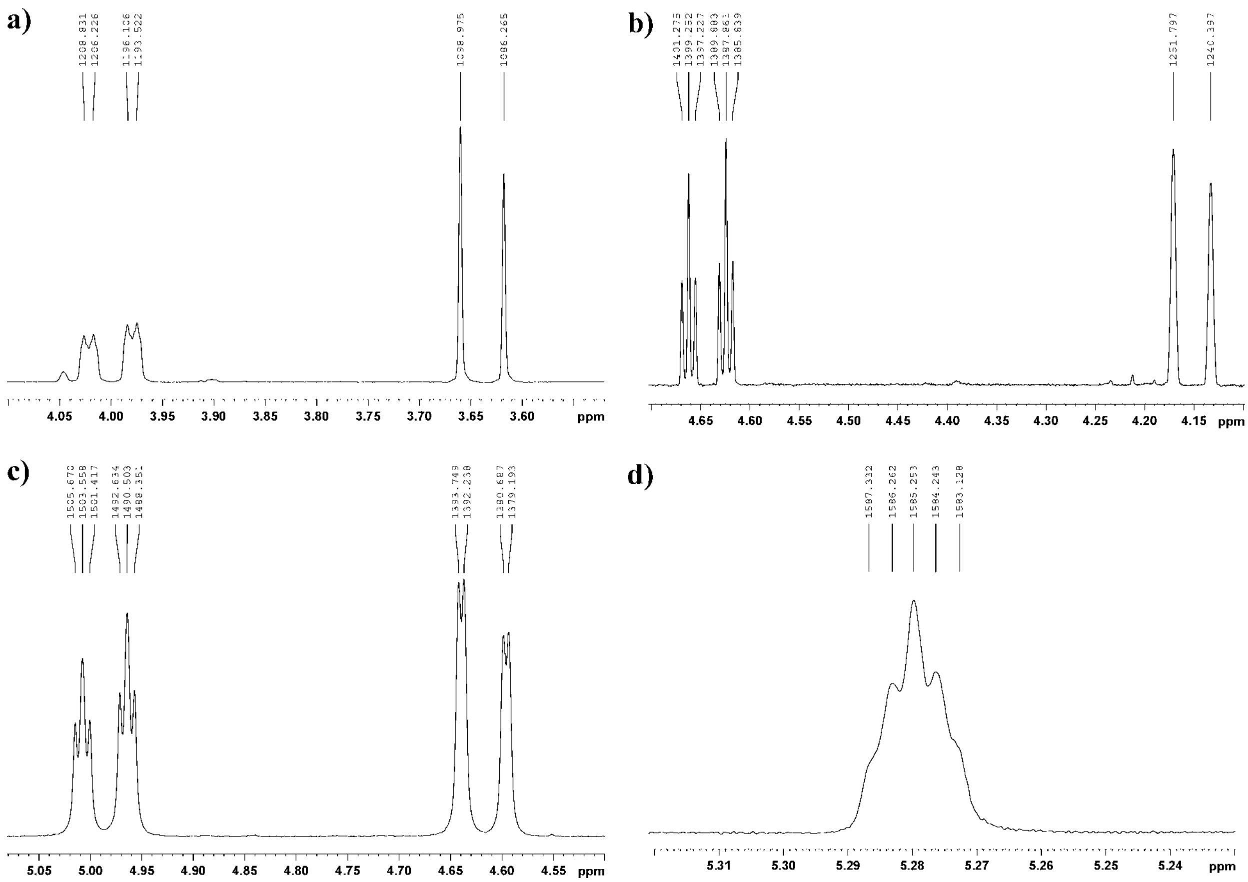

Figure 3. ^{1}H NMR signals for H_2 axial (low frequency) and equatorial (high frequency) for: (a) 1,3-dithiane-1-oxide (**2**); (b) *cis*-1,3-dithiane-1,3-dioxide (**3**); (c) 1,3-dithiane-1,1,3-trioxide (**4**); and (d) 1,3-dithiane-1,1,3,3-tetraoxide (**5**).

with H_{2ax} and the two four-bond couplings with H_{4eq} and H_{6ax}. A similar pattern is observed for H_{2eq} in **4**, however in this case a long-range coupling, $^4J_{H_{2ax}H_{6ax}}$ is also observed for H_{2ax}, which suggests that the presence of the S=O moiety in axial orientation enhances the ability of this coupling pathway for transmitting that long-range SSCC.

To get insight into the influence of an S=O group and its orientation for enhancing the four-bond J_{HH} coupling pathways in dithiane derivatives measured in this work, hyperconjugative interactions involving either bond and/or antibonding orbitals belonging to those pathways are studied performing the relevant NBO calculations.

$^4J_{H_{2eq}-H_{6eq}}$ SSCCs could be measured in **2**−**5**. It is observed that in **5** this SSCC is less than one-half those measured in **2**−**4**. On the other hand, $^4J_{H_{2eq}-H_{4eq}}$ could be measured in **3**−**5**. Again, in **5** this SSCC is less than one-half of those measured in **3** and **4**.

To verify if $H_{2eq}-C_2-S_1-C_6-H_{6eq}$ and $H_{2eq}-C_2-S_3-C_4-H_{4eq}$ coupling pathways are enhanced when either or both S_1 and S_3 are oxidized, in Table 2 are listed hyperconjugative interactions within both pathways. In this Table is shown the sum of each hyperconjugative interaction and its respective back-donation because they are considered to be adequate descriptors to compare how efficient are the respective coupling pathways. Data in Table 2 show similar hyperconjugative interactions along the $^4J_{H_{eq}-H_{eq}}$ coupling pathways for **1**−**5**, the result of which is not in line with experimental $^4J_{H_{eq}-H_{eq}}$ SSCCs displayed in Table 1. Therefore, a different type of coupling pathway enhancement should be sought.

For instance, in **2** the $^4J_{H_{2eq}-H_{6eq}}$ coupling pathway is notably enhanced in comparison with that of $^4J_{H_{2eq}H_{4eq}}$, which could not be measured. This suggests that the strong hyperconjugative interactions (LP(O_{1eq}) → $\sigma^*_{C_2-S_1}$ = 22.6 kcal/mol and LP(O_{1eq}) → $\sigma^*_{C_6-S_1}$ = 20.1 kcal/mol) that take place within the sulfinyl group enhances the $^4J_{H_{2eq},H_{6eq}}$ coupling pathway in **2**, $^4J_{H_{eq},H_{eq}}$ SSCCs measured in **3** seem to support this assumption, although both $^4J_{H_{eq},H_{eq}}$ SSCCs are smaller than in **2**. In **4**, experimental $^4J_{H_{2eq},H_{6eq}}$ and $^4J_{H_{2eq},H_{4eq}}$ SSCCs are equal, although the coupling pathway in the former bears two sulfinyl group. For similar coupling pathways in **5**, both of $^4J_{H_{2eq},H_{6eq}}$ and $^4J_{H_{2eq},H_{4eq}}$ SSCCs are notably smaller, suggesting that the second sulfinyl group with an axial orientation yields an inhibition of that coupling pathway. No measurement could be carried out to verify the efficiency of a coupling pathway bearing only a sulfinyl group in the axial position.

TABLE 2: Hyperconjugative Interactions within the $H_{2eq}-C_2-S_1-C_6-H_{6eq}$ and $H_{2eq}-C_2-S_3-C_4-H_{4eq}$ Coupling Pathways of $^4J_{H_{2eq},H_{6eq}}$ and $^4J_{H_{2eq},H_{4eq}}$, Respectively; in This Table Each Entry Corresponds to the Sum of the Interaction Shown at Left and Its Respective Back-Donation Interaction (in kcal/mol)

	interactions	1	2	3	4	5
1	$\sigma_{C_2-H_{eq}} \rightarrow \sigma^*_{C_6-S_1}$	3.2	2.9	2.9	3.1	2.8
2	$\sigma_{C_6-H_{eq}} \rightarrow \sigma^*_{S_1-C_2}$	3.3	2.8	3.2	3.4	3.4
3	$\sigma_{C_2-H_{eq}} \rightarrow \sigma^*_{C_4-S_3}$	3.2	3.4	2.9	2.8	2.8
4	$\sigma_{C_4-H_{eq}} \rightarrow \sigma^*_{S_3-C_2}$	3.3	3.5	3.2	3.2	3.4

The rationalization of the transmission of $^4J_{H_{ax},H_{ax}}$ SSCCs in **4** and **5** is rather straightforward. It must be highlighted that these coupling pathways are quite similar to those of homoallylic couplings.[45] The difference rests on this fact, whereas in homoallylic couplings the intermediate antibonding orbital is of π^* symmetry; in **4** and **5** they are of σ^* symmetry. Such

TABLE 3: Interactions (in kcal/mol) that Define the Coupling Pathway Transmission of $^4J_{H_{ax},H_{ax}}$ SSCCs in 4 and 5

	interactions[a]	4	5
A	$\sigma_{C_2-H_{ax}} \rightarrow \sigma^*_{S_1=O_{ax}}$	2.8	2.6
B	$\sigma_{C_6-H_{ax}} \rightarrow \sigma^*_{S_1=O_{ax}}$	3.0	3.0
C	$\sigma_{C_2-H_{ax}} \rightarrow \sigma^*_{S_3=O_{ax}}$		2.6
D	$\sigma_{C_4-H_{ax}} \rightarrow \sigma^*_{S_3=O_{ax}}$		3.0

[a] Back-donation interactions are summed to interactions quoted in the second column.

interactions are displayed in Table 3, where it is noted that interactions A and B define the coupling pathway for $^4J_{H_{2ax},H_{6ax}}$, whereas interactions C and D define the coupling pathway for $^4J_{H_{2ax},H_{4ax}}$.

Conclusions

In the present study, rationalizations for the transmission mechanisms involving the long-range $^4J_{HH}$ coupling constant for 1,3-dithiane derivatives are presented. It was observed that these long-range couplings are very sensitive to the sulfur oxidation because the $^4J_{H_{eq}-H_{eq}}$ coupling transmission mechanism involves interactions between $LP_O \rightarrow \sigma_{C-S}$, which is present only when the respective sulfur atom is oxidized. Besides, $^4J_{HH}$ coupling constants are also sensitive to the orientation of S═O bond because the $^4J_{H_{ax}-H_{ax}}$ coupling transmission mechanism involves the hyperconjugative interactions of types $\sigma_{C_4-H_{4ax}} \rightarrow \sigma^*_{S=O}$, $\sigma_{C_6-H_{6ax}} \rightarrow \sigma^*_{S=O}$ and $\sigma_{C_2-H_{2ax}} \rightarrow \sigma^*_{S=O}$, which take place only when the S═O bond is in axial orientation. Therefore, long-range $^4J_{HH}$ coupling constants can be used to determine the orientation of S═O bonds in sulfur derivatives compounds, which are difficult tasks in structural assignments.

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