The Synthesis of 2-Cyano-cyanothioformanilides from 2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles Using DBU

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Abstract: A series of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles were prepared from the reaction of 4,5-dichloro-1,2,3-dithiazolium chloride (Appel salt) and the corresponding anilinolamines. Reaction of the 1,2,3-dithiazolimines with DBU (3 equiv) at –5 °C gave the corresponding 2-cyano-cyanothioformanilides in near quantitative yields. Treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile with DBU (4 equiv) at –5 to 5% at 20 °C gave 2-isothiocyanatobenzonitrile in 96% yield. The latter compound was also formed directly from 2-cyano-cyanothioformanilide on treatment with DBU (1 equiv) in 95% yield. A tentative mechanism for the DBU-mediated dithiazole to cyanothioformanilide transformation is proposed and all compounds were fully characterized.

Key words: Appel salt, DBU, Cyanothioformanilide, isothiocyanate

Cyanothioformanilides (thioxanilonitriles) demonstrate herbicidal activity,1 and have been used extensively for the preparation of various heterocycles including pyrroles,2a,b imidazoles,3 oxazoles,4 1,3,4-thiadiazoles,5 quinazolines,6 and other fused heterocycles.7 Furthermore, cyanothioformanilides participate in Diels–Alder and ene-reactions,8 and in nucleophilic (thiophilic) reagents such as aqueous hydrogen sulfide or hydroxylamine to the nitrile, afford aminooxothioacetylanilines, aminothiooxoacetylanilines (N-arylthiioxamides)4c,11 or amidinothioformylanilines,4e,12 respectively.

Cyanothioformanilides are traditionally prepared by the reaction of N-aryl isothiocyanates with cyanoacetanilides,3j,4a,b,7g,h,13 or bis(dialkylamino)acetonitriles14 and also via dethiohydration of N-arylthiooximides,3d,15 thionation–dethiohydration of N-arylthiooxamides,15 and thionation–dehydration of aryloxalamides.16 More recent methods involve treating 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzenes with either the oxidizing agent m-chloroperoxybenzoic acid (MCPBA),16 the reducing agent sodium cyanoborohydride (NaBH₄CN),17 or with nucleophilic (thiophilic) reagents such as aqueous sodium hydroxide,18 hydroxylamine,19 tert-butylamine,20 tryptamine,21 o-aminophenethylation and o-phenylenediamine,22 triphenylphosphoranylidene,23 triphenylphosphine in moist dichloromethane,24 and through the use of ethylmagnesium bromide (1 equiv).24h,25

While the use of triphenylphosphine (2 equiv) was reported to give good yields of the cyanothioformanilides, it was not possible to obtain 2-cyano-cyanothioformanilide (2a) from the reaction of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a) despite the preparation of the 4,5-dimethoxy analogue in high yield.26 Nevertheless Kim et al. successfully isolated 2-cyano-cyanothioformanilide (2a) from the reaction of the dithiazoline 1a with either NH₂OH·HCl (4 equiv) in pyridine at ~20 °C for 4 h (27%)19 or as a by-product from reaction with phosphoranylidene in low yield (8%).23 As part of our ongoing investigations of 4,5-dichloro-1,2,3-dithiazolium chloride (Appel salt)26 and our desire to study the chemistry of 2-cyano-cyanothioformanilides 2, we required an efficient synthesis that tolerated a range of aryl substituents. Here, we describe the reaction of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles 1 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which affords the desired 2-cyano-cyanothioformanilides 2 in near quantitative yields.

Treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a) with only DBU (3 equiv) in dichloromethane at ca. –5 °C gave near quantitative conversion of dithiazolimine 1a into 2-cyano-cyanothioformanilide (2a) and no sulfur formation could be observed by TLC. The use of an additional equivalent of DBU led to the clean formation of 2-isothiocyanatobenzonitrile (3) which could also be formed directly from a pure sample of 2-cyano-cyanothioformanilide 1a (Scheme 1). No reaction occurred between the dithiazoline 1a and three equivalents of either pyridine, 1,4-diazabicyclo[2.2.2]octane (DABCO), 4-((N,N-dimethylamino)pyridine (DMAP) or triethylamine in dichloromethane at ~20 °C.

The high-yielding formation of the isothiocyanate 3 is worthy of note; since 1995, only four reports have appeared on the conversion of 2-(4-chloro-5H-1,2,3-dithia-

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Scheme 1  Reagents and conditions: (i) DBU (3 equiv), CH₂Cl₂, –5 °C, 5 min, 93%; (ii) DBU (1 equiv), 20 °C, 0.5 h, 95%; (iii) DBU (4 equiv), CH₂Cl₂, –5 to +20 °C, 0.5 h, 96%.

[Diagram of Scheme 1]
The facile conversion of 1,2,3-dithiazolimine 1a into 2-cyano-cyanothioformanilide (2a) was extended to a wider range of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles 1b–g, which were readily prepared from the corresponding anthranilonitriles 4a–g and 4,5-dichloro-1,2,3-dithiazolium chloride 5 (Table 1).

In general, the reaction of the dithiazolimines 1 with DBU (3 equiv) at ca. −5 °C rapidly gave the desired 2-cyano-cyanothioformanilides 2 in high yield (Table 2). In a couple of examples where the yield was significantly lower than 90%, the reactions could be initiated at ca. −78 °C and, under these conditions, the products were obtained in yields >90%.

A tentative mechanistic rationale for the reaction can be proposed as follows. Nucleophilic attack via the DBU amidine nitrogen at the dithiazole S(2) ring sulfur and subsequent ring-opening can afford the disulfide 6. A second equivalent of DBU could then abstract HCl to give the neutral disulfide 7. Further nucleophilic attack by a third equivalent of DBU could cleave the disulfide S–S bond to ultimately give the cyanothioformanilide and the neutral sulfane 8 (Scheme 2).

Table 1 Reaction of Anthranilonitriles 4 with 4,5-Dichloro-1,2,3-dithiazolium Chloride (5) Followed by Treatment with Pyridine

<table>
<thead>
<tr>
<th>R</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>H</td>
<td>1a</td>
</tr>
<tr>
<td>4b</td>
<td>6-Me</td>
<td>1b</td>
</tr>
<tr>
<td>4c</td>
<td>5-O₂N</td>
<td>1c</td>
</tr>
<tr>
<td>4d</td>
<td>4-Cl</td>
<td>1d</td>
</tr>
<tr>
<td>4e</td>
<td>5-Cl</td>
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</tr>
<tr>
<td>4f</td>
<td>4-MeO</td>
<td>1f</td>
</tr>
<tr>
<td>4g</td>
<td>4,5-(MeO)₂</td>
<td>1g</td>
</tr>
</tbody>
</table>

a Reaction conditions: 4 (0.65 mmol), 5 (1 equiv), CH₂Cl₂, −20 °C, 1 h then pyridine (2 equiv), −20 °C, 2 h.

Table 2 Reaction of 2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitriles 1 with DBU

<table>
<thead>
<tr>
<th>R</th>
<th>Temp (°C)</th>
<th>Time (min)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>−5</td>
<td>5</td>
<td>2a</td>
</tr>
<tr>
<td>1b</td>
<td>6-Me</td>
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</tr>
<tr>
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<td>5-O₂N</td>
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<td>45</td>
<td>2e</td>
</tr>
<tr>
<td>1d</td>
<td>4-Cl</td>
<td>−5</td>
<td>15</td>
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<td>1f</td>
<td>4-MeO</td>
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<tr>
<td>1g</td>
<td>4,5-(MeO)₂</td>
<td>−5</td>
<td>15</td>
<td>2g</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1 (0.40 mmol), DBU (3 equiv), anhyd CH₂Cl₂ (2 mL).
Cl

cyanothioformanilides found to date.13 Pprovides the most efficient route to this class of nitrile (1

zonitrile (1b) were protected from atmospheric moisture by CaCl₂ drying tubes. CH₂Cl₂ was freshly distilled from CaH₂ under argon. Reactions from N to C(6) and similar N–P to C(6)–P migrations are protected from atmospheric moisture by CaCl₂ drying tubes. CH₂Cl₂ was freshly distilled from CaH₂ under argon. Reactions from N to C(6) and similar N–P to C(6)–P migrations were not successful, the need for three equivalents of DBU in confirmed, since the use of less than this amount gave incomplete conversion of the anticipated sulfane. It is worthy of note that the sulfane sulfur could migrate from the reaction mixture tentatively added support to the starting dithiazolimine. The absence of elemental sulfur for an additional 2 h. The reaction mixture was adsorbed onto silica was not successful, the need for three equivalents of DBU in confirmed, since the use of less than this amount gave incomplete conversion of the anticipated sulfane. It is worthy of note that the sulfane sulfur could migrate from the reaction mixture tentatively added support to the starting dithiazolimine. The absence of elemental sulfur for an additional 2 h. The reaction mixture was adsorbed onto silica and chromatography (hexane) gave S₈ (traces). Further elution for an additional 2 h. The reaction mixture was adsorbed onto silica and chromatography (hexane) gave S₈ (traces). Further elution (hexane–CH₂Cl₂, 8:2) gave 4-chloro-5H-1,2,3-dithiazole-5-thione (9; 10 mg, 6%) and (hexane–CH₂Cl₂, 2:8) gave the title compound 1a.

Yield: 395 mg (92%); yellow crystals; mp 125–126 °C (Lit. 21 128 °C) (cyclohexane–CH₂Cl₂).

IR: 3088 (w), 3025 (w; ArCH), 2238 (m; C≡N).

1H NMR (300 MHz, CDCl₃): δ = 7.80 (d, 1 H, ArH–d₁), 7.76–7.65 (m, 2 H, ArH), 7.35–7.29 (m, 2 H, ArH).

13C NMR (75 MHz, CDCl₃): δ = 161.5, 153.2, 148.0, 134.4 (ArCH), 134.0 (ArCH), 126.3 (ArCH), 117.4 (ArCH), 116.3 (C≡N), 106.0 (CC≡N).

13C NMR (75 MHz, DEPT-135, DMSO-d₆): δ = 134.4 (ArCH), 134.0 (ArCH), 125.3 (ArCH), 117.4 (ArCH).

MS (El): m/z (%) = 255 (35) [M⁺ + 2], 253 (84) [M⁺], 192 (99), 160 (12), 154 (18), 128 (11), 125 (10), 116 (4), 102 (71), 93 (13), 75 (33), 64 (100), 51 (31).

UV/Vis (CH₂Cl₂); λ max (log ε) = 231 (3.33), 268 (inf; 2.79), 302 (2.65), 379 (2.92), 398 (inf; 2.85), 423 nm (inf; 2.56); identical to an authentic sample.

2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)-6-methylbenzonitrile (1b) Similar treatment of 2-amino-6-methylbenzonitrile (4b; 200 mg, 1.52 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 315.9 mg, 1.52 mmol) and pyridine (245.9 μl, 2 equiv) in CH₂Cl₂ (4 mL) gave the title compound 1b.

Yield: 369.3 mg (91%); yellow cotton fibers; mp 109–110 °C (cyclohexane–EtOH).

IR: 2232 (w; C≡N), 1601 (m–s), 1579 (m), 1547 (s), 1480 (s), 1431 (m), 1283 (s), 1248 (s), 1231 (s), 1147 (s), 1115 (s), 1082 (s), 1049 (s), 980 (s), 878 (m), 847 (s), 770 (s), 738 (s), 723 (s), 680 (w), 641 (s), 605 (w).
Yield: 324.2 mg (80%); red powder; mp 181–182 °C (EtOH).

MS (EI): m/z (%) = 300 (6) [M + + 2], 298 (14) [M+] , 237 (15), 205 (9), 157 (9), 127 (10), 102 (13), 93 (8), 76 (11), 64 (55), 50 (7).

UV/Vis (CH2Cl2): λ max (log ε) = 291 (5) [M + + 4], 289 (26) [M + + 2], 287 (37) [M+] , 228 (21), 226 (47), 194 (9), 188 (7), 162 (9), 136 (12), 127 (7), 125 (6), 109 (5), 100 (31), 93 (8), 75 (10), 70 (8), 64 (100), 50 (8).

UV/Vis (CH3Cl2): λ max (log ε) = 430 (inf; 2.39), 383 (2.78), 313 (2.97), 247 (2.96), 229 nm (3.00).

Anal. Calcd for C10H6ClN3S2: C, 44.9; H, 2.3; N, 15.7.

5-Chloro-2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1e)

Similar treatment of 2-amino-5-chlorobenzonitrile (4f; 200 mg, 1.35 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 281.8 mg, 1.35 mmol) and pyridine (218 µL, 2.70 mmol, 2 equiv) in CH2Cl2 (4 mL) gave the title compound 1e.

Yield: 282.7 mg (74%); orange needles; mp 163–164 °C (cyclohexane–CH2Cl2).

IR: 2965 (w) and 2835 (w; CH3), 2221 (s; C≡N).

UV/Vis (CH2Cl2): λ max (log ε) = 233 (3.25), 272 (inf; 2.76), 337 nm (2.78).

Anal. Calcd for C10HCl3ClN3O2S2: C, 42.3; H, 2.1; N, 14.8. Found: C, 42.4; H, 2.0; N, 14.8.

2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)4-methoxybenzonitrile (1f)

Similar treatment of 2-amino-4-methoxybenzonitrile (4f; 200 mg, 1.35 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 281.8 mg, 1.35 mmol) and pyridine (218 µL, 2.70 mmol, 2 equiv) in CH2Cl2 (4 mL) gave the title compound 1f.

Yield: 282.7 mg (74%); orange needles; mp 163–164 °C (cyclohexane–CH2Cl2).

IR: 2965 (w) and 2835 (w; CH3), 2221 (s; C≡N), 1589 (s), 1495 (s), 1249 (s), 1095 (s), 821 (s), 756 (s) cm⁻¹.

UV/Vis (CH2Cl2): λ max (log ε) = 300 (6) [M + + 2], 298 (14) [M+] , 237 (15), 205 (9), 157 (9), 127 (10), 102 (13), 93 (8), 76 (11), 64 (55), 50 (7).

UV/Vis (CH3Cl2): λ max (log ε) = 430 (inf; 2.39), 383 (2.78), 313 (2.97), 247 (2.96), 229 nm (3.00).

Anal. Calcd for C10H6ClN3O2S2: C, 44.9; H, 2.3; N, 15.7.

5-Chloro-2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1e)

Similar treatment of 2-amino-5-chlorobenzonitrile (4e; 200 mg, 1.31 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 273.1 mg, 1.31 mmol) and pyridine (212 µL, 2.62 mmol, 2 equiv) in CH2Cl2 (4 mL) gave the title compound 1e.

Yield: 323.3 mg (86%); yellow cotton fibers; mp 147–148 °C (cyclohexane–CH2Cl2).

IR: 3071 (w; ArCH), 2237 (w; C≡N), 1589 (s), 1495 (s), 1249 (s), 1095 (s), 821 (s), 756 (s) cm⁻¹.

UV/Vis (CH2Cl2): λ max (log ε) = 233 (3.25), 272 (inf; 2.76), 337 nm (2.78).

Anal. Calcd for C10HCl3ClN3O2S2: C, 42.3; H, 2.1; N, 14.8. Found: C, 42.4; H, 2.0; N, 14.8.

2-(4-Chloro-5H-1,2,3-dithiazol-5-ylideneamino)4,5-dimethoxybenzonitrile (1g)

Similar treatment of 2-amino-4,5-dimethoxybenzonitrile (4g; 200 mg, 1.12 mmol), 4,5-dichloro-1,2,3-dithiazolium chloride (5; 233.5 mg, 1.12 mmol) and pyridine (181 µL, 2.24 mmol, 2 equiv) in CH2Cl2 (4 mL) gave the title compound 1g.

Yield: 266.4 mg (76%); orange crystals; mp 156–157 °C (cyclohexane–EtOH).
IR: 3002 (w; ArCH), 2961 (w), 2829 (w; CH₃), 2224 (m, C≡N), 1591 (s), 1498 (s), 1281 (s), 1103 (s), 902 (s), 763 (s) cm⁻¹. 31H NMR (300 MHz, CDCl₃): δ = 7.12 (s, 1 H, ArH-6), 6.81 (s, 1 H, ArH-3), 3.93 (s, 3 H, CH₃O), 3.93 (s, 3 H, CH₂O). 31C NMR (75 MHz, DMSO-d₆): δ = 133.8 (ArCH), 124.6 (ArCH), 20.0 (CH₃). MS (EI): m/z (%): 201 (56) [M⁺], 200 (31), 186 (14), 174 (100), 168 (15), 149 (14), 142 (17), 131 (6), 116 (87), 104 (16), 89 (43), 73 (75), 70 (24), 63 (25), 51 (15). UV/Vis (CH₃Cl): λmax (log ε) ≈ 226 (3.71), 254 (2.97), 283 (2.75), 332 (2.79), 348 nm (2.85).


2-(Cyanothioformamido)-5-nitrobenzonitrile (2c) Similarly, treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylidene)amine-5-nitrobenzonitrile (1c; 100 mg, 0.34 mmol) cooled to ca. –78 °C with DBU gave, after chromatography (CH₂Cl₂–tert-butyl methyl ether, 50:50), the title compound 2c.
Yield: 74.9 mg (95%); red powder; mp >300 °C (pentane–CH₂Cl₂).
IR: 3611 (w), 3399 (w; NH), 3053 (w; ArCH), 2236 (w; C≡N), 1597 (m), 1483 (s), 1443 (s), 1346 (s), 1261 (m), 1177 (m), 843 (m), 733 (m) cm⁻¹. 31H NMR (300 MHz, CD₂Cl₂): δ = 8.58 (d, J = 2.7 Hz, 1 H, ArH-6), 7.6 (d, J = 9.0 Hz, 1 H, ArH-3); NH missing.
13C NMR (75 MHz, DMSO-d₆): δ = 162.7, 160.75, 141.5, 128.85 (ArCH, 128.0 (ArCH), 122.85 (ArCH), 117.7 (C≡N), 116.1 (C≡N), 105.7 (C≡N).

13C NMR (75 MHz, DEPT-135, DMSO-d₆): δ = 128.9 (ArCH), 122.85 (ArCH).

MS (EI): m/z (%): 232 (19) [M⁺], 205 (100), 199 (8), 186 (6), 175 (36), 159 (37), 147 (24), 132 (14), 115 (26), 97 (9), 94 (14), 88 (17), 85 (21), 70 (16), 64 (21), 57 (14), 50 (13).
UV/Vis (CH₃Cl): λmax (log ε) ≈ 226 (3.10), 254 (2.97), 283 (2.75), 332 (2.79), 348 nm (2.85).
Anal. Calcd for C₁₀H₉N₂S: C, 46.55; H, 1.7; N, 24.1. Found: C, 46.5; H, 1.8; N, 24.1.
5-Chloro-2-(cyanothioformamido)benzonitrile (2e)

Similarly, treatment of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)-5-chlorobenzonitrile (1e; 100 mg, 0.35 mmol) cooled to ca. –5 °C with DBU gave, after chromatography (CH₂Cl₂), the title compound 2e.

Yield: 98.4 mg (89%); dark-red crystals; mp 131–132 ºC (cyclohexane).

IR: 3271 (m; ν(NH)), 1516 (C=S), 1514 (ν(C=O)), 1468 (ν(NH)), 1163 (ν(OH)), 1076 (s), 841 (s) cm⁻¹.

1H NMR (300 MHz, CD₂Cl₂); δ = 7.83 (s, 1 H, ArH-3), 7.16 (s, 1 H, ArH-5), 3.97 (s, 3 H, CH₃O), 3.96 (3 H, CH₃O); NH missing.

13C NMR (75 MHz, DMSO-d₆); δ = 165.3 (C=S), 153.0 (ArC), 148.4 (ArC), 133.5 (ArC), 116.1 (C≡N), 114.6 (ArCH), 113.5 (C≡N), 110.4 (ArCH), 100.5 (C≡C), 56.3 (CH₃O), 56.2 (CH₃O).

13C NMR (75 MHz, DEPT-135, DMSO-d₆); δ = 114.6 (ArCH), 110.4 (ArCH), 56.3 (CH₃O), 56.2 (CH₃O).

MS (EI); m/z (%) = 247 (100) [M⁺], 232 (7), 214 (15), 205 (27), 195 (35), 180 (21), 177 (28), 162 (13), 150 (10), 134 (13), 119 (17), 104 (13), 90 (7), 83 (7), 76 (15), 70 (23), 50 (11).

UV/Vis (CH₂Cl₂); λmax (log ε) = 230 (3.56), 265 (3.48), 277 (inf; 3.51), 287 (3.56), 331 (inf; 3.07), 347 (3.11), 375 (3.16), 395 nm (inf; 3.07).

Anal. Calcd for C₁₃H₁₁N₃O₂: C, 54.3; H, 3.7; N, 17.0. Found: C, 53.4; H, 3.8; N, 16.9.

2-Isothiocyanatobenzonitrile (3) from 2-(Cyanothioformamido)benzonitrile (2a)

To a stirred solution of 2-(4-chloro-5H-1,2,3-dithiazol-5-ylideneamino)benzonitrile (1a) (100 mg, 0.53 mmol) in distilled CH₂Cl₂ (2 mL) at ~20 °C and protected with a CaCl₂ drying tube, was added dropwise, DBU (79.3 µL, 0.53 mmol, 1 equiv). The mixture was then allowed to stir at ~20 °C, until no starting material remained (TLC). The reaction mixture was adsorbed onto silica and purified by chromatography (CH₂Cl₂–tert-butyl methyl ether, 9:1) to give the title compound 3.

Yield: 81.4 mg (96%); colorless needles; mp 66–67 ºC (Lit. 64 ºC) (cyclohexane).

IR: 2232m (C≡N); 1784, 1749, 1723 (C=O); 3453 (OH); 2930 (C–H); 1592, 1478, 1336 (Ar–C); 1214 (CH₃O); 1102, 994 (C–C).

Anal. Calcd for C₁₃H₁₁N₃O₂S: C, 40.0; H, 3.7; N, 17.0. Found: C, 40.1; H, 3.7; N, 17.0.

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