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# Proton Abstraction from 4-Nitrophenyl[bis(ethylsulphonyl)]methane with TMG, TBD and MTBD Bases in Acetonitrile

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4-Nitrophenyl[bis(ethylsulphonyl)]methane has been synthesized and used in kinetic studies of proton abstraction induced by 1,1,3,3-tetramethylguanidine (TMG), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) bases in acetonitrile. The $pK_a$ values of this carbon acid in water and in acetonitrile solvents are 10.08 and 22.8 respectively. The electronic spectra of 4-nitrophenyl[bis(ethylsulphonyl)]methane and its anion are well defined and temperature dependent. The rates of proton abstraction are large as the reaction occurs in the range of microseconds. The relaxation times were studied by spectrophotometric temperature-jump technique. The rate constants for proton transfer reaction promoted by TMG, TBD and MTBD bases in acetonitrile are: $1.39\times10^5$–$2.11\times10^5$; $8.8\times10^6$–$19.2\times10^6$; $0.84\times10^5$–$2.43\times10^5$ [$dm^3\ mol^{-1}\ s^{-1}$] respectively between 20–40°C. The enthalpies of activation are: $\Delta H^{\neq}$ = 18.1, 28.7 and 40.0 [kJ $mol^{-1}$] for TMG, TBD and MTBD respectively. The entropies of activation are all negative: $\Delta S^{\neq}$ = –84.9, –13.6, –14.3 [J $mol^{-1}$ $deg^{-1}$] for the same sequence of bases reacting with 4-nitrophenyl[bis(ethylsulphonyl)]methane in acetonitrile solvent. The general discussion of the results obtained and their comparison with those for proton transfer reaction carried out with "normal" C-acids is given.

**Key words:** kinetics, proton transfer, T-jump, 4-nitrophenyl[bis(ethylsulphonyl)]methane, TMG, TBD, MTBD bases, activation parameters

The rates of proton abstraction depend on the type of the proton donor used. Generally two extreme cases can be considered. The first is a "normal" acid, where the proton is bound to strongly electronegative atom as oxygen, and the second, where the proton is bound to carbon atom that is substituted with electron withdrawing group making carbon acid. The first type of the acids reveals very fast dissociation and therefore the rate of proton abstraction frequently is not a rate-determining step, due to very low intrinsic energy barrier [1–4]. The second types are carbon acids that are mostly derivatives of methane substituted by strongly electron withdrawing groups. The proton may be abstracted from carbon atom of C-acid or from the oxygen atom of its aci-isomer [1,5]. However, the proton abstractions from the latter are exceptions.

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Predominantly the mechanisms of proton transfer reactions in solution concerns with carbon acids of different structure and strength [1,2,6–10]. The proton abstraction from C-acids is relatively slow, what enabled precise measure of the rate constant being in the range of milliseconds. This is attributable to the extreme electronic re-arrangement accompanying proton loss of carbon acid [11,12] revealing in the formation of a number of nitronates, which could be hydrogen bonded to some bases [5,10,13–16]. The variety of C-acids towards their strength, type of electron withdrawing group and steric hindrance in the vicinity of reaction center, used in kinetic and equilibrium experiments, is advisable to evaluate the factors influencing rate constants and primary deuterium kinetic isotope effects (KIE) [9,10]. In the kinetic experiments prevails 4-nitrophenyl-1-nitroalkanes [17–20]. The variety derivatives having acidic properties as: nitrophenylcyanomethanes [9,21,22], nitrophenylacetates [23–25], nitrophenylmalonate [26], malononitriles [27] and 2,4,6-trinitrotoluene (TNT) [28,29] were also used. The C-acids with sulfonyl electron withdrawing groups have the acid-base properties more alike "normal acids" than nitro or cyano-derivatives [30–32].

The main purpose of this research is to find the possible structure of the activated complex formed in the reaction of 4-nitrophenyl[bis(ethylsulphonyl)]methane with 1,1,3,3-tetramethylguanidine (TMG), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) in acetonitrile. We already found the drastic difference in the rates of proton abstraction induced by TBD and MTBD bases [13]. This large ratio of $k_{TBD}/k_{MTBD}$ was accounted for different structures of the hydrogen bonded transition states [13]. For nitrosubstituted C-acids, formation of a pyramidal carbanion as an intermediate was postulated by Bordwell and Boyle [33]. This was converted to alkanenitronate, a true carbanion for nitro-substituted C-acid [41]. In case of 4-nitrophenyl[bis(ethylsulphonyl)]methane one can expect a different structure of the transition state and final carbanion. Then the kinetics of the proton transfer of sulfonyl C-acid with TMG, TBD and MTBD bases could be sensitive to the different structure of the transition state [30]. The carbanion of 4-nitrophenyl[bis(ethylsulphonyl)]methane would involve delocalization of the negative charge to the electronegative atoms more alike it was observed for C-acids activated by nitro groups than for normal acids. Some attempts to study of the acid/base properties of 4-nitrophenyl[bis(ethylsulphonyl)]methane were already made by Sørensen *et al*. [30]. They also measured its value of $pK_a = 10.08$ in water while in acetonitrile is 22.8 [34]. The proton abstraction from 4-nitrophenyl[bis-(ethylsulphonyl)]methane with TMG, TBD, MTBD in acetonitrile is fast and the equilibrium temperature dependent. Then the deprotonation of 4-nitrophenyl[bis-(ethylsulphonyl)]methane with these bases in acetonitrile could be measured by means of a temperature-jump relaxation technique [30,35,36].

## EXPERIMENTAL

4-Nitrophenyl[bis(ethylsulphonyl)]methane was synthesized according to modified method described by Cronyn [37]. The general procedure was to mix the ethyl mercaptan and benzaldehyde or aryl substituted benzaldehyde with benzene. Toluene-p-sulfonic acid was added as a catalyst and the mixture was refluxed during 2–3 hours using Dean – Stark trap for continuous removal of water and a dry ice-aceton cooled condenser. $^1$H NMR (Gemini 300VT Varian) and MS (AMD 604/402) spectroscopy checked the purity of resulting C-acid. The spectral data of synthesized 4-nitrophenyl[bis(ethylsulphonyl)]methane were: $^1$H NMR ($CDCl_3$) $\delta_H$: 1.5 (6H, m, 2×$CH_3$); 3.5 (4H, m, 2×$CH_2$); 5.21 (H, s, ×CH); 7.3–7.7 ArH. M/z = 321 ($M^{+\bullet}$), 229, 136, 77 and m.p. = 199–202°C. The melting point, MS and NMR spectra were in accordance with the literature [30]. Spectroscopic grade acetonitrile from Romil was purified by shaking it with $CaH_2$, followed by fractional distillation from $P_2O_5$ and final fractional distillation from $CaH_2$. The middle fraction was collected and stored under nitrogen free from moisture and $CO_2$. 1,1,3,3-Tetramethylguanidine (TMG) from Aldrich was distilled under reduced pressure (10 mm Hg), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) from Aldrich were used without any further purification. The purity of the samples of the bases as tested by NMR spectroscopy [24] and titration was satisfactory. Due to poor solubility of 4-nitrophenyl[bis(ethylsulphonyl)]methane in acetonitrile, originally its 0.025 M stock solution in dioxane was prepared and then the calculated volume of this solution was transferred to acetonitrile to make $2\times10^{-4}$ M substrate solution. The stock solutions of carbon acid and bases were freshly prepared before experiments and handled with precautions to protect them from carbon dioxide and moisture. The spectra of neutral and ionized form of 4-nitrophenyl[bis(ethylsulphonyl)]methane in acetonitrile (Fig. 1) were measured using a Hewlett Packard Diode–Array Spectrophotometer (HP 8452A) fitted with a thermostated cell holder to keep the temperature constant within ± 0.1°C.

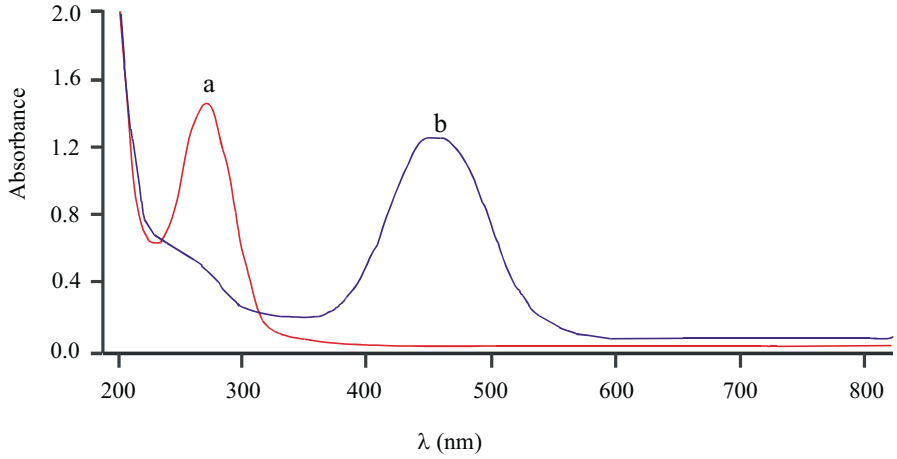



**Figure 1.** Electronic spectra of 4-nitrophenyl[bis(ethylsulphonyl)]methane (a) and its anion (b) in acetonitrile.

Temperature dependence of the ionization of 4-nitrophenyl[bis(ethylsulphonyl)]methane with TMG ($\lambda_{max}$ = 446 nm) in acetonitrile is characterized by a change of equilibrium constants K [$dm^3\ mol^{-1}$] equal to 7.1–9.6 for temperature range 20–40°C. Rates of ionization of C-acid were measured by a temperature-jump technique using the Hi-Tech Scientific IS-2 apparatus. The observation cell with 3 mm light path, constructed of quartz and thermostated, was connected with the capacitor *via* two stainless electrodes. The discharge of capacitor of 13 kV, heated the 100 µl volume of solution giving the temperature rise in acetonitrile ΔT = 19.3°C. Temperature rise $\Delta T = C\cdot V^2/2\cdot Q_s\cdot m_s$ (°C); where C = capacitance F, V = voltage across capacitor V, $Q_s$ = 2.23 J $g^{-1}$ $deg^{-1}$ specific heat of acetonitrile, $m_s$ = mass of solvent, heating time < 5 µs. The syringes were used to fill up the measuring cell and to drain used solution. The constant temperature of the cell within ± 0.1°C was achieved with an external liquid circulating bath. Spectral

changes after the temperature jump were recorded and analyzed by a computer. Up to ten results were taken to have an average value of the rate constant. The example of the relaxation curve made for the reaction system consisting 4-nitrophenyl[bis(ethylsulphonyl)]methane [$2\times10^{-4}$ M] and TMG [$3.2\times10^{-3}$ M] in acetonitrile is demonstrated in Fig. 2.

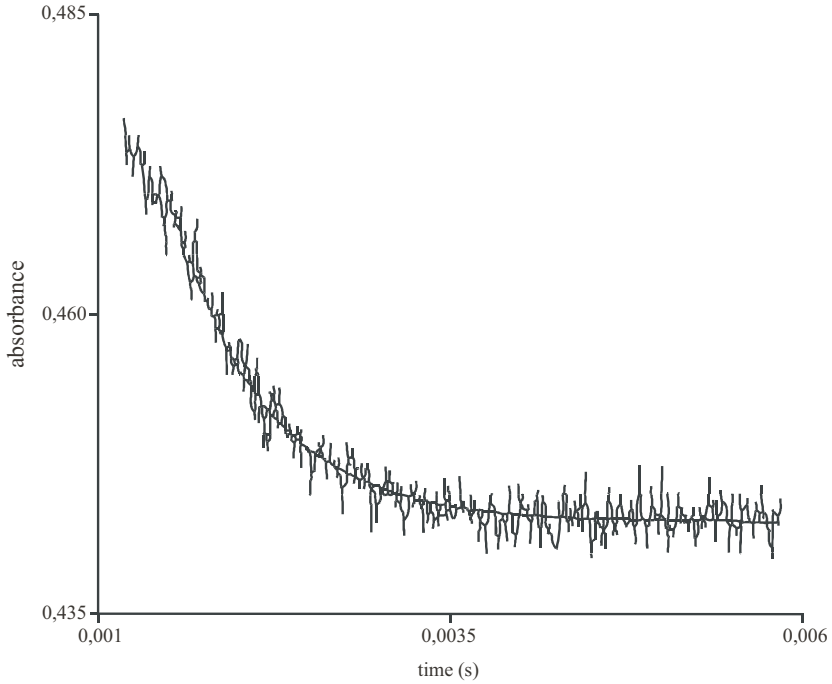
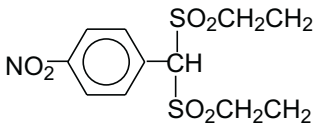
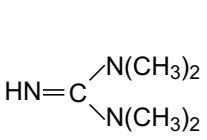



**Figure 2.** Relaxation curve for the system of reaction consisting of 4-nitrophenyl[bis(ethylsulphonyl)]methane [$2\times10^{-4}$ M] and TMG [$3.2\times10^{-3}$ M] in acetonitrile at 20°C.

The system under study consists of 4-nitrophenyl[bis(ethylsulphonyl)]methane and strong bases with different steric hindrance.

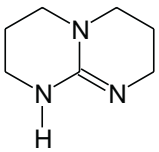



$pK_a$ = 22,8 [34]



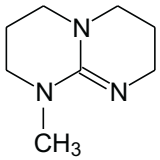

TMG

$pK_a$ = 23,3 [38]




TBD

$pK_a$ =25,96 [39]




MTBD

$pK_a$ = 25,0 [39]

## RESULTS AND DISCUSSION

The reaction of 4-nitrophenyl[bis(ethylsulphonyl)]methane with strong nitrogen bases gives the anion showing intense visible absorption at $\lambda_{max}$ = 446 nm in acetonitrile solvent (Fig. 1 a and b). The product of reaction of TMG, TBD and MTBD is highly dissociated into free carbanion as seen from electronic spectra with equal $\lambda_{max}$ = 446 nm for each base.

The product of reaction of C-acids is usually dissociated into free ions in both water and acetonitrile solvents [20,30,40]. However, the structure of the transition state for the proton transfer reactions between nitrophenylalkanes and TBD and MTBD bases are not alike implicating large differences in the rates of proton transfer reactions [13,41]. The rate ratios for proton transfer between 1-nitro-1-(4-nitrophenyl)alkanes and TBD and MTBD bases were $k_{TBD}/k_{MTBD}$ 118 to 287 depending on the steric hindrance close to reaction center of reacting C-acid [13]. These large differences in the rate constants were attributed to the structure of the transition state with two hydrogen bonds in the case of TBD and single hydrogen bond for the MTBD base. This phenomenon is a result of interaction between electronegative oxygen atoms of the nitro-group of C-acid and TBD or MTBD base. Much faster reaction of TBD than MTBD bases of equal strength shows that the Brönsted relationship does not hold for reactions of nitroalkanes with bicyclic guanidines/amidines. Such breakdowns frequently indicate steric hindrance but for TBD/MTBD reactions prove different reaction mechanism *via* two various structures of the transition state [13,16,24,41].

Using 4-nitrophenyl[bis(ethylsulphonyl)]methane as a C-acid, we expected to study the effect of interaction of oxygen atoms of sulfonyl groups of this C-acid with TBD, MTBD and TMG bases, to make different transition states and therefore different rates of proton abstraction. The measured rate constants $k_{obs}$ and $k_2$ of the proton abstraction from 4-nitrophenyl[bis(ethylsulphonyl)]methane and TBD and MTBD bases are collected in Table 1.

As we predicted, the fastest reaction in the group takes place with TBD base $k_{TBD}$ =$110\times10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ while the MTBD reaction is much slower $k_{MTBD} = 1\times10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$. Then the Brönsted relation does not hold as TBD and MTBD bases, having almost the same basicity in acetonitrile ($pK_a^{MTBD}$ = 25.43, $pK_a^{TBD}$ = 25.96) caused proton abstraction from 4-nitrophenyl[bis(ethylsulphonyl)]methane differing in rate constants by two orders of magnitude (Table 1). As follows from Table 1, similar values of the rate of proton abstraction from 4-nitrophenyl[bis(ethylsulphonyl)]methane are observed for two other bases TMG and MTBD, in spite of their significant difference in strength ($pK_a^{TMG}$ = 23.3, $pK_a^{MTBD}$ = 25.43), with a tendency to be faster for the weaker TMG base. Such breakdowns frequently indicate steric hindrance but in this case the different mechanism of the reaction must be considered. This also stems from the values of activation parameters collected in Table 2. For the reaction of TMG and MTBD free enthalpy of activation $\Delta G^{\neq}$ are equal (Table 2) resulting similar values of rate constant (Table 1), however, the negative values of entropy of activation $\Delta S^{\neq}$ are different, indicating more ordered transition state for TMG reaction.

**Table 1.** Rate constants for the reactions of 4-nitrophenyl[bis(ethylsulphonyl)]methane with TMG,TBD and MTBD bases in acetonitrile solvent.

| T [°C] | $C_{base}$ [M]·$10^2$ | $k_{obs}$ [$s^{-1}$]·$10^{-3}$ | $k_2$ [$dm^3$ $mol^{-1}$ $s^{-1}$]·$10^{-5}$ |
|---|---|---|---|
| **MTBD** | | | |
| 20 | 2–5 | 0.22–0.46 | 0.84±0.02 |
| 25 | 2–5 | 0.31–0.62 | 1.00±0.05 |
| 30 | 2–5 | 0.48–0.89 | 1.36±0.22 |
| 35 | 2–5 | 0.80–1.35 | 1.95±0.33 |
| 40 | 2–5 | 1.06–1.82 | 2.43±0.19 |
| **TBD** | | | |
| 20 | 2–5 | 19.6–45.6 | 88.0±8.7 |
| 25 | 2–5 | 25.8–57.0 | 110±16 |
| 30 | 2–5 | 31.5–71.0 | 136±12 |
| 35 | 2–5 | 43.0–97.0 | 179±28 |
| 40 | 2–5 | 58.0–113.9 | 192±13 |
| **TMG** | | | |
| 20 | 2.4–6.4 | 1.31–1.85 | 1.39±0.98 |
| 25 | 2.4–6.4 | 1.87–2.49 | 1.56±0.34 |
| 30 | 2.4–6.4 | 2.40–3.10 | 1.74±0.36 |
| 35 | 2.4–6.4 | 2.82–3.66 | 2.11±0.61 |

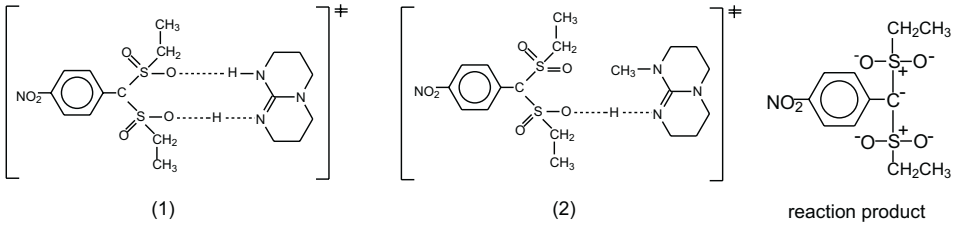
**Table 2.** Activation parameters for proton transfer reaction between 4-nitrophenyl[bis(ethylsulphonyl)]methane and TMG, TBD and MTBD bases in acetonitrile.

| Bases | $\Delta H^{\neq}$ [kJ $mol^{-1}$] | $\Delta S^{\neq}$ [J $mol^{-1}$ $deg^{-1}$] | $\Delta G^{\neq}$ [kJ $mol^{-1}$] |
|---|---|---|---|
| MTBD | 40.0±2.8 | –14.3±9.2 | 44.4±2.8 |
| TBD | 28.7±2.6 | –13.6±8.5 | 32.8±2.6 |
| TMG | 18.1±2.2 | –84.9±7.4 | 43.4±2.2 |

The TBD and MTBD reactions seem to follow similar reaction mechanism, although the enthalpy of activation values differ by 11 kJ $mol^{-1}$, what is manifested in smaller values of the rate constants for MTBD reaction. Taking into account that these two bases have almost the same strength, then the reduction of the rate constants in case of MTBD could be attributed to steric reasons. However, the decrease of $k_2$ observed (Table 1) is much larger than could be accounted for this effect. Then we presume that this is attributable to two different structures of the transition states for TBD and MTBD reactions (Scheme).

We already have confirmed the structure of 4-nitrophenyl[bis(ethylsulphonyl)]methane/TBD 1:1 complex, that has two hydrogen bonds to oxygen atoms of both sulphonyl groups and nitrogen atoms of TBD [42]. However, they are much weaker than those already found for nitroalkanes [16]. Due to steric reasons, this structure could not be formed in the case of MTBD reaction [13,41], what causes the drastic, two orders of magnitude reduction of the rate constants (Table 1). Then the kinetic behaviour of methanedisulphone C-acid is certainly not as different compared

to nitroalkanes as was already suggested [30 and ref. therein]. The general suggestion was that the ionization of methanedisulphone C-acid is not accompanied by any considerable changes in bonding or shift in charge away from carbon atom as observed for nitroalkanes [30]. However, it is visible that the proton loss from methanedisulphone C-acid is also accompanied by electronic rearrangement to stabilize the anion formed. Since 4-nitrophenyl[bis(ethylsulphonyl)]methane is rather strong C-acid $pK_a = 22.8$ [34], then the proton abstraction with strong TBD and MTBD bases gives the substrate-like transitions state (Scheme). The product of this reaction in polar acetonitrile is entirely dissociated into free anions, what is consistent with the strong ability of the groups to stabilize the "true" carbanion electrostatically (Scheme) [30].




**Scheme.** Transition states and the product for the reaction of 4-nitrophenyl[bis(ethylsulphonyl)]methane with TBD (1) and MTBD (2) in acetonitrile.

Rather different reaction mechanism operates for the proton abstraction with TMG base. The values of the rate constants are close to the MTBD reaction (Table 1), however the activation parameters (Table 2) are very different with large negative value of entropy of activation $\Delta S^{\neq} = -84.9$ J mol$^{-1}$ deg$^{-1}$. In the case of ionogenic reactions carried out in solutions, the values of the enthalpy of activation are compensated by the solvation effects stabilizing the charged activated complex. The solvation shell of this is better organized showing more negative entropy value. As can be seen (Table 2), similar values of free enthalpy of activation for MTBD and TMG reactions are composed with two different $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values. Then the compensating effects of entropy of activation caused that free enthalpy of activation $\Delta G^{\neq}_{MTBD} = 44.4$ kJ mol$^{-1}$ and $\Delta G^{\neq}_{TMG} = 43.4$ kJ mol$^{-1}$ are alike within standard deviation. So, in the case of the TMG reaction, the transition state is much more ordered in comparison with the substrate.

The TMG base in acetonitrile solvent has a low value of homoconjugation constant $K_{HOMO} = 3.3$ [43]. This stems from better delocalization of the positive charge in guanidinium than amidinium cations. Thus, guanidinium cations are worse hydrogen bond donors [43]. Then, at the kinetic concentrations used in this study, large concentration of TMG, $2.4–6.4\times10^{-3}$ M, one can consider a very fast equilibrium between free ions and ion pairs as already postulated [20]. In conclusion, we claim that the acid-base properties of 4-nitrophenyl[bis(ethylsulphonyl)]methane in the proton abstraction reaction promoted with strong guanidine/amidine bases in acetonitrile are

intermediate in behaviour, located between "normal" acids in which case anions formed, have the negative charge residing primarily on a single carbon atom (true carbanions) and carbon acids with negative charge delocalized to electronegative atoms, such as oxygen of nitro groups (nitroalkanes). These acid-base properties are manifested in the presence of the strong bases of different ability to form various transition states, showing different kinetic pattern of the proton transfer reaction, although leading to the same, final ionic product (Scheme).

Acknowledgments

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