

Creatininium dihydrogenarsenate

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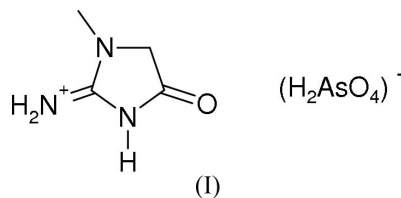
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.027
 wR factor = 0.069
Data-to-parameter ratio = 26.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $(\text{C}_4\text{H}_8\text{N}_3\text{O})[\text{H}_2\text{AsO}_4]$, contains a network of creatininium cations and dihydrogenarsenate anions [mean $\text{As}-\text{O} = 1.681(2)$ Å]. The crystal packing involves anion-to-anion $\text{O}-\text{H}\cdots\text{O}$, cation-to-anion $\text{N}-\text{H}\cdots\text{O}$ and cation-to-cation $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, resulting in a chain structure.

Comment

The title compound, (I) (Fig. 1), was prepared as part of our ongoing structural studies of hydrogen-bonding interactions in protonated-amine (di)hydrogen arsenate molecular salts (Wilkinson & Harrison, 2004; Todd & Harrison, 2005). The $[\text{H}_2\text{AsO}_4]^-$ dihydrogenarsenate group in (I) shows a normal tetrahedral geometry [mean $\text{As}-\text{O} = 1.681(2)$ Å], with the protonated $\text{As1}-\text{O3}$ and $\text{As1}-\text{O4}$ vertices showing their usual lengthening relative to the unprotonated $\text{As1}-\text{O1}$ and $\text{As1}-\text{O2}$ bonds, which have formal partial double-bond character (Table 1).



The creatininium cation is approximately planar [r.m.s. deviation for the non-H atoms = 0.031 Å; maximum deviation from the mean plane = 0.0597 (16) Å for N2]. The three C1–N bond distances (Table 1) are distinctly different, with C1–N1 much longer than the other two. This configuration perhaps indicates that the canonical form of the molecule, with a formal double bond in the C1–N1 position and a formal positive charge on N1, is of less importance than the forms that place the double bond in the C1–N2 and C1–N3 positions and the positive charge on the respective N atoms. However, the rather short C2–N1 bond length suggests that some conjugation involving the C2=O5 group may also be significant. In the structure of creatininium dipicolinate monohydrate (Moghimi *et al.*, 2004), the creatininium cation is constrained to be planar by mirror symmetry and an almost identical pattern of C–N bond lengths is observed.

As well as electrostatic attractions, the component species in (I) interact by means of a network of cation-to-anion $\text{N}-\text{H}\cdots\text{O}$, anion-to-anion $\text{O}-\text{H}\cdots\text{O}$ and cation-to-cation $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). The $[\text{H}_2\text{AsO}_4]^-$ units are linked into polymeric chains (Fig. 2) propagating along [100] by way of inversion-generated pairs of $\text{O3}-\text{H1}\cdots\text{O2}^i$ and

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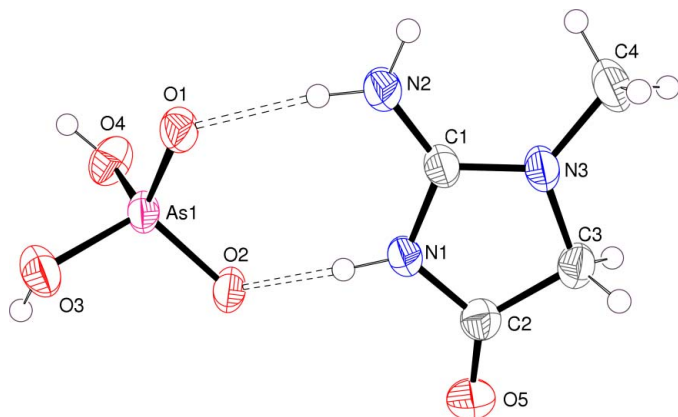


Figure 1
View of the asymmetric unit of (I), showing 50% probability displacement ellipsoids, with hydrogen bonds indicated by dashed lines.

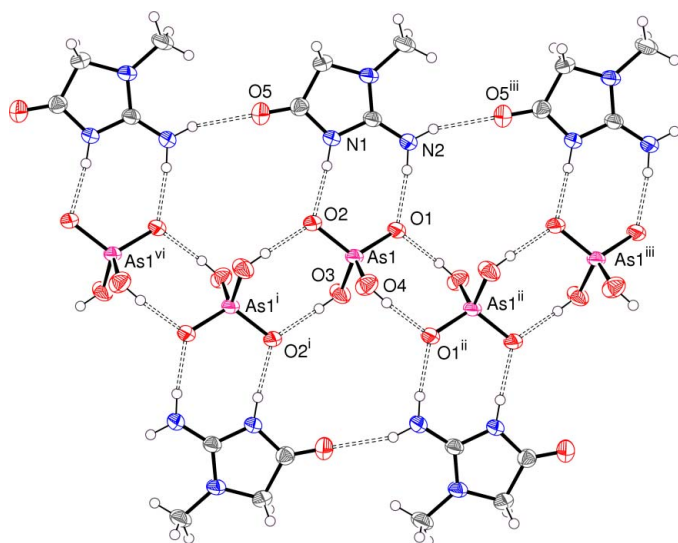


Figure 2
Detail of a hydrogen-bonded chain in (I). Hydrogen bonds are indicated by dashed lines. [Symmetry codes as in Table 2; additionally, (vi) $x - 1, y, z$.]

O4—H2 \cdots O1ⁱⁱ bonds (see Table 2 for symmetry codes). In graph-set notation (Bernstein *et al.*, 1995), each inter-tetrahedral linking motif corresponds to an $R_2^2(8)$ loop. The As1 \cdots As1ⁱ and As1 \cdots As1ⁱⁱⁱ separations are 4.0608 (3) and 3.9286 (3) Å, respectively.

The organic species interacts with the dihydrogenarsenate chains by way of two N—H \cdots O hydrogen bonds (Fig. 1), such that both sides of each [100] chain are decorated by the creatinium cations. The third creatinium N—H group is involved in a cation-to-cation N—H \cdots O bond (Fig. 2) that appears to reinforce the chains. Overall, a chain structure along the *a* axis arises for (I), as shown in Fig. 3. Atoms O1 and O2 accept two hydrogen bonds each (bond angle sums about these atoms are 358.3 and 359.3°, respectively). A PLATON (Spek, 2003) analysis of (I) flagged the possible presence of two short C—H \cdots O interactions (Table 2), although their structural significance is not clear.

PLATON also flagged a short C2 \cdots C2^v [symmetry code: (v) $-x, 1 - y, -z$] intermolecular contact of 3.158 (3) Å,

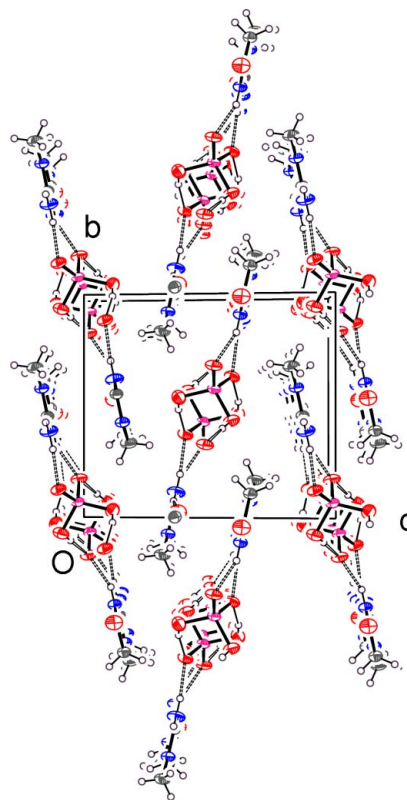


Figure 3
Projection of the packing of (I) along the *a* axis. Hydrogen bonds are indicated by dashed lines.

compared with a van der Waals radius sum of 3.40 Å (Bondi, 1964). This close contact might arise as part of a carbonyl-carbonyl interaction, as described by Allen *et al.* (1998). In the notation of these workers, the situation in (I) corresponds to a 'sheared antiparallel' or motif II interaction (Fig. 4), generated by a centre of symmetry. Here, the O5=C2 \cdots O5^v and C2=O5 \cdots C2^v interaction angles are 100.50 (14) and 79.50 (13)°, respectively, compared with the nominal values of $2 \times 90^\circ$ for a perfect rectangle of the four constituent atoms. This is slightly more distorted than the mean O=C \cdots O and C=O \cdots C angles of 96.5 (4) and 83.5 (4)° based on 553 contributors, as cited by Allen *et al.* (1998). The C2 \cdots O5^v separation of 3.147 (3) Å in (I) is slightly less than the C \cdots O van der Waals separation of 3.22 Å.

The dihydrogenarsenate chain motif in (I) replicates that seen in *t*-butylammonium dihydrogenarsenate (Wilkinson & Harrison, 2004). However, a different cation-to-anion hydrogen-bonding scheme leads to a layered structure in this phase. The intrachain As \cdots As separations of 4.2662 (3) and 4.3002 (4) Å in the *t*-butylammonium compound are significantly larger than those seen in (I).

Experimental

A 0.5 M aqueous creatine solution (10 ml) was added to a 0.5 M aqueous H₃AsO₄ solution (20 ml) to result in a clear solution. A mass of block-like crystals of (I) grew as the water evaporated over the course of a few days. The creatine transformed to creatinine under the low-pH conditions of the reaction.

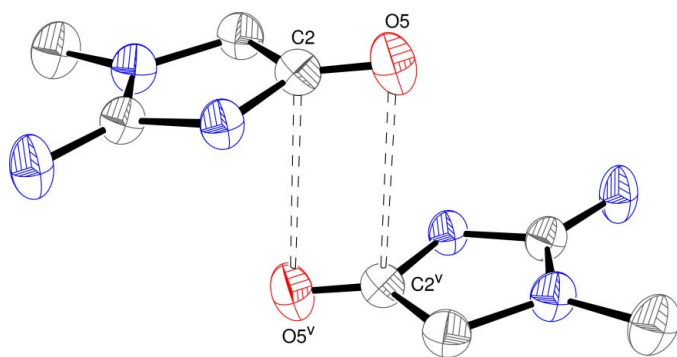


Figure 4
Detail of (I), showing the possible carbonyl-carbonyl interaction, with H atoms omitted for clarity. Hydrogen bonds are indicated by dashed lines. [Symmetry code: (v) $-x, 1 - y, -z$.]

Crystal data

(C₄H₈N₃O)[H₂AsO₄]
M_r = 255.07
 Monoclinic, *P*2₁/*n*
a = 7.3576 (3) Å
b = 10.4263 (5) Å
c = 11.9471 (5) Å
 β = 102.908 (1)°
V = 893.33 (7) Å³
Z = 4

D_x = 1.897 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5020 reflections
 θ = 2.6–32.2°
 μ = 3.80 mm⁻¹
T = 293 (2) K
 Chunk, colourless
 0.49 × 0.33 × 0.24 mm

Data collection

Bruker SMART 1000 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
*T*_{min} = 0.223, *T*_{max} = 0.401
 11192 measured reflections

3202 independent reflections
 2403 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.029
 θ_{max} = 32.5°
h = -11 → 11
k = -15 → 15
l = -17 → 18

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.027
wR(*F*²) = 0.069
S = 1.00
 3202 reflections
 119 parameters

H-atom parameters constrained
w = 1/[σ²(*F*_o²) + (0.0381*P*)²]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 0.59 e Å⁻³
 Δρ_{min} = -0.52 e Å⁻³

Table 1

Selected interatomic distances (Å).

As1—O1	1.6512 (13)	C1—N2	1.305 (2)
As1—O2	1.6563 (12)	C1—N3	1.321 (2)
As1—O4	1.7013 (15)	C1—N1	1.374 (2)
As1—O3	1.7134 (13)	C2—N1	1.367 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H1···O2 ⁱ	0.85	1.77	2.618 (2)	177
O4—H2···O1 ⁱⁱ	0.82	1.79	2.598 (2)	169
N1—H3···O2	0.86	1.89	2.703 (2)	158
N2—H4···O5 ⁱⁱⁱ	0.86	2.16	2.983 (2)	161
N2—H5···O1	0.86	1.89	2.747 (2)	172
C3—H6···O1 ^{iv}	0.97	2.46	3.334 (2)	149
C3—H7···O2 ^v	0.97	2.46	3.384 (2)	159

Symmetry codes: (i) $-x, -y + 2, -z$; (ii) $-x + 1, -y + 2, -z$; (iii) $x + 1, y, z$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x, -y + 1, -z$.

The hydroxy H atoms were found in difference maps and refined as riding on their carrier O atoms in their as-found relative positions. The H atoms bonded to C and N atoms were placed in idealized positions (C—H = 0.96–0.97 Å and N—H = 0.86 Å) and refined as riding, allowing for free rotation of the -CH₃ group. The constraint *U*_{iso}(H) = 1.2*U*_{eq}(carrier) or 1.5*U*_{eq}(methyl carrier) was applied.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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supporting information

Acta Cryst. (2005). E61, m1228–m1230 [https://doi.org/10.1107/S1600536805016144]

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Hall symbol: -*P* 2₁ *n*

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β = 102.908 (1)°

V = 893.33 (7) Å³

Z = 4

F(000) = 512

D_x = 1.897 Mg m⁻³

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Cell parameters from 5020 reflections

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T = 293 K

Chunk, colourless

0.49 × 0.33 × 0.24 mm

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Bruker SMART 1000 CCD
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Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
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T_{min} = 0.223, *T_{max}* = 0.401

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2403 reflections with *I* > 2σ(*I*)

R_{int} = 0.029

θ_{max} = 32.5°, θ_{min} = 2.6°

h = -11 → 11

k = -15 → 15

l = -17 → 18

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.027

wR(*F*²) = 0.069

S = 1.00

3202 reflections

119 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0381*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 0.59 e Å⁻³

Δρ_{min} = -0.52 e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
As1	0.26213 (2)	0.928771 (15)	0.019997 (18)	0.03047 (7)
O1	0.46360 (18)	0.87172 (12)	0.09239 (13)	0.0373 (3)
O2	0.08787 (18)	0.82749 (11)	0.01759 (13)	0.0398 (3)
O3	0.2283 (2)	1.06885 (12)	0.08753 (15)	0.0438 (3)
H1	0.1274	1.1029	0.0514	0.053*
O4	0.2634 (2)	0.96492 (14)	-0.11868 (13)	0.0444 (3)
H2	0.3451	1.0179	-0.1198	0.053*
C1	0.3742 (2)	0.54747 (15)	0.13831 (17)	0.0311 (4)
C2	0.0711 (3)	0.51202 (17)	0.13441 (17)	0.0338 (4)
C3	0.1748 (3)	0.38752 (17)	0.16057 (18)	0.0355 (4)
H6	0.1640	0.3537	0.2344	0.043*
H7	0.1294	0.3240	0.1016	0.043*
C4	0.5201 (3)	0.33417 (18)	0.1848 (2)	0.0446 (5)
H8	0.4793	0.2528	0.1506	0.067*
H9	0.5636	0.3239	0.2662	0.067*
H10	0.6196	0.3664	0.1527	0.067*
N1	0.2003 (2)	0.60209 (13)	0.12221 (14)	0.0316 (3)
H3	0.1761	0.6817	0.1067	0.038*
N2	0.5212 (2)	0.61337 (15)	0.12952 (17)	0.0430 (4)
H4	0.6280	0.5763	0.1395	0.052*
H5	0.5112	0.6939	0.1138	0.052*
N3	0.3657 (2)	0.42406 (13)	0.16181 (15)	0.0345 (3)
O5	-0.0931 (2)	0.53087 (16)	0.12300 (15)	0.0489 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.02924 (9)	0.01985 (8)	0.03993 (12)	-0.00035 (7)	0.00263 (7)	0.00260 (7)
O1	0.0290 (6)	0.0275 (6)	0.0517 (9)	0.0024 (5)	0.0011 (6)	0.0088 (6)
O2	0.0305 (6)	0.0231 (5)	0.0629 (10)	-0.0022 (5)	0.0042 (6)	0.0075 (6)
O3	0.0382 (7)	0.0294 (6)	0.0582 (10)	0.0038 (6)	-0.0012 (7)	-0.0102 (6)
O4	0.0428 (8)	0.0446 (7)	0.0421 (9)	-0.0107 (6)	0.0013 (7)	0.0051 (6)
C1	0.0325 (8)	0.0231 (7)	0.0364 (10)	0.0023 (6)	0.0051 (7)	0.0003 (6)
C2	0.0349 (9)	0.0316 (8)	0.0351 (10)	-0.0010 (7)	0.0085 (8)	-0.0012 (7)
C3	0.0384 (10)	0.0263 (7)	0.0418 (11)	-0.0038 (7)	0.0089 (8)	0.0015 (7)
C4	0.0440 (11)	0.0260 (8)	0.0602 (14)	0.0085 (8)	0.0039 (10)	0.0030 (8)
N1	0.0298 (7)	0.0230 (6)	0.0418 (9)	0.0031 (5)	0.0077 (6)	0.0028 (6)
N2	0.0282 (8)	0.0269 (7)	0.0722 (13)	0.0026 (6)	0.0077 (8)	0.0076 (8)
N3	0.0356 (8)	0.0216 (6)	0.0449 (10)	0.0017 (6)	0.0062 (7)	0.0021 (6)
O5	0.0340 (7)	0.0476 (8)	0.0678 (11)	0.0002 (7)	0.0176 (7)	0.0017 (8)

Geometric parameters (Å, °)

As1—O1	1.6512 (13)	C2—C3	1.503 (3)
As1—O2	1.6563 (12)	C3—N3	1.452 (2)
As1—O4	1.7013 (15)	C3—H6	0.9700
As1—O3	1.7134 (13)	C3—H7	0.9700
O3—H1	0.8488	C4—N3	1.451 (2)
O4—H2	0.8185	C4—H8	0.9600
C1—N2	1.305 (2)	C4—H9	0.9600
C1—N3	1.321 (2)	C4—H10	0.9600
C1—N1	1.374 (2)	N1—H3	0.8600
C2—O5	1.202 (2)	N2—H4	0.8600
C2—N1	1.367 (2)	N2—H5	0.8600
O1—As1—O2	112.36 (6)	C2—C3—H7	111.2
O1—As1—O4	112.96 (7)	H6—C3—H7	109.1
O2—As1—O4	107.28 (7)	N3—C4—H8	109.5
O1—As1—O3	105.56 (7)	N3—C4—H9	109.5
O2—As1—O3	111.00 (7)	H8—C4—H9	109.5
O4—As1—O3	107.62 (8)	N3—C4—H10	109.5
As1—O3—H1	108.6	H8—C4—H10	109.5
As1—O4—H2	109.2	H9—C4—H10	109.5
N2—C1—N3	127.51 (17)	C2—N1—C1	110.36 (14)
N2—C1—N1	122.20 (16)	C2—N1—H3	124.8
N3—C1—N1	110.29 (15)	C1—N1—H3	124.8
O5—C2—N1	125.52 (18)	C1—N2—H4	120.0
O5—C2—C3	128.01 (18)	C1—N2—H5	120.0
N1—C2—C3	106.45 (15)	H4—N2—H5	120.0
N3—C3—C2	102.73 (14)	C1—N3—C4	126.66 (16)
N3—C3—H6	111.2	C1—N3—C3	110.16 (15)
C2—C3—H6	111.2	C4—N3—C3	123.18 (15)
N3—C3—H7	111.2		
O5—C2—C3—N3	179.0 (2)	N2—C1—N3—C4	0.9 (3)
N1—C2—C3—N3	0.8 (2)	N1—C1—N3—C4	-179.61 (18)
O5—C2—N1—C1	-178.5 (2)	N2—C1—N3—C3	-178.4 (2)
C3—C2—N1—C1	-0.2 (2)	N1—C1—N3—C3	1.0 (2)
N2—C1—N1—C2	179.00 (19)	C2—C3—N3—C1	-1.1 (2)
N3—C1—N1—C2	-0.5 (2)	C2—C3—N3—C4	179.53 (18)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H1...O2 ⁱ	0.85	1.77	2.618 (2)	177
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