

There are no intermolecular distances shorter than the sum of the van der Waals radii. Fig. 1 shows a perspective view of (I), with the atom-numbering scheme.

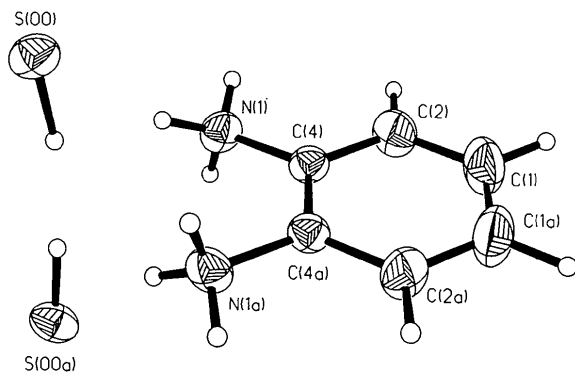


Fig. 1. A view of the title molecule with the atom-numbering scheme. Atoms are represented as 50% probability ellipsoids.

Experimental

Dark red crystals suitable for X-ray study were grown from a 2-propanol solution by slow evaporation of the solvent.

Crystal data

C₆H₁₀N₂²⁺·2HS⁻

M_r = 176.31

Monoclinic

*C*2/*c*

a = 7.341 (1) Å

b = 14.518 (3) Å

c = 8.010 (2) Å

β = 94.01 (3)°

V = 851.6 (9) Å³

Z = 4

D_x = 1.375 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 9 reflections

θ = 12–13°

μ = 0.554 mm⁻¹

T = 293 K

Block

0.4 × 0.2 × 0.2 mm

Dark red

*R*_{int} = 0.0259

θ_{max} = 25°

h = 0 → 11

k = 0 → 23

l = -12 → 12

2 standard reflections

monitored every 98

reflections

intensity decay: 7%

Data collection

Siemens P3/PC diffractometer

2θ–θ scans

Absorption correction: none

1917 measured reflections

1804 independent reflections

1119 observed reflections

[*F* > 6σ(*F*)]

Refinement

Refinement on *F*²

R = 0.037

wR = 0.043

S = 1.73

1119 reflections

64 parameters

H atoms riding with fixed isotropic *U*

w = 1/[σ²(*F_o*) + 0.0003*F_o*²]

(Δ/σ)_{max} = 0.197

Δρ_{max} = 0.44 e Å⁻³

Δρ_{min} = -0.47 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)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S	0.0232 (1)	0.1767 (1)	-0.0099 (1)	0.037 (1)
N(1)	-0.1880 (2)	0.3323 (1)	-0.2069 (2)	0.035 (1)
C(1)	-0.0885 (3)	0.5828 (1)	-0.2253 (2)	0.053 (1)
C(2)	-0.1787 (2)	0.5008 (1)	-0.2017 (2)	0.042 (1)
C(4)	-0.0889 (2)	0.4181 (1)	-0.2264 (2)	0.029 (1)

Table 2. Selected geometric parameters (Å, °)

C(4)—C(4')	1.384 (2)	C(4)—C(2)	1.391 (2)
C(1)—C(1')	1.384 (4)	C(2)—C(1)	1.381 (2)
N(1)—C(4)	1.457 (2)		
N(1)—C(4)—C(2)	118.6 (1)	C(4)—C(2)—C(1)	119.2 (1)
C(2)—C(4)—C(4')	120.3 (1)	C(2)—C(1)—C(1')	120.5 (1)
N(1)—C(4)—C(4')	121.1 (1)		

Symmetry codes: (i) -*x*, *y*, -½ - *z*.

The structure was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1991). After non-H atoms were refined anisotropically, positions of all H atoms were located from a Δ*F* map and included in the refinement with fixed isotropic displacement parameters. Ten strong reflections with (*F_o* - *F_c*)/σ > 4.0 were excluded from the last refinement cycles.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VS1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Sheldrick, G. M. (1991). *SHELXTL-Plus*. PC Version. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1995). **C51**, 2644–2647

Muscarinic Antagonist: 8,8-Dimethyl-3',3'-diphenylspiro(8-azoniabicyclo[3.2.1]octane-3,2'-1',3'-dioxolane)-4'-one Iodide

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(Received 10 May 1995; accepted 3 July 1995)

Abstract

The molecular structure of the title compound, C₂₃H₂₆NO₃⁺.I⁻, BVT44Me, has been compared to that of the related compound 8,8-dimethyl-3,3-diphenyl-

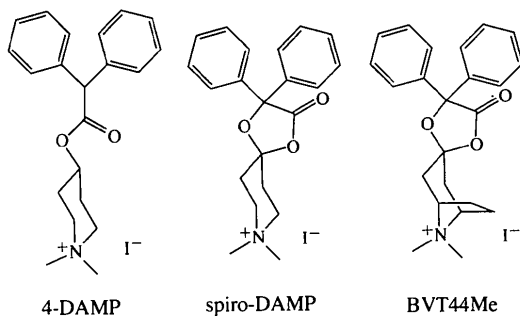
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1,4-dioxo-8-azoniaspiro[4.5]decan-2-one iodide, spiro-DAMP [Sabatino, Recanatini, Tumiatti & Melchiorre (1994), *Acta Cryst.* C50, 640–645]. The dioxolane ring adopts an envelope conformation in spiro-DAMP (the ether O atom being out of the plane of the ring) and a twist conformation in BVT44Me (the ether O and the C atom at the spiro position being out of the plane of the ring). This makes the spatial orientations of the substituents of the dioxolane ring slightly different. The crystal packing in BVT44Me is stabilized by electrostatic interactions and van der Waals contacts. Charge–charge interactions place the I^- ion close to the quaternary ammonium group. These interactions may be classified as hydrogen bonds ($CH \cdots I$).

Comment

For some time much interest has been focused on the research and development of selective muscarinic agonists and antagonists. At present, four different muscarinic receptor subtypes are pharmacologically defined: M1, M2, M3 and M4 (Fisher & Barak, 1994, and references therein). Receptor subtype-selective ligands may provide information on the chemical and spatial requirements at the receptor sites.

4-DAMP is a well known M3-selective muscarinic antagonist (Barlow, Berry, Glenton, Nikolaou & Soh, 1976). Spiro-DAMP and the title compound, BVT44Me, are conformationally restrained analogues of 4-DAMP and have been synthesized in order to determine the structural requirements at the receptor sites. The structure determination of BVT44Me has been performed in order to elucidate the exact three-dimensional molecular structure (Fig. 1).



The crystal packing of BVT44Me (Fig. 2) is stabilized by electrostatic interactions and van der Waals contacts. The positive charge of the quaternary ammonium group is highly delocalized and the H atoms of the two methyl and the two methine moieties connected to the quaternary N atom have partial positive charges (Meotner & Deakyne, 1985*a,b*). Favourable interactions are therefore observed between the negatively charged I and the positively charged H atoms (Table 3). Furthermore, contacts are observed to the carbonyl O atom (O2)

(Table 3). One contact is intramolecular, from a benzene ring to the carbonyl O atom (C32—H32 \cdots O2), and another contact is intermolecular, from the piperidine ring to the carbonyl O atom (C10—H102 \cdots O2) (Table 3). The described contacts may be classified as C—H \cdots O hydrogen bonds (Jeffrey & Saenger, 1991).

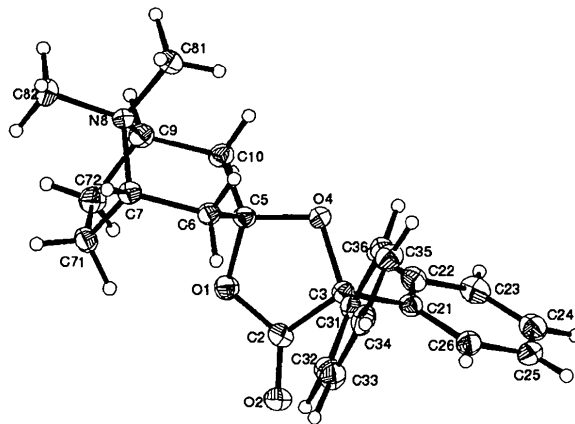


Fig. 1. Perspective drawing of BVT44Me with atomic labelling (ORTEP11; Johnson, 1976). Non-H atoms are represented by displacement ellipsoids at the 50% probability level.

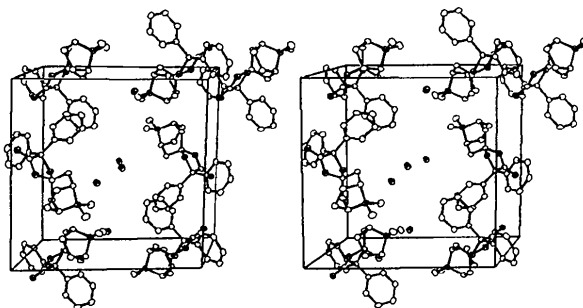


Fig. 2. Stereoview of the unit cell (*a* horizontal, *b* vertical, *c* out of the plane of the paper).

In the molecular structure of BVT44Me, the ester moiety of the dioxolane ring is observed in an axial position with respect to the piperidine ring and the two phenyl groups are situated almost perpendicular to each other [$85.43(9)^\circ$].

The conformation of BVT44Me (Fig. 1) has been compared to the conformation observed for spiro-DAMP (Sabatino, Recanatini, Tumiatti & Melchiorre, 1994) (Fig. 3). The dioxolane ring in spiro-DAMP adopts an envelope conformation with the ether atom O4 0.29 Å above the least-squares plane passing through the remaining four atoms. In BVT44Me, the dioxolane ring adopts a twist conformation with the ether atom O4 above [$0.266(7) \text{ \AA}$] and the spiro atom C5 below [$0.214(7) \text{ \AA}$] the plane through the remaining atoms of the dioxolane ring [pseudorotation parameters: $Q_2 = 0.296(3) \text{ \AA}$, $\varphi_2 = 122.6(6)^\circ$ (PLATON92; Spek, 1990)].

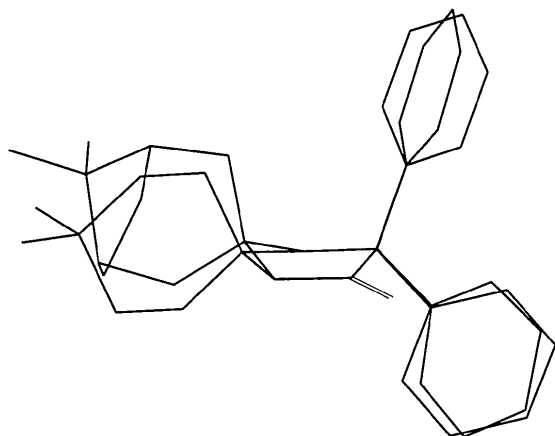


Fig. 3. Comparison of BVT44Me and spiro-DAMP (SYBYL; Tripos Associates Inc., 1994). The ester moieties of the dioxolane rings are superimposed.

The conformational flexibility of this type of compound has to be examined carefully before any conclusions can be made concerning the receptor-active conformation of the compounds. The dioxolane ring of these compounds can obviously adopt different conformations and the intramolecular distances between essential parts of the molecule may change (Sabatino *et al.*, 1994). Fig. 3 illustrates how the difference in the conformation of the dioxolane ring in these two compounds changes the spatial orientation of the substituents.

Experimental

The compound was kindly donated by Professor C. Melchiorre, University of Bologna, Italy. The compound was synthesized by Dr Tumiatti (details to be published elsewhere together with the pharmacological data). Single crystals were obtained by vapour diffusion of diethyl ether into a solution of the compound in ethanol; m.p. 493–495 K (uncorrected).

Crystal data

C₂₃H₂₆NO₃·I⁻

$M_r = 491.35$

Monoclinic

$P2_1/c$

$a = 14.615 (3) \text{ \AA}$

$b = 14.625 (3) \text{ \AA}$

$c = 10.330 (2) \text{ \AA}$

$\beta = 107.67 (2)^\circ$

$V = 2103.8 (7) \text{ \AA}^3$

$Z = 4$

$D_x = 1.551 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4
diffractometer

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 20

reflections

$\theta = 38.71\text{--}44.30^\circ$

$\mu = 12.144 \text{ mm}^{-1}$

$T = 112 (2) \text{ K}$

Prism

$0.22 \times 0.20 \times 0.05 \text{ mm}$

Colourless

$R_{\text{int}} = 0.0266$

$\theta_{\text{max}} = 75.02^\circ$

$\omega/2\theta$ scans

Absorption correction:

ABSORB (Blessing, 1987,
1989)

$T_{\text{min}} = 0.129$, $T_{\text{max}} =$
0.571

8933 measured reflections

4178 independent reflections

3773 observed reflections

$[I > 2\sigma(I)]$

Refinement

Refinement on F^2

$R(F) = 0.0322$

$wR(F^2) = 0.0811$

$S = 1.067$

4178 reflections

331 parameters

Only coordinates of H atoms
refined

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2$
 $+ 1.4417P]$

where $P = (F_o^2 + 2F_c^2)/3$

$h = -18 \rightarrow 17$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 12$

5 standard reflections

monitored every 600
reflections

frequency: 167 min

intensity decay: 7.5%
(corrected)

$(\Delta/\sigma)_{\text{max}} = 0.005$

$\Delta\rho_{\text{max}} = 0.706 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -1.804 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992),
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

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

	x	y	z	U_{eq}
I	0.60180 (1)	0.92264 (1)	0.80127 (2)	0.02505 (8)
O4	0.1764 (1)	0.9944 (1)	0.3603 (2)	0.0194 (4)
C3	0.1266 (2)	0.9080 (2)	0.3502 (3)	0.0182 (6)
C2	0.0898 (2)	0.9130 (2)	0.4745 (3)	0.0198 (6)
O1	0.1325 (2)	0.9848 (1)	0.5516 (2)	0.0216 (4)
C5	0.2075 (2)	1.0200 (2)	0.4983 (3)	0.0185 (6)
O2	0.0319 (2)	0.8653 (2)	0.5023 (2)	0.0239 (5)
C21	0.0423 (2)	0.9085 (2)	0.2213 (3)	0.0198 (6)
C22	-0.0149 (2)	0.9868 (2)	0.1893 (3)	0.0223 (6)
C23	-0.0919 (2)	0.9893 (2)	0.0713 (4)	0.0269 (7)
C24	-0.1132 (2)	0.9143 (2)	-0.0144 (4)	0.0272 (7)
C25	-0.0575 (2)	0.8367 (2)	0.0173 (3)	0.0248 (6)
C26	0.0203 (2)	0.8328 (2)	0.1358 (3)	0.0223 (6)
C31	0.1976 (2)	0.8297 (2)	0.3601 (3)	0.0185 (6)
C32	0.2006 (2)	0.7514 (2)	0.4365 (3)	0.0228 (6)
C33	0.2711 (2)	0.6851 (2)	0.4457 (3)	0.0253 (6)
C34	0.3380 (2)	0.6969 (2)	0.3757 (3)	0.0246 (6)
C35	0.3331 (2)	0.7741 (2)	0.2955 (4)	0.0258 (6)
C36	0.2648 (2)	0.8406 (2)	0.2885 (3)	0.0225 (6)
C6	0.3028 (2)	0.9763 (2)	0.5784 (3)	0.0195 (6)
C7	0.3475 (2)	1.0244 (2)	0.7138 (3)	0.0203 (6)
N8	0.3682 (2)	1.1240 (2)	0.6875 (3)	0.0199 (5)
C9	0.2665 (2)	1.1628 (2)	0.6441 (3)	0.0224 (6)
C10	0.2097 (2)	1.1241 (2)	0.5048 (3)	0.0216 (6)
C71	0.2787 (2)	1.0345 (2)	0.8000 (3)	0.0219 (6)
C72	0.2269 (2)	1.1275 (2)	0.7558 (4)	0.0250 (6)
C81	0.4222 (2)	1.1378 (2)	0.5867 (4)	0.0256 (6)
C82	0.4291 (3)	1.1661 (2)	0.8183 (3)	0.0271 (7)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O4—C5	1.409 (4)	C31—C32	1.384 (4)
O4—C3	1.447 (3)	C31—C36	1.406 (4)
C3—C21	1.515 (4)	C32—C33	1.397 (4)
C3—C31	1.528 (4)	C33—C34	1.393 (4)
C3—C2	1.536 (4)	C34—C35	1.388 (5)
C2—O2	1.197 (4)	C35—C36	1.380 (4)
C2—O1	1.351 (4)	C6—C7	1.524 (4)
O1—C5	1.462 (3)	C7—N8	1.528 (4)
C5—C10	1.523 (4)	C7—C71	1.540 (4)

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 ^v	0.93 (5)	3.22 (5)	4.014 (3)	144 (4)
C82—H821...I ⁱⁱ	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 ⁱⁱ	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).

The authors thank Mr Flemming Hansen for collecting the X-ray data. The Alfred Benzon and the Lundbeck Foundations are acknowledged for financial support.

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°.