

C5—C6	1.529 (4)	N8—C81	1.499 (4)
C21—C26	1.391 (4)	N8—C82	1.506 (4)
C21—C22	1.397 (4)	N8—C9	1.525 (4)
C22—C23	1.386 (5)	C9—C72	1.529 (4)
C23—C24	1.385 (5)	C9—C10	1.534 (4)
C24—C25	1.377 (5)	C71—C72	1.557 (4)
C25—C26	1.396 (5)		
C5—O4—C3	107.8 (2)	C32—C31—C36	119.2 (3)
O4—C3—C21	108.5 (2)	C32—C31—C3	124.1 (3)
O4—C3—C31	109.4 (2)	C36—C31—C3	116.7 (3)
C21—C3—C31	114.7 (2)	C31—C32—C33	120.5 (3)
O4—C3—C2	101.2 (2)	C34—C33—C32	119.9 (3)
C21—C3—C2	109.7 (2)	C35—C34—C33	119.5 (3)
C31—C3—C2	112.5 (2)	C36—C35—C34	120.6 (3)
O2—C2—O1	123.0 (3)	C35—C36—C31	120.1 (3)
O2—C2—C3	128.7 (3)	C7—C6—C5	111.7 (2)
O1—C2—C3	108.3 (2)	C6—C7—N8	109.2 (2)
C2—O1—C5	108.4 (2)	C6—C7—C71	113.6 (2)
O4—C5—O1	103.9 (2)	N8—C7—C71	102.2 (2)
O4—C5—C10	107.9 (2)	C81—N8—C82	106.0 (2)
O1—C5—C10	110.1 (2)	C81—N8—C9	114.7 (2)
O4—C5—C6	113.4 (2)	C82—N8—C9	111.7 (2)
O1—C5—C6	108.2 (2)	C81—N8—C7	115.2 (2)
C10—C5—C6	113.0 (2)	C82—N8—C7	108.9 (2)
C26—C21—C22	119.7 (3)	C9—N8—C7	100.4 (2)
C26—C21—C3	121.6 (3)	N8—C9—C72	102.2 (2)
C22—C21—C3	118.7 (3)	N8—C9—C10	109.9 (2)
C23—C22—C21	119.8 (3)	C72—C9—C10	111.3 (3)
C24—C23—C22	120.4 (3)	C5—C10—C9	114.1 (3)
C25—C24—C23	119.9 (3)	C7—C71—C72	105.0 (2)
C24—C25—C26	120.4 (3)	C9—C72—C71	104.7 (2)
C21—C26—C25	119.7 (3)		
O1—C2—C3—O4	-10.8 (3)	O4—C3—C21—C22	-43.9 (3)
C2—C3—O4—C5	27.2 (3)	O4—C3—C31—C32	136.6 (3)
C3—O4—C5—O1	-33.3 (3)	O1—C5—C6—C7	-81.1 (3)
O4—C5—O1—C2	25.9 (3)	O1—C5—C10—C9	82.6 (3)
C5—O1—C2—C3	-8.9 (3)		

Table 3. Hydrogen-bonding 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>
C10—H102...O2'	1.06 (5)	2.55 (5)	3.513 (4)	152 (4)
C7—H7...I	1.02 (5)	2.89 (5)	3.847 (3)	157 (4)
C71—H711...I ⁱⁱ	0.97 (5)	3.06 (5)	4.005 (3)	163 (4)
C82—H823...I ⁱⁱⁱ	0.98 (5)	2.98 (5)	3.933 (4)	167 (4)
C24—H24...I ^{iv}	0.94 (6)	3.25 (5)	4.022 (3)	140 (4)
C36—H36...I ^v	0.96 (5)	3.39 (5)	4.213 (3)	145 (4)
C9—H9...I ^{vi}	0.95 (5)	3.36 (5)	4.220 (3)	152 (4)
C81—H812...I ^{vii}	0.93 (5)	3.22 (5)	4.014 (3)	144 (4)
C82—H821...I ^{viii}	0.96 (5)	3.41 (5)	4.291 (4)	155 (4)
C25—H25...O2 ⁱⁱ	0.90 (5)	2.62 (5)	3.252 (4)	128 (4)
C26—H26...O2 ⁱⁱⁱ	0.94 (5)	2.63 (5)	3.236 (4)	123 (4)
C32—H32...O2	0.96 (5)	2.57 (5)	3.213 (4)	125 (4)

Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $1 - x, 2 - y, 2 - z$; (iii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $x - 1, y, z - 1$; (v) $1 - x, 2 - y, 1 - z$; (vi) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

The position of the I⁻ ion was found using the Patterson method and the positions of all other atoms were found in subsequent difference electron density maps. In the final refinement residual density was observed close to the I⁻ ion.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREADD* (Blessing, 1987, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1064). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(E)- and (Z)-Enamine Dewar Pyrimidinones

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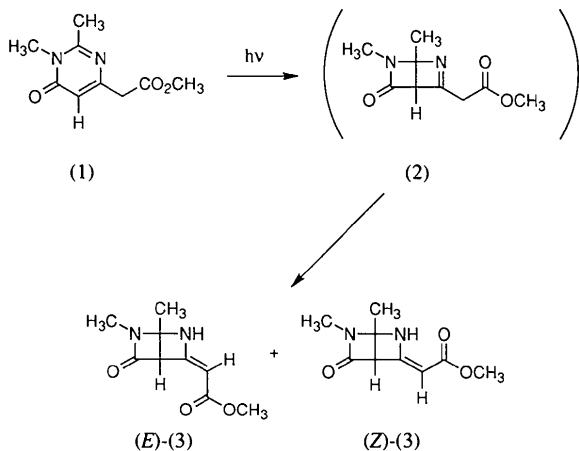
(Received 3 January 1995; accepted 2 May 1995)

Abstract

The structures of (E)- and (Z)-methyl 1,6-dimethyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-3-ylideneacetate, C₉H₁₂N₂O₃, have been established by X-ray diffraction analyses. The 2-azetidinone ring, azetidine ring and enamine moiety in both isomers are quite planar. The dihedral angles between the least-squares planes of the 2-azetidinone and azetidine rings in the two Dewar isomers are almost 112°.

Comment

The title compounds (enamine Dewar 4-pyrimidinones) were formed in the photolysis of methyl 1,2-dimethyl-6-oxo-1,6-dihydro-3-pyrimidinacetate, (1), via the unstable photoproduct imine Dewar isomer (2) (Hirokami, Takahashi, Kurosawa, Nagata & Yamazaki, 1985). The stereochemistry about the enamine double bond of both (*E*)-(3) and (*Z*)-(3) was confirmed unambiguously by the present X-ray analysis.



Figs. 1 and 2 show *ORTEP*II (Johnson, 1976) drawings of the Dewar isomers (*E*)-(3) and (*Z*)-(3) with the respective crystallographic numbering systems. The 2-azetidinone and azetidine rings of the *E* isomer have similar conformations to those of the *Z* isomer. The bond distances and angles are almost identical. The 2-azetidinone ring is quite planar in the *E* isomer and is

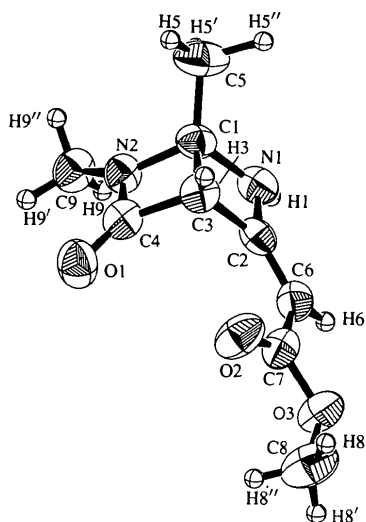


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the *E* Dewar isomer. Displacement ellipsoids are drawn at the 50% probability level. Isotropic H-atom displacement parameters are represented by spheres of arbitrary size.

almost planar in the *Z* isomer, with mean deviations of 0.005 (5) and 0.0146 (17) Å, respectively. The sum of the angles at the amide N atom is 358.9° in the *E* isomer and 357.7° in the *Z* isomer. Thus, the configuration at the amide N atom is almost planar in both isomers. This indicates sp^2 hybridization of the atom. The azetidine ring is also almost planar in the *Z* isomer, but is slightly bent in the *E* isomer. The sums of the bond angles at the enamine N atom are 354 and 350° in the *Z* and *E* isomers, respectively. The results show that the configuration of the enamine N atom is more pyramidal than that of the amide N atom. The N1—C1—N2 and C2—C3—C4 bond angles in the *E* isomer are 114.6 (3)

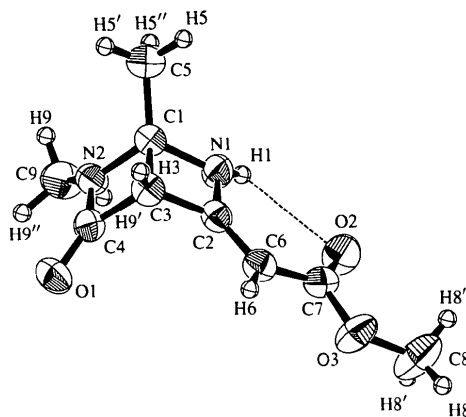


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of the *Z* Dewar isomer. Displacement ellipsoids are drawn at the 50% probability level. Isotropic H-atom displacement parameters are represented by spheres of arbitrary size. The dotted line indicates the intramolecular hydrogen bond.

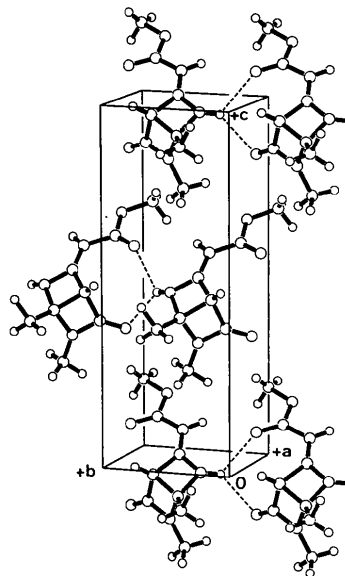


Fig. 3. Packing diagram of the *E* Dewar isomer. Intramolecular hydrogen bonds are drawn as dotted lines.

and 110.2(3)°, and those in the *Z* isomer are 113.8(1) and 110.3(1)°, respectively, indicating that the dihedral angles between the 2-azetidinone and azetidine rings in the two Dewar isomers are close to the tetrahedral angle.

The enamine moieties are almost planar in the *E* and *Z* isomers with mean deviations of 0.023(6) and 0.0146(17) Å, respectively, from the least-squares plane through N1, C2, C3, C6 and C7.

The enamine N1 atom in the *E* isomer is involved in two intermolecular hydrogen bonds: one with the β -lactam carbonyl O atom O1(*x*, *y* + 1, *z*) and the other with the ester carbonyl O atom O2(*x*, *y* + 1, *z*), with lengths of 3.042(5) and 2.983(5) Å, respectively. The *Z* isomers are linked by an intermolecular hydrogen bond between N1 and O2(1 - *x*, 1 - *y*, 2 - *z*) of length 2.976(2) Å. A weak intramolecular hydrogen bond of length 2.913(2) Å is formed between the enamine N1 atom and the ester carbonyl O2 atom.

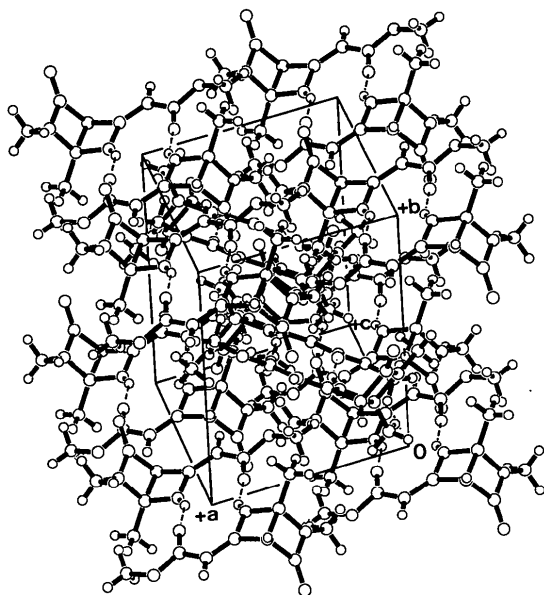


Fig. 4. Packing diagram of the *Z* Dewar isomer. Intramolecular hydrogen bonds are drawn as dotted lines.

Experimental

The compounds (*E*)-(3) and (*Z*)-(3) were prepared by the photochemical reaction of methyl 1,2-dimethyl-6-oxo-1,6-dihydro-3-pyrimidinacetate, (1), in ethanol solution at 253–258 K. The starting compound and photochemical products were separated by a column of Sephadex LH-20 (Pharmacia Fine Chemicals AB) with distilled acetone as an eluent, at room temperature. Single crystals of (*E*)-(3) and (*Z*)-(3) were grown from a dichloromethane–hexane solution.

Compound (*E*)-(3)

Crystal data

C₉H₁₂N₂O₃
M_r = 196.21

Mo K α radiation
 λ = 0.7107 Å

Monoclinic
Pc
a = 5.558(1) Å
b = 5.7557(8) Å
c = 15.656(2) Å
 β = 92.61(1)°
V = 500.3(1) Å³
Z = 2
D_x = 1.302 Mg m⁻³

Data collection

AFC-7R diffractometer
 $\omega/2\theta$ scans
Absorption correction:
refined from ΔF
(DIFABS; Walker &
Stuart, 1983)
1407 measured reflections
1283 independent reflections
776 observed reflections
[*I* > 3 σ (*I*)]

Refinement

Refinement on *F*
R = 0.035
wR = 0.049
S = 1.20
776 reflections
173 parameters
All H-atom parameters
refined
 $w = 1/[\sigma^2(F) + 0.0009F^2]$

Cell parameters from 25
reflections
 θ = 13.49–18.20°
 μ = 0.099 mm⁻¹
T = 295 K
Prism
0.34 × 0.31 × 0.12 mm
Colourless

*R*_{int} = 0.051
 θ_{\max} = 27.50°
h = 0 → 7
k = 0 → 7
l = -20 → 20
3 standard reflections
monitored every 150
reflections
intensity decay: 0.34%

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max}$ = 0.11 e Å⁻³
 $\Delta\rho_{\min}$ = -0.15 e Å⁻³
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (*E*)-(3)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O1	0.6175	0.0186(6)	0.3561	0.0685(10)
O2	0.7320(9)	-0.0180(5)	0.5793(3)	0.0730(10)
O3	1.0206(9)	0.1775(5)	0.6537(3)	0.0664(10)
N1	0.4843(10)	0.6185(6)	0.4718(3)	0.0528(10)
N2	0.4406(10)	0.3861(6)	0.3387(3)	0.0475(9)
C1	0.3221(10)	0.4899(7)	0.4121(3)	0.0493(10)
C2	0.5718(10)	0.4248(6)	0.5123(3)	0.0455(10)
C3	0.398(1)	0.2671(7)	0.4628(3)	0.0471(10)
C4	0.508(1)	0.1875(7)	0.3796(4)	0.0484(10)
C5	0.078(1)	0.593(1)	0.3927(5)	0.076(1)
C6	0.752(1)	0.3930(8)	0.5709(4)	0.0496(10)
C7	0.825(1)	0.1653(7)	0.5993(3)	0.0528(11)
C8	1.118(2)	-0.040(1)	0.6840(5)	0.085(3)
C9	0.506(1)	0.4837(9)	0.2571(3)	0.0578(13)

Table 2. Selected geometric parameters (Å, °) for (*E*)-(3)

O1—C4	1.213(5)	N2—C9	1.458(5)
O2—C7	1.209(5)	C1—C3	1.556(5)
O3—C7	1.353(4)	C1—C5	1.500(6)
O3—C8	1.438(7)	C2—C3	1.513(5)
N1—C1	1.469(6)	C2—C6	1.340(6)
N1—C2	1.362(5)	C3—C4	1.533(6)
N2—C1	1.476(6)	C6—C7	1.436(6)
N2—C4	1.354(5)		
C7—O3—C8	116.3(4)	N1—C2—C6	132.1(4)
C1—N1—C2	94.5(3)	C3—C2—C6	135.2(4)
C1—N2—C4	95.6(3)	C1—C3—C2	85.3(3)
C1—N2—C9	131.7(3)	C1—C3—C4	85.6(3)
C4—N2—C9	131.6(4)	C2—C3—C4	110.2(3)

N1—C1—N2	114.6 (3)	O1—C4—N2	131.7 (4)
N1—C1—C3	87.0 (3)	O1—C4—C3	136.2 (4)
N1—C1—C5	117.0 (4)	N2—C4—C3	92.1 (3)
N2—C1—C3	86.7 (3)	C2—C6—C7	121.8 (4)
N2—C1—C5	115.7 (4)	O2—C7—O3	122.0 (4)
C3—C1—C5	130.7 (4)	O2—C7—C6	127.3 (3)
N1—C2—C3	92.7 (3)	O3—C7—C6	110.7 (3)

Compound (Z)-(3)*Crystal data*C₉H₁₂N₂O₃M_r = 196.21

Monoclinic

P2₁/a

a = 9.076 (4) Å

b = 9.925 (3) Å

c = 11.833 (3) Å

β = 109.61 (2)°

V = 1004.1 (5) Å³

Z = 4

D_x = 1.298 Mg m⁻³

Mo Kα radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 18.23–19.86°

μ = 0.099 mm⁻¹

T = 294 K

Prism

0.63 × 0.46 × 0.32 mm

Colourless

Data collection

AFC-7R diffractometer

ω/2θ scans

Absorption correction:

refined from ΔF
(DIFABS; Walker &
Stuart, 1983)

2235 measured reflections

2107 independent reflections

1380 observed reflections

[I > 3σ(I)]

R_{int} = 0.020θ_{max} = 27.49°

h = 0 → 11

k = 0 → 12

l = -15 → 14

3 standard reflections

monitored every 150

reflections

intensity decay: 0.41%

Refinement

Refinement on F

R = 0.037

wR = 0.057

S = 1.39

1380 reflections

176 parameters

All H-atom parameters

refined

w = 1/[σ²(F) + 0.0009F²](Δ/σ)_{max} = 0.002Δρ_{max} = 0.15 e Å⁻³Δρ_{min} = -0.12 e Å⁻³

Extinction correction:

Zachariasen (1967) type

2 Gaussian isotropic

Extinction coefficient:

1.555 × 10⁻⁶

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (Z)-(3)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
O1	0.1798 (2)	0.6994 (1)	0.5379 (1)	0.0597 (5)
O2	0.6746 (2)	0.5510 (2)	0.9699 (1)	0.0581 (5)
O3	0.8332 (2)	0.6581 (2)	0.8897 (1)	0.0613 (5)
N1	0.3849 (2)	0.4497 (2)	0.7976 (1)	0.0439 (4)
N2	0.1317 (2)	0.5278 (1)	0.6567 (1)	0.0429 (4)
C1	0.2452 (2)	0.4172 (2)	0.6933 (2)	0.0408 (5)
C2	0.4630 (2)	0.5110 (2)	0.7314 (1)	0.0394 (5)
C3	0.3320 (2)	0.4833 (2)	0.6144 (2)	0.0423 (5)
C4	0.2058 (2)	0.5929 (2)	0.5905 (2)	0.0439 (5)
C5	0.1814 (3)	0.2778 (2)	0.6875 (2)	0.0555 (6)
C6	0.6024 (2)	0.5730 (2)	0.7596 (2)	0.0428 (5)
C7	0.7012 (2)	0.5905 (2)	0.8811 (2)	0.0432 (5)
C8	0.9375 (4)	0.6875 (4)	1.0079 (2)	0.0830 (10)
C9	0.0127 (3)	0.5704 (3)	0.7039 (3)	0.0616 (8)

Table 4. Selected geometric parameters (Å, °) for (Z)-(3)

O1—C4	1.209 (2)	N2—C9	1.436 (3)
O2—C7	1.219 (2)	C1—C3	1.554 (2)
O3—C7	1.346 (2)	C1—C5	1.493 (3)
O3—C8	1.431 (3)	C2—C3	1.516 (3)
N1—C1	1.478 (2)	C2—C6	1.345 (2)
N1—C2	1.364 (2)	C3—C4	1.536 (3)
N2—C1	1.467 (2)	C6—C7	1.427 (3)
N2—C4	1.356 (2)		
C7—O3—C8	117.1 (2)	C3—C2—C6	133.9 (2)
C1—N1—C2	94.8 (1)	C1—C3—C2	85.9 (1)
C1—N2—C4	95.2 (1)	C1—C3—C4	85.0 (1)
C1—N2—C9	130.6 (2)	C2—C3—C4	110.3 (1)
C4—N2—C9	131.9 (2)	O1—C4—N2	131.7 (2)
N1—C1—N2	113.8 (1)	O1—C4—C3	135.9 (2)
N1—C1—C3	86.8 (1)	N1—C2—C6	133.5 (2)
N1—C1—C5	116.8 (2)	N2—C4—C3	92.3 (1)
N2—C1—C3	87.4 (1)	C2—C6—C7	121.8 (2)
N2—C1—C5	117.2 (2)	O2—C7—O3	121.6 (2)
C3—C1—C5	129.1 (2)	O2—C7—C6	126.2 (2)
N1—C2—C3	92.5 (1)	O3—C7—C6	112.3 (2)

The structure was solved by direct methods and expanded using Fourier techniques. Refinement was carried out by full-matrix least-squares methods.

For both compounds, data collection: *MSC/AFC Diffractometer Control* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985), *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structures: *TEXSAN LS*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN FINISH*.

The authors thank Dr Motoo Shiro of Rigaku Corporation for helpful suggestions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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