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# The Molecular and Crystal Structure of Tricyclazole, $C_9H_7N_3S$

**Keun Il Park, Yong Kie Kim, Sung Il Cho and Man Hyung Yoo**

*Department of Chemical Engineering, Junnong-dong 90, University of Seoul, Korea*

# Tricyclazole, $C_9H_7N_3S$의 분자 및 결정구조

**박권일 · 김용기 · 조성일 · 유만형**

서울시립대학교 화학공학과

## Abstract

The molecular and crystal structure of Tricyclazole, $C_9H_7N_3S$, has been determined by single crystal x-ray diffraction study. Crystallographic data for title compound: $Pca2_1$, $a$ = 14.889(1) Å, $b$ = 7.444(1) Å, $c$ = 15.189(2) Å, $V$ = 1683.3(3) Å$^3$, $Z$ = 8. The molecular structure model was solved by direct methods and refined by full-matrix least-squares. The final reliable factor, $R$, is 0.047 for 1533 independent reflections ($F_o^2 > 4\sigma(F_o^2)$). The asymmetry unit contains two molecules which are in plate conformation, parallel to each other and related by a pseudo four-fold screw on the $b$-direction.

## 요 약

X-선 회절법을 이용하여 Tricyclazole, $C_9H_7N_3S$의 분자 및 결정 구조를 규명하였다. 화합물의 결정학 자료: Orthorhombic 공간군 $Pca2_1$, $a$ = 14.889(1) Å, $b$ = 7.444(1) Å, $c$ = 15.189(2) Å, $V$ = 1683.3(3) Å$^3$, $Z$ = 8. 분자 구조는 직접법으로 풀었고 완전최소자승법으로 정밀화하여 1533 ($F_o^2 > 4\sigma(F_o^2)$)인 독립회절반점에 대하여 최종 신뢰도 값 $R$ = 0.047을 얻었다. 구조 해석 결과 두 분자가 asymmetric 단위로 구성되어 있으며 각각의 분자는 서로 거의 평형을 이루면서 $b$축 방향으로 유사 4-fold screw를 이루고 있었다.

## 1. Introduction

Title compound is benzothiazole derivative and has biological activity as a systemic fungicide which is rapidly absorbed on root and translate through the plant.[1] It inhibits appressorial penetration probably due to the lack of melanization in appressoria.[2)3)]

The characteristic structure of this compound shown in this paper, which is the first report to our certain knowledge, might offer an important information to elucidate the relationship between the crystal structure and biological activity.

## 2. Experimental

Single crystal of this compound were grown from a saturated toluene solution. A transparent crystal of dimension 0.55×0.35×0.30 mm was mounted at the tip of a glass fiber. The accurate cell parameters were obtained by least-squares refinement from 25 reflections in the ranges $12^\circ < \theta < 26^\circ$ measured with graphite-monochromated Mo Kα radiation on Enraf-Nonious CAD4 Diffractometer at 293 ± 3 K.[4)]

X-ray intensity data were collected by ω-2θ scan method (ω-scan width = 0.8 + 0.35 tanθ°) with 2θ = 49.89° in the ranges of $0 \le h \le 17$, $0 \le k \le 18$, $0 \le l \le 8$. Three standard reflections monitored every 100 reflections showed maximum 3% deviation of intensity during the course of data collection. All reflections were corrected for Lp effect[5)] but not for absorption effect because of the small linear absorption coefficient (0.33/mm). Crystallographic details

**Table 1. X-ray data collection and structure refinement**

| | |
|---|---|
| *Crystal size | : 0.55×0.35×0.30 mm |
| *Lattice parameter determination | : 25 reflections of θ = 12°-26° |
| *Diffractometer | : Enraf Nonius CAD4 Diffractometer |
| *Radiation | : Graphate mono-chromated Mo-Kα (λ = 0.7107 Å) |
| *Data collection temperature | : 293 ± 3 K |
| *Index range | : $0 \le h \le 17$, $0 \le k \le 18$, $0 \le l \le 8$ (Maximum 2θ = 49.89°) |
| *Scane method | : ω-2θ (ω-scane width = 0.8 + 0.35 tanθ°) |
| *Orientation | : Three standard reflections are used which has 3.0%/1 hr maximum variation |
| *Data | : 1533 unique reflections are collected |
| *Data conversion | : Correction of Lorentz and polarization is applied to intensity data |
| *Molecular formula | : $C_9H_7N_3S$ |
| *Molecular weight | : 189.2 g/mol |
| *Density(calculated) | : 1.493 g/cm$^3$ |
| *Crystal system | : Orthorhombic |
| *Cell parameter | : $a$ = 14.899(1) Å, $b$ = 7.444(1) Å, $c$ = 15.189(2) Å |
| *Space group | : $Pca2_1$ |
| *Volume | : 1683.3(3) Å$^3$ |
| *Z | : 8 |
| *Absorption coefficient | : 0.33/mm |
| *F(000) | : 784.0 |
| *Structure | : Direct method (SHELXL-86 program) |
| *Refine | : Full-matrix least square method (SHELXL-93 program) |
| *Hydrogen atom | : Ideal geometry (SHELXL-93 program) |
| *Final R factor | : 0.047 for $F_o^2 > 4\sigma(F_o^2)$ data (1533) |
| *Goo. F. | : 1.105 |

and data collection parameters are given in Table 1. The structure was solved by the application of direct methods using SHELXS-86[6] and refined by full-matrix least-squares on $F_o^2$ using SHELXL-93[7] with anisotropic displacement factors for all 14 non-H atoms. The H atoms were located by geometrical

**Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for non-hydrogen atom of tricyclazole, $C_9H_7N_3S$**

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

| atom | $x$ | $y$ | $z$ | $U_{eq}$ | atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| S(1) | 0.8723 (1) | 0.0216 (1) | 0.4815 (9) | .0529(4) | S(1') | 0.9341 (1) | 0.0098 (1) | 0.2287 (1) | .0546(4) |
| C(2) | 0.8748 (2) | −0.1933 (5) | 0.5307 (2) | .039(1) | C(2') | 0.9212 (2) | −0.2034 (5) | 0.2787 (2) | .039(1) |
| C(3) | 0.8009 (2) | −0.2916 (6) | 0.5566 (3) | .045(1) | C(3') | 0.9888 (2) | −0.3166 (6) | 0.3038 (2) | .045(1) |
| C(4) | 0.8154 (3) | −0.4601 (7) | 0.5926 (3) | .047(1) | C(4') | 0.9656 (3) | −0.4789 (6) | 0.3408 (3) | .045(1) |
| C(5) | 0.9027 (3) | −0.5254 (6) | 0.6033 (2) | .041(1) | C(5') | 0.8764 (4) | −0.5265 (6) | 0.3520 (3) | .052(1) |
| C(6) | 0.9777 (2) | −0.4280 (6) | 0.5777 (2) | .037(1) | C(6') | 0.8075 (2) | −0.4151 (5) | 0.3287 (2) | .037(1) |
| C(7) | 0.9610 (2) | −0.2597 (5) | 0.5421 (2) | .036(1) | C(7') | 0.8318 (2) | −0.2501 (5) | 0.2912 (2) | .0331(9) |
| N(8) | 1.0244 (2) | −0.1339 (4) | 0.5104 (2) | .040(1) | N(8') | 0.7750 (2) | −0.1119 (4) | 0.2620 (2) | .0393(8) |
| C(9) | 1.1151 (3) | −0.1081 (9) | 0.4998 (3) | .055(1) | C(9') | 0.6859 (3) | −0.0696 (8) | 0.2562 (3) | .054(1) |
| N(10) | 1.1307 (3) | 0.0420 (7) | 0.4632 (3) | .065(1) | N(10') | 0.6781 (3) | 0.0891 (7) | 0.2180 (3) | .068(1) |
| N(11) | 1.0507 (3) | 0.1281 (6) | 0.4471 (3) | .068(1) | N(11') | 0.7619 (3) | 0.1548 (5) | 0.1994 (3) | .061(1) |
| C(12) | 0.9906 (4) | 0.0164 (5) | 0.4759 (4) | .048(1) | C(12') | 0.8182 (3) | 0.0352 (6) | 0.2268 (4) | .049(1) |
| C(13) | 1.0716 (3) | −0.5007 (8) | 0.5892 (4) | .051(1) | C(13') | 0.7117 (3) | −0.4646 (7) | 0.3428 (4) | .054(1) |

**Table 3. Bond distances (Å), bond angles (°), selected torsion angles (°) and Least squares planes. The e.s.d.'s are in parentheses. Tricyclazole, $C_9H_7N_3S$**

| | | | |
|---|---|---|---|
| Bond distances (Å) | | | |
| S(1)-C(2) | 1.767 (7) | S(1')-C(2') | 1.771 (5) |
| S(1)-C(10) | 1.765 (6) | S(1')-C(10') | 1.738 (15) |
| C(2)-C(3) | 1.379 (6) | C(2')-C(3') | 1.367 (7) |
| C(2)-C(8) | 1.387 (6) | C(2')-C(8') | 1.387 (6) |
| C(3)-C(4) | 1.385 (7) | C(3')-C(4') | 1.377 (7) |
| C(4)-C(5) | 1.398 (6) | C(4')-C(5') | 1.385 (8) |
| C(5)-C(6) | 1.389 (6) | C(5')-C(6') | 1.367 (7) |
| C(6)-C(7) | 1.509 (7) | C(6')-C(7') | 1.489 (7) |
| C(6)-C(8) | 1.388 (6) | C(6')-C(8') | 1.402 (6) |
| C(8)-N(9) | 1.414 (5) | C(8')-N(9') | 1.404 (5) |
| N(9)-C(10) | 1.334 (6) | N(9')-C(10') | 1.378 (6) |
| N(9)-C(13) | 1.373 (5) | N(9')-C(13') | 1.367 (7) |
| C(10)-N(11) | 1.297 (7) | C(10')-N(11') | 1.292 (7) |
| N(11)-N(12) | 1.372 (7) | N(11')-N(12') | 1.370 (7) |
| N(12)-C(13) | 1.273 (9) | N(12')-C(13') | 1.320 (8) |
| Bond angles (°) | | | |
| C(3)-C(2)-S(1) | 125.8 (3) | C(3')-C(2')-S(1') | 126.3 (3) |
| C(4)-C(3)-C(2) | 118.0 (3) | C(4')-C(3')-C(2') | 118.0 (3) |
| C(5)-C(4)-C(3) | 120.4 (4) | C(5')-C(4')-C(3') | 121.0 (4) |
| C(6)-C(5)-C(4) | 122.3 (4) | C(6')-C(5')-C(4') | 122.2 (4) |
| C(6)-C(7)-C(2) | 122.5 (3) | C(6')-C(7')-C(2') | 121.5 (3) |
| C(7)-C(2)-S(1) | 113.3 (3) | C(7')-C(2')-S(1') | 112.8 (3) |
| C(7)-C(2)-C(3) | 120.9 (3) | C(7')-C(2')-C(3') | 120.9 (3) |
| C(7)-C(6)-C(5) | 115.9 (3) | C(7')-C(6')-C(5') | 116.3 (3) |
| N(8)-C(7)-C(2) | 109.8 (3) | N(8')-C(7')-C(2') | 110.5 (3) |
| N(8)-C(7)-C(6) | 127.7 (3) | N(8')-C(7')-C(6') | 128.0 (3) |
| N(8)-C(12)-S(1) | 112.1 (4) | N(8')-C(12')-S(1') | 111.8 (3) |
| C(9)-N(8)-C(7) | 142.1 (4) | C(9')-N(8')-C(7') | 140.7 (4) |
| N(10)-C(9)-N(8) | 110.8 (5) | N(10')-C(9')-N(8') | 108.7 (4) |
| N(11)-N(10)-C(9) | 109.3 (4) | N(11')-N(10')-C(9') | 109.3 (4) |
| N(11)-C(12)-S(1) | 133.7 (4) | N(11')-C(12')-S(1') | 136.5 (4) |
| N(11)-C(12)-N(8) | 114.2 (5) | N(11')-C(12')-N(8') | 111.7 (4) |
| C(12)-S(1)-C(2) | 88.8 (2) | C(12')-S(1')-C(2') | 89.8 (2) |
| C(12)-N(8)-C(7) | 115.9 (4) | C(12')-N(8')-C(7') | 115.1 (3) |
| C(12)-N(8)-C(9) | 102.0 (4) | C(12')-N(8')-C(9') | 104.2 (4) |
| C(12)-N(11)-N(10) | 103.8 (4) | C(12')-N(11')-N(10') | 106.2 (4) |
| C(13)-C(6)-C(5) | 121.7 (4) | C(13')-C(6')-C(5') | 122.1 (4) |
| C(13)-C(6)-C(7) | 122.4 (4) | C(13')-C(6')-C(7') | 121.5 (3) |

calculations. The final R value was 0.047 with 1533 ($F_o^2 4\sigma(F_o^2)$) observed reflections and 292 variables. The final positions and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 2. In the Table 3, crystal geometric properties are listed.

## 3. Results and Discussion

The X-ray structure ORTEP-III drawing[8] of the

**Table 3. Continued**

| Torsion angles (°) | | | |
|---|---|---|---|
| C(12)-S(1)-C(2)-C(3) | −179.4 (6) | C(12')-S(1')-C(2')-C(3') | −179.2 (4) |
| C(12)-S(1)-C(2)-C(7) | .7 (3) | C(12')-S(1')-C(2')-C(7') | .9 (3) |
| C(2)-S(1)-C(12)-N(8) | −1.2 (4) | C(2')-S(1')-C(12')-N(8') | −.3 (3) |
| C(2)-S(1)-C(12)-N(11) | −179.7 (8) | C(2')-S(1')-C(12')-N(11') | −178.6 (6) |
| S(1)-C(2)-C(3)-C(4) | 178.7 (6) | S(1')-C(2')-C(3')-C(4') | −179.1 (5) |
| C(7)-C(2)-C(3)-C(4) | −1.3 (4) | C(7')-C(2')-C(3')-C(4') | .8 (3) |
| S(1)-C(2)-C(7)-C(6) | −178.5 (5) | S(1')-C(2')-C(7')-C(6') | 179.0 (4) |
| S(1)-C(2)-C(7)-N(8) | .0 (4) | S(1')-C(2')-C(7')-N(8') | −1.2 (2) |
| C(3)-C(2)-C(7)-C(6) | 1.6 (3) | C(3')-C(2')-C(7')-C(6') | −.9 (3) |
| C(3)-C(2)-C(7)-N(8) | −180.0 (5) | C(3')-C(2')-C(7')-N(8') | 178.9 (5) |
| C(2)-C(3)-C(4)-C(5) | 1.1 (4) | C(2')-C(3')-C(4')-C(5') | .2 (4) |
| C(3)-C(4)-C(5)-C(6) | −1.0 (4) | C(3')-C(4')-C(5')-C(6') | −1.2 (4) |
| C(4)-C(5)-C(6)-C(7) | 1.1 (4) | C(4')-C(5')-C(6')-C(7') | 1.1 (4) |
| C(4)-C(5)-C(6)-C(13) | −179.7 (6) | C(4')-C(5')-C(6')-C(13') | −178.5 (7) |
| C(5)-C(6)-C(7)-C(2) | −1.4 (3) | C(5')-C(6')-C(7')-C(2') | .0 (4) |
| C(5)-C(6)-C(7)-N(8) | −179.6 (5) | C(5')-C(6')-C(7')–N(8') | −179.7 (5) |
| C(13)-C(6)-C(7)-C(2) | 179.4 (6) | C(13')-C(6')-C(7')-C(2') | 179.5 (5) |
| C(13)-C(6)-C(7)-N(8) | 1.2 (4) | C(13')-C(6')-C(7')-N(8') | −.2 (4) |
| C(2)-C(7)-N(8)-C(9) | −179.4 (7) | C(2')-C(7')-N(8')-C(9') | −178.7 (6) |
| C(2)-C(7)-N(8)-C(12) | −1.0 (4) | C(2')-C(7')-N(8')-C(12') | 1.0 (3) |
| C(6)-C(7)-N(8)-C(9) | −1.0 (5) | C(6')-C(7')-N(8')-C(9') | 1.0 (5) |
| C(6)-C(7)-N(8)-C(12) | 177.4 (5) | C(6')-C(7')-N(8')-C(12') | −179.3 (5) |
| C(7)-N(8)-C(9)-N(10) | 178.7 (8) | C(7')-N(8')-C(9')-N(10') | −178.6 (7) |
| C(12)-N(8)-C(9)-N(10) | .2 (5) | C(12')-N(8')-C(9')-N(10') | 1.6 (4) |
| C(7)-N(8)-C(12)-S(1) | 1.5 (4) | C(7')-N(8')-C(12')-S(1') | −.4 (3) |
| C(7)-N(8)-C(12)-N(11) | −179.6 (6) | C(7')-N(8')-C(12')-N(11') | 178.4 (5) |
| C(9)-N(8)-C(12)-S(1) | −179.5 (5) | C(9')-N(8')-C(12')-S(1') | 179.5 (4) |
| C(9)-N(8)-C(12)-N(11) | −.6 (5) | C(9')-N(8')-C(12')-N(11') | −1.8 (4) |
| N(8)-C(9)-N(10)-N(11) | .3 (4) | N(8')-C(9')-N(10')-N(11') | −1.0 (4) |
| C(9)-N(10)-N(11)-C(12) | −.7 (5) | C(9')-N(10')-N(11')-C(12') | −.1 (4) |
| N(10)-N(11)-C(12)-S(1) | 179.3 (8) | N(10')-N(11')-C(12')-S(1') | 179.5 (7) |
| N(10)-N(11)-C(12)-N(8) | .8 (4) | N(10')-N(11')-C(12')-N(8') | 1.2 (4) |

| Least squares planes | |
|---|---|
| Benzene ring of molecule **1** | |
| −.04385 x + −.41038 y + −.91086 z = −7.32813 | |
| C(2) | .005 (3) |
| C(3) | −.005 (5) |
| C(4) | .003 (5) |
| C(5) | −.003 (3) |
| C(6) | .005 (3) |
| C(7) | −.006 (3) |
| Thiazole ring of molecule **1** | |
| .04140 x + .42884 y + .90243 z = 7.19628 | |
| S(1) | .010 (2) |
| C(2) | .000 (3) |
| C(7) | −.003 (3) |
| N(8) | .004 (3) |
| C(12) | −.010 (6) |

**Table 3. Continued**

| Least squares planes | |
|---|---|
| Triazole ring of molecule **1** | |
| −.04470 x + −.43559 y + −.89903 z = −7.21630 | |
| N(8) | −.001 (3) |
| C(9) | −.000 (5) |
| N(10) | .003 (5) |
| N(11) | −.004 (5) |
| C(12) | .005 (6) |
| Benzene ring of molecule **2** | |
| .01429 x + .41821 y + .90824 z = 3.41256 | |
| C(2') | −.005 (3) |
| C(3') | .003 (3) |
| C(4') | .003 (5) |
| C(5') | −.009 (6) |
| C(6') | .002 (3) |
| C(7') | .003 (3) |
| Thiazole ring of molecule **2** | |
| .03192 x + .42313 y + .90551 z = 3.62087 | |
| S(1') | −.001 (1) |
| C(2') | .010 (3) |
| C(7') | −.008 (3) |
| N(8') | −.002 (3) |
| C(9') | .010 (5) |
| Triazole ring of molecule **2** | |
| −.03273 x + −.43460 y + −.90003 z = −3.60177 | |
| N(8') | .004 (3) |
| C(9') | −.010 (5) |
| N(10') | .003 (5) |
| N(11') | .004 (4) |
| C(12') | −.011 (6) |
| Least square plane of molecule **1** | |
| .04625 x + .41932 y + .90666 z = 7.30166 | |
| S(1) | −.003 (1) |
| C(2) | .006 (3) |
| C(3) | .005 (5) |
| C(4) | −.016 (5) |
| C(5) | −.012 (3) |
| C(6) | −.009 (3) |
| C(7) | .015 (3) |
| N(8) | .015 (3) |
| C(9) | .012 (5) |
| N(10) | −.013 (5) |
| N(11) | −.021 (5) |
| C(12) | −.015 (6) |
| C(13) | −.013 (6) |

**Table 3. Continued**

| Least squares planes | |
|---|---|
| Least square plane of molecule **2** | |
| −.02577 x + −.42389 y + −.90535 z = −3.53728 | |
| S(1') | .003 (1) |
| C(2') | −.007 (3) |
| C(3') | −.021 (3) |
| C(4') | −.009 (5) |
| C(5') | .022 (5) |
| C(6') | .017 (3) |
| C(7') | .003 (3) |
| N(8') | −.010 (3) |
| C(9') | −.029 (5) |
| N(10') | −.002 (5) |
| N(11') | .014 (4) |
| C(12') | −.007 (6) |
| C(13') | −.016 (6) |
| Dihedral angle A and B ring of molecule **1**: | 1.2° |
| Dihedral angle B and C ring of molecule **1**: | 0.5° |
| Dihedral angle A and C ring of molecule **1**: | 1.6° |
| Dihedral angle A and B ring of molecule **2**: | 1.1° |
| Dihedral angle B and C ring of molecule **2**: | 0.7° |
| Dihedral angle A and C ring of molecule **2**: | 1.5° |
| Dihedral angle molecule **1** and **2**: | 1.3° |

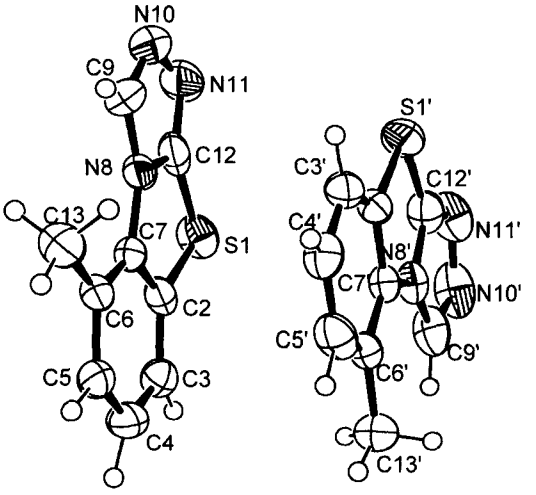


**Fig. 1. Molecular structure of title compound showing 50% probability displacement ellipsoids.**

molecule with the numbering and packing are presented in Fig. 1 and Fig. 2 respectively. This compound is composed of benzene (A), thiazole (B) and triazole (C) ring. Each ring's bond lengths and bond angles are normal within experimental error. Each ring is in planer conformation. In molecule **1**, the dihedral angle between A and B rings is 1.2°, A and C rings is 0.5°, B and C rings is 1.6°. In molecular **2**, A and B rings is 1.1°, B and C rings is 0.7°, A and C rings is 1.5°. The three rings constitute a

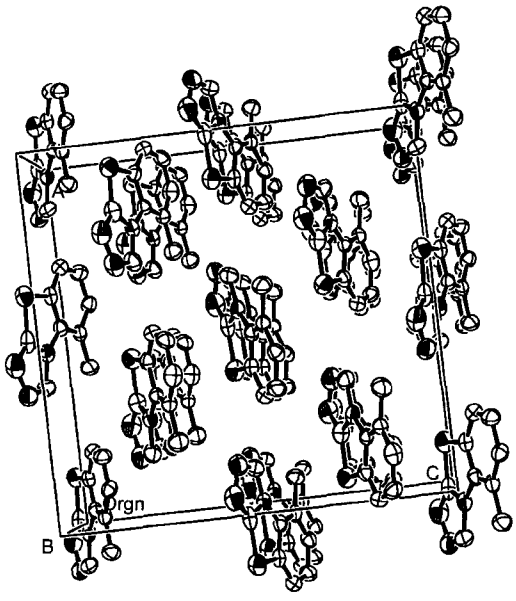


**Fig. 2. Packing diagram viewed down the *b* axis.**

single plane in molecule **1** and **2** (maximum shift from least square plane of molecule **1** is N11: 0.021(5) Å; molecule **2** is C9':-0.029(5) Å), and two molecules parallel to each other (dihedral angle of molecule **1** and **2** is 1.3°). There is an asymmetry unit composed of the two molecules. The asymmetry unit has a pseudo 2-fold symmetry on *b* direction and nearly 4.0 Å transition to the *c* axis direction.

The molecules in the crystal are arranged zigzag along to the *b* axis and held by van der Waals force interaction.

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