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TETRAHEDRON

Synthesis and Characterization of a Planarized, Trimethylenemethane-Type Bis(Semiquinone) Biradical

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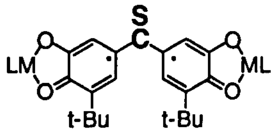
Abstract: The synthesis and characterization of a biradical in which two semiquinone rings are held rigidly co-planar and are attached in a geminal fashion to a carbon-carbon double bond is described. The results of cyclic voltammetry and variable-temperature EPR studies are interpreted in terms of the interaction of the two semiquinones through the carbon-carbon double bond coupling unit. © 1999 Elsevier Science Ltd. All rights reserved.

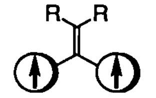
Keywords: benzoquinone; conformation; electrochemistry; molecular design; radicals

INTRODUCTION

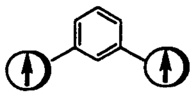
The synthesis of novel paramagnetic ligands is critical to preparation of metal complexes and coordination polymers exhibiting new and interesting magnetic and optical properties. Along these lines, we recently described the synthesis and characterization of several exchange-coupled (via the π-topology of **SC**, below)[1] bis(semiquinone)s[2] and dinuclear metal complexes of one such ligand.[3] The reported series of bis(semiquinone)s includes trimethylenemethane-type (TMM-type) and *meta*-phenylene-type biradicals.



Dinuclear Complex of an
$S = 1$, Bis(Semiquinone) Biradical Dianion

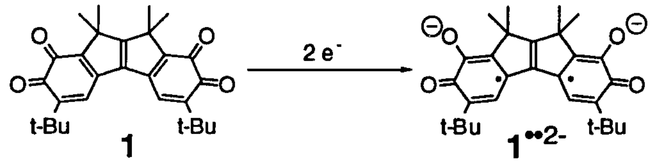


Generalized
TMM-type Biradical



Generalized
meta-Phenylene-type Biradical

Within the TMM-type bis(semiquinone) series, we prepared several molecules with different spin-protecting "R" groups to vary steric interactions between "R" and the semiquinone rings to continue our study of conformational J-modulation in TMM-type biradicals.[2a,4-6] The compound lacking in our previous report was one in which two semiquinone rings were held rigidly co-planar. Herein, we report the synthesis and characterization of such a planar bis(semiquinone), $1^{\bullet\bullet 2-}$.



RESULTS AND DISCUSSION

Synthesis

Recently, we reported the preparation of a planarized TMM-type dinitroxide biradical;[6] however, the bis(quinone) synthesis required modification. The planar TMM-type biradical precursor, bis(quinone) 1

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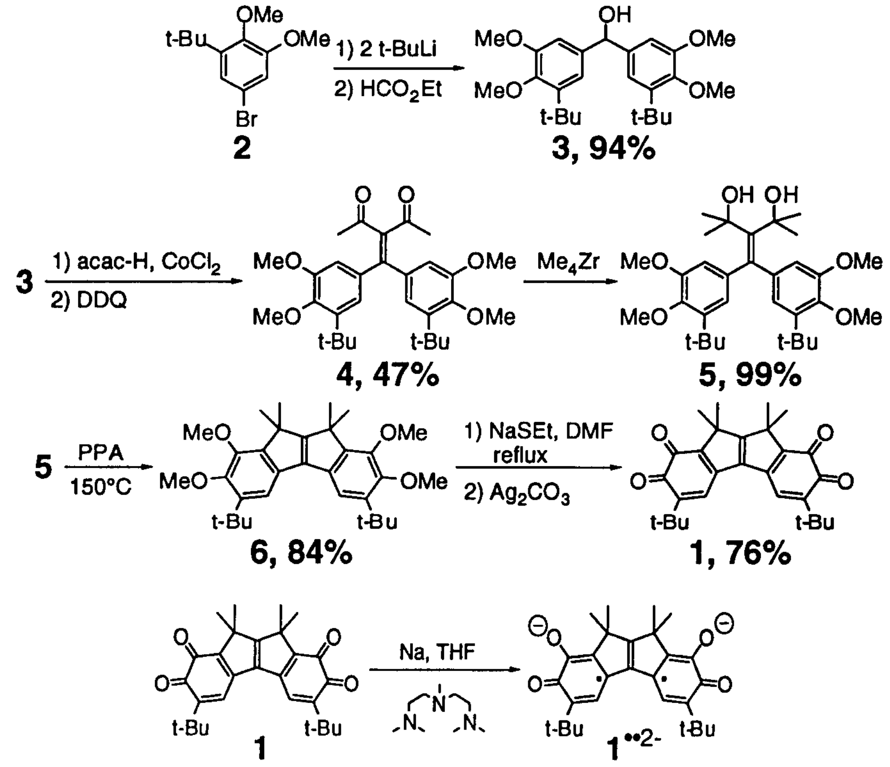
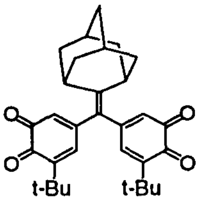
was prepared as shown below. Bromide **2**[2b] was converted to the lithium reagent and reacted with ethyl formate to give carbinol **3**. Diarylcarbinol **3** was reacted with acetylacetone in the presence of anhydrous cobaltous chloride,[7] followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to give conjugated ene-dione **4**. The DDQ oxidation was preferable to the NBS-bromination/elimination protocol used previously,[6] and should be generally applicable if the aryl groups are electron-rich as in the present case. In addition, direct formation of **4** by condensation of acetylacetone and the benzophenone derivative obtained by oxidation of **3** gave no **4**.[8] Dione **4** was converted into diol **5** by reaction with two equivalents of tetramethylzirconium.[9,10] Reaction of **4** with the Cerium(III) reagent from MeLi and $CeCl_3$ gave a poor yield of the desired diol. Ring-closure of **5** to indeno[1,2-*a*]indene derivative **6** was affected by stirring the diol with poly[phosphoric acid] at 150°C. Demethylation was achieved using sodium ethanethiolate in refluxing DMF, and the resulting bis(catechol) was oxidized using Fétizon's reagent.[11] Bis(semiquinone) $(Na^+)_2\mathbf{1}^{\bullet\bullet 2-}$ was prepared from **1** by reduction over Na mirror in the presence of excess pentamethyldiethylenetriamine, PMDTA, which slows precipitation of coordination polymers.[2a,12]



Electrochemistry

Bis(quinone) **1** exhibits several redox waves associated with quinone/semiquinone and semiquinone/catecholate redox couples.[2] The first two redox couples occur at -0.83 and -1.11 volts *vs.* Ag/AgNO$_3$ and are assigned to the (**1** to $\mathbf{1}^{\bullet -}$) and ($\mathbf{1}^{\bullet -}$ to $\mathbf{1}^{\bullet\bullet 2-}$) redox couples. These data along with those for bis(quinone)s **7** — **10**[2a] are collected in Table 1.



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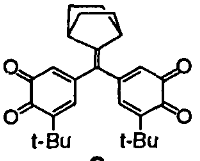

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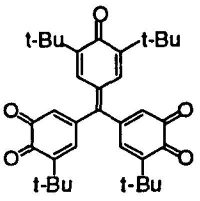

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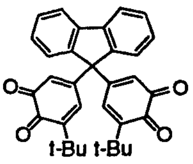

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Table 1. Cyclic Voltammetric Data for Bis(quinones).[a]

Bis(Quinone)	$E_{1/2}(1)$[b]	$E_{1/2}(2)$[c]	$\Delta E_{1/2}$[d]
1	**-0.83**	**-1.11**	**-0.28**
7	-0.73	-0.94	-0.21
8	-0.72	-0.94	-0.22
9	-0.52	-0.77	-0.25
10	-0.73	-0.93	-0.20

[a] 0.5 mM bis(quinone) in THF, 100 mM n-Bu$_4$NPF$_6$ electrolyte; potentials in Volts *vs.* Ag/AgNO$_3$; scan rate = 200 mV/s; data for **7** — **10** from ref 2a. [b] Redox potential for bis(quinone) / (quinone-semiquinone) couple; $E_{1/2} = (E_{p,c}-E_{p,a})/2$. [c] Redox potential for (quinone-semiquinone) / bis(semiquinone) couple; $E_{1/2} = (E_{p,c}-E_{p,a})/2$. [d] $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$.

The greater separation between $E_{1/2}(1)$ and $E_{1/2}(2)$ for **1** indicates greater coulombic repulsion of the charges due to greater delocalization compared to the other bis(quinone)s. In addition, both $E_{1/2}(1)$ and $E_{1/2}(2)$ for **1** are shifted to more negative potentials because of the additional electron-donating alkyl group attached to the quinone rings.

The 280 mV redox splitting indicates that electron-electron repulsion in $\mathbf{1}^{\bullet\bullet 2-}$ is the greatest in our series of bis(semiquinone)s. This result suggests mixed-valency for $\mathbf{1}^{\bullet -}$ and related species, and studies along these lines are underway.

EPR Spectroscopy

Figure 1 shows the EPR spectra of $\mathbf{1}^{\bullet\bullet 2-}$ recorded at 77 K in THF. The spectra are consistent with randomly-oriented triplet species[13] along with a doublet monoradical impurity near $g = 2$ (3300 G). The zero-field-splitting parameters for the biradical, obtained by simulation,[2a] are given in Table 2.

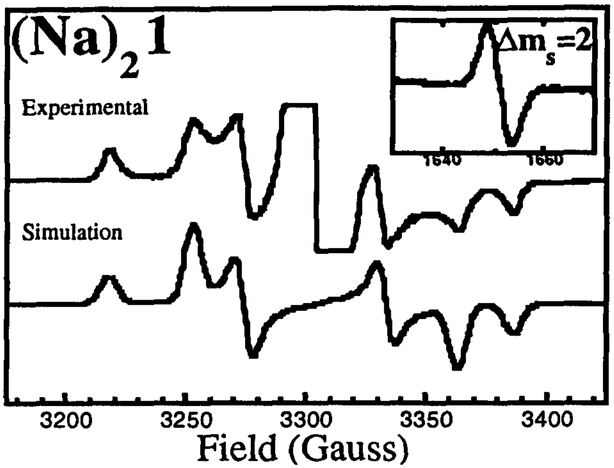

Figure 1. X-band EPR spectra of biradical $1^{\bullet\bullet 2-}$ as a frozen solution in THF at 77 K (upper) and spectral simulation (lower). Inset: $\Delta m_S = 2$ transition.

Table 2. Zero-Field-Splitting Parameters and Results of VT-EPR Studies for Bis(Semiquinones)[a]

Biradical	$\lvert D/hc\rvert$ /10^{-4} cm^{-1}	$\lvert E/hc\rvert$ /10^{-4} cm^{-1}	Curie Plot[b]
$1^{\bullet\bullet 2-}$	**78.9**	**8.80**	**linear**
$7^{\bullet\bullet 2-}$	94.7	6.30	linear
$8^{\bullet\bullet 2-}$	91.0	5.75	linear
$9^{\bullet\bullet 2-}$	86.0	6.70	linear
$10^{\bullet\bullet 2-}$	*ca.* 115	---	curved, $J \approx -100$ cal/mol[c]

[a] Zero-field-splitting parameters estimated by simulation. Data for $7^{\bullet\bullet 2-}$ — $10^{\bullet\bullet 2-}$ from ref 2a. [b] Linear Curie plots indicate either a triplet ground-state, or a singlet triplet degeneracy; curved Curie plots indicate a singlet ground state. [c] The J-value is one-half the singlet-triplet gap.

The zero-field splitting parameters for $1^{\bullet\bullet 2-}$ and previously reported bis(semiquinone)s are consistent with their electronic structures: greater delocalization results in smaller D-values.[14,15] Indeed, biradicals $1^{\bullet\bullet 2-}$, $7^{\bullet\bullet 2-}$ — $9^{\bullet\bullet 2-}$ that have conjugating groups attached to the semiquinone rings have D-values less than $10^{\bullet\bullet 2-}$. The D-value of $1^{\bullet\bullet 2-}$ is the smallest in the series consistent with the planarity of the π-system.

The Curie plot for the doubly-integrated $\Delta m_S = 2$ signal of $1^{\bullet\bullet 2-}$ is shown in Figure 2, and all results are summarized in Table 2. Biradicals $1^{\bullet\bullet 2-}$, $7^{\bullet\bullet 2-}$ — $9^{\bullet\bullet 2-}$ give a linear responses, consistent with $J > 0$ (ferromagnetic coupling) or $J = 0$ (singlet-triplet degeneracy).[16]

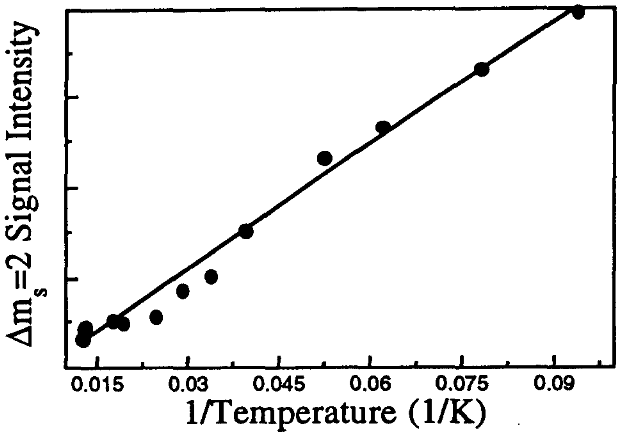

Figure 2. Curie plot for biradical $1^{\bullet\bullet2-}$. The data points were collected between 8 and 150 K and represent normalized signal intensities obtained by double integration of the Δm_S=2 signal.

CONCLUSIONS

A new, planar bis(semiquinone) has been prepared by two-electron reduction of the corresponding bis(quinone). The results of cyclic voltammetry indicate substantial interaction of the two semiquinone units, in line with the zero-field-splitting parameter, *D*, that suggests maximum delocalization of spin/charge density into the exchange coupling ethene unit.

EXPERIMENTAL

Unless noted otherwise, reactions were carried out in oven-dried glassware under an argon atmosphere. THF was distilled under nitrogen from sodium benzophenone ketyl, toluene was distilled from sodium metal under nitrogen, and methylene chloride were distilled from CaH_2 under nitrogen. *tert*-Butyl lithium (1.5M in pentane) was used as received from Acros Chemical. Other chemicals were purchased from Aldrich Chemical Company. Electrochemical experiments and X-Band EPR spectroscopy were performed as described previously.[17] NMR spectra were recorded at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR. Elemental analysis was performed by Atlantic Microlab, Inc, Norcross, GA. Mass Spectra were obtained at the NC State University Mass Spectrometry Facility.

Bis(3-*tert*-butylphenyl-4,5-dimethoxyphenyl)methanol, 3. A 200 mL Schlenk flask containing 1-bromo-3,4-dimethoxy-5-*t*-butyl-benzene (5.00 g, 18.30 mmol) in THF (70 mL) was cooled to –78°C, and *t*-butyllithium (1.5M, 24.4 mL, 36.6 mmol) was added slowly. The reaction mixture was stirred for 1 h at -78°C. Ethylformate (740 µL, 9.15 mmol) was added, and the reaction mixture was stirred for 2 h at -78°C and for 6.5 h at room temperature. Saturated brine was added and the mixture was poured into a separatory funnel. The mixture was extracted with ether (3X), and the ether washings combined, dried with Na_2SO_4, filtered, and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, 15-20% EtOAc:petroleum ether) to give **3** as colorless oil, (3.564 g, 94%). This material was used directly in the next step. ^1H NMR ($CDCl_3$) δ (ppm): 6.94 (s, 2H), 6.87 (s, 2H), 5.67 (s, 1H), 3.86 (s, 6H), 3.80 (s, 6H), 2.98 (s, 1H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 153.2, 147.7, 142.8, 138.5, 117.3, 109.1, 76.4, 60.3, 55.7, 35.2, 30.6. IR (film from CH_2Cl_2) ν (cm^{-1}): 3420, 2956, 2831, 1582, 1481, 1451, 1420, 1313, 1235, 1141, 1071, 1009.

3-[Bis-(3'-*tert*-butyl-4',5'-dimethoxyphenyl)methylene]pentane-2,4-dione, 4. In a glove box, carbinol **3** (3.36 g, 8.1 mmol), 2,4-pentadione (1.65 mL, 16.2 mmol), and anhydrous $CoCl_2$ (420 mg, 3.24 mmol) were added to a 50 mL Schlenk flask. The flask was removed from the glove box, connected to a Schlenk line, and the contents heated to reflux for 1 h. The reaction mixture was then cooled to room temperature, CH_2Cl_2 was added, and the mixture was filtered to remove inorganic salts. Solvent was removed by rotary evaporation and the residue was rinsed with petroleum ether to give the intermediate dione as a white solid, (3.23 g, 80%). ^1H NMR ($CDCl_3$) δ (ppm): 6.81 (s, 2H), 6.67 (s, 2H), 4.63 (s, 2H), 3.80 (s, 12H), 1.97 (s, 6H), 1.33 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 203.3, 153.3, 147.3, 143.3, 135.6, 117.8, 110.5, 75.3, 60.3, 55.7, 51.9, 35.2, 30.6, 29.9. IR (film from CH_2Cl_2) ν (cm^{-1}): 2956, 1698, 1580, 1482, 1452, 1423, 1357, 1313, 1235, 1147, 1069, 1008. Anal. Calcd for $C_{30}H_{42}O_6$: C, 72.26; H, 8.48. Found: C, 71.99; H, 8.42.

A 100 mL Schlenk flask containing the product from the previous reaction (2.58 g, 5.18 mmol), DDQ (3.53 g, 15.5 mmol), and 100 mL toluene was heated until the mixture reached reflux for 20 h, and reaction progress was monitored by TLC. When the reaction was judged complete, and after cooling the reaction mixture, toluene was removed by rotary evaporation. After adding CH_2Cl_2, the reduced DDQ was removed by filtration. The crude product was purified by column chromatography (SiO_2, 2.5-5% THF:petroleum ether), and then crystallized from ether and petroleum ether to give **4** as white crystals, (1.52 g, 59%). ^1H NMR ($CDCl_3$) δ (ppm): 6.79 (d, J = 1.89, 2H), 6.59 (d, J = 1.83, 2H), 3.92 (s, 6H), 3.76 (s, 6H), 1.93 (s, 6H), 1.33 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 204.1, 153.1, 150.8, 150.4, 143.3, 142.0, 133.5, 122.3, 112.7, 60.6, 55.9, 35.3, 31.2, 30.5. IR (film from CH_2Cl_2) ν (cm^{-1}): 2953, 1688, 1665, 1567, 1471, 1411, 1353, 1241, 1067, 1006, 907, 733. Anal. Calcd for $C_{30}H_{40}O_6$: C, 72.55; H, 8.12. Found: C, 72.54; H, 8.12.

3-[Bis-(3'-*tert*-butyl-4',5'-dimethoxyphenyl)methylene]-2,4-dimethyl-pentane-2,4-diol, 5. A 100 mL flask containing $ZrCl_4$ (737 mg, 3.16 mmol) and a stir bar was prepared in the glove box. The flask was removed from the glove box, connected to a Schlenk line. Freshly distilled THF (25 mL) was added and the mixture was cooled to -25 °C. An aliquot of 1.5 M methyllithium (8.60 mL, 12.05 mmol) was added via syringe and the reaction mixture was stirred for 10 min at -20 °C, 10 min at 25 °C, and then stirred 1h at -15 °C. Dione, **4**, (748 mg, 1.51 mmol) as a solution in THF (30 mL) was added by cannulation, keeping the temperature at -20 °C. The reaction mixture was stirred for 1.5 h at -20 °C, and cooled to -78 °C and then quenched by pouring onto saturated brine. The resulting mixture was extracted with ether (3X), and the extracts combined and dried over Na_2SO_4. After filtering and removing the solvent, the crude product was crystallized to give the intermediate diol, **5**, as a white solid, (789 mg, 99%). IR (film from CH_2Cl_2)

ν (cm^{-1}): 3326 (br), 2957, 1568, 1462, 1410, 1358, 1303, 1232, 1188, 1132, 1068, 1006, 953. Anal. Calcd for $C_{32}H_{48}O_6$: C, 72.69; H, 9.15. Found: C, 72.42; H, 8.99.

3,6-Di-*tert*-butyl-1,2,7,8-tetramethoxy-9,9,10,10-tetramethyl-9,10-dihydro-indeno[1,2-*a*]indene, 6. A 50 mL round-bottom flask containing diol **5** (789 mg, 1.49 mmol) and excess poly[phosphoric acid] (18 g) was heated to 150-160 °C for 0.5 h. When the reaction was judged complete by TLC, the reaction was cooled and carefully poured onto water/crushed ice with stirring. The resulting mixture was extracted with ether (3X) and the combined organic extracts were dried with Na_2SO_4, filtered, and evaporated to dryness. The residue was crystallized with ether/petroleum ether to give **6** as white crystals, (622 mg, 84%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.30 (s, 2H), 3.92 (s, 6H), 3.90 (s, 6H), 1.61 (s, 12H), 1.45 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 168.8, 150.9, 150.1, 147.3, 142.2, 140.0, 132.9, 112.5, 59.8, 49.1, 35.1, 30.7, 23.5. IR (film from CH_2Cl_2) ν (cm^{-1}): 2964, 1440, 1377, 1017. Anal. Calcd for $C_{32}H_{44}O_4$: C, 78.01; H, 9.00. Found: C, 77.76; H, 9.02.

3,6-Di-*tert*-butyl-9,9,10,10-tetramethyl-9,10-dihydro-indeno[1,2-*a*]indene-1,2,7,8-tetraone, 1. A 25 mL Schlenk flask containing **6** (100 mg, 0.203 mmol) and sodium ethanethiolate (683 mg, 8.12 mmol) was prepared in a glove box. The flask was removed from the glove box, connected to a Schlenk line, anhydrous DMF (10 mL) was added, and the mixture was refluxed for 31 h. When the reaction was judged complete by ^{1}H-NMR, the reaction mixture was cooled to room temperature quenched with deionized water and then 1M HCl. The resulting mixture was extracted with ether (3X), the extracts combined and dried over Na_2SO_4, and evaporated to dryness to give the intermediate bis(catechol) as a light red solid. The bis(catechol), excess Ag_2CO_3 (Fétizon's reagent: 150 mg, *ca.* 2.90 mmol Ag), and 10 mL of THF were combined in a 50 mL round bottom flask and the mixture was stirred for 20 h. The remaining solids were removed by filtration and the crude product was purified by radial chromatography (SiO_2, 20% ether:petroleum ether) and crystallization from a 1:1:1 mixture of CH_2Cl_2, ether, and petroleum ether to give purple needle crystals of **1**, (67 mg, 76%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.18 (s, 2H), 1.57 (s, 12H), 1.34 (s, 18H). ^{13}C NMR ($CDCl_3$) δ (ppm): 194.5, 181.8, 173.5, 152.8, 149.4, 146.3, 140.3, 127.3, 51.9, 35.8, 29.2, 22.6. IR (film from CH_2Cl_2) ν (cm^{-1}): 2966, 1678, 1624, 1601, 1538, 1443, 1364, 1197, 890. Anal. Calcd for $C_{28}H_{32}O_4$: C, 77.74; H, 7.45. Found: C, 77.54; H, 7.47. UV-Vis (CH_2Cl_2) λ_{max} (log ε): 230 (4.42), 284 (4.17), 400 (3.92), 498 (3.89).

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