Tableau 1. *Coordonnées atomiques et facteurs d'agitation thermique isotrope équivalents* (Å$^2$)

$$U_{éq} = \tfrac{1}{3}\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{éq}$ |
|---|---|---|---|---|
| C1 | 0,1672 (6) | 0,6526 (5) | 0,8282 (4) | 0,038 (3) |
| C2 | 0,1529 (6) | 0,8124 (5) | 0,7250 (4) | 0,040 (3) |
| O3 | 0,3827 (5) | 0,8874 (4) | 0,6999 (3) | 0,048 (2) |
| C4 | 0,4269 (6) | 0,9801 (6) | 0,5857 (4) | 0,050 (3) |
| C5 | 0,2900 (6) | 0,9123 (5) | 0,4676 (4) | 0,043 (3) |
| N6 | 0,0896 | 0,7776 | 0,4921 | 0,042 (3) |
| C7 | 0,0322 (5) | 0,7332 (5) | 0,6055 (4) | 0,039 (3) |
| C8 | −0,1450 (6) | 0,5650 (6) | 0,6306 (4) | 0,045 (3) |
| C9 | −0,0708 (6) | 0,4426 (5) | 0,7466 (4) | 0,045 (3) |
| C10 | −0,0597 (6) | 0,5425 (6) | 0,8714 (4) | 0,045 (3) |
| C11 | 0,1830 (6) | 0,4796 (5) | 0,7585 (4) | 0,047 (3) |
| C12 | −0,0220 (7) | 0,4126 (7) | 0,9922 (5) | 0,067 (4) |
| C13 | −0,2477 (7) | 0,6373 (7) | 0,8971 (4) | 0,068 (4) |
| C14 | 0,0639 (8) | 0,9767 (6) | 0,7674 (4) | 0,064 (4) |
| O4 | 0,5899 (6) | 1,0986 (5) | 0,5807 (3) | 0,075 (3) |
| C2′ | 0,2411 (7) | 1,0774 (6) | 0,3743 (4) | 0,053 (4) |
| C3′ | 0,1430 (7) | 1,0071 (7) | 0,2461 (4) | 0,061 (4) |
| C4′ | 0,2876 (7) | 0,9017 (7) | 0,1816 (4) | 0,061 (4) |
| C5′ | 0,3407 (7) | 0,7373 (6) | 0,2737 (4) | 0,054 (4) |
| C6′ | 0,4368 (6) | 0,8034 (6) | 0,4038 (4) | 0,049 (3) |
| C21 | 0,0954 (9) | 1,1921 (7) | 0,4293 (5) | 0,080 (5) |
| C22 | 0,4892 (9) | 1,0304 (7) | 0,1299 (5) | 0,083 (5) |
| C23 | 0,4898 (8) | 0,6240 (7) | 0,2216 (5) | 0,078 (5) |

Tableau 2. *Paramètres géométriques* (Å, °)

| | | | |
|---|---|---|---|
| C1—C2 | 1,529 (5) | C7—C8 | 1,512 (5) |
| C1—C10 | 1,573 (5) | C8—C9 | 1,536 (6) |
| C1—C11 | 1,542 (5) | C9—C10 | 1,550 (6) |
| C2—O3 | 1,473 (5) | C9—C11 | 1,552 (6) |
| C2—C7 | 1,515 (5) | C10—C12 | 1,542 (6) |
| C2—C14 | 1,531 (6) | C10—C13 | 1,524 (6) |
| O3—C4 | 1,345 (5) | C2′—C3′ | 1,525 (6) |
| C4—C5 | 1,514 (6) | C2′—C21 | 1,527 (7) |
| C4—O4 | 1,208 (6) | C3′—C4′ | 1,526 (6) |
| C5—N6 | 1,465 (6) | C4′—C5′ | 1,541 (6) |
| C5—C2′ | 1,543 (6) | C4′—C22 | 1,530 (7) |
| C5—C6′ | 1,550 (6) | C5′—C6′ | 1,528 (6) |
| N6—C7 | 1,268 (6) | C5′—C23 | 1,521 (7) |
| C2—C1—C10 | 114,7 (3) | C7—C8—C9 | 109,5 (3) |
| C2—C1—C11 | 107,0 (3) | C8—C9—C10 | 110,6 (3) |
| C10—C1—C11 | 86,8 (3) | C8—C9—C11 | 108,0 (3) |
| C1—C2—O3 | 103,9 (3) | C10—C9—C11 | 87,2 (3) |
| C1—C2—C7 | 108,9 (3) | C1—C10—C9 | 85,3 (3) |
| C1—C2—C14 | 115,2 (3) | C1—C10—C12 | 109,2 (3) |
| O3—C2—C7 | 109,6 (3) | C1—C10—C13 | 123,4 (3) |
| O3—C2—C14 | 105,3 (3) | C9—C10—C12 | 112,2 (3) |
| C7—C2—C14 | 113,5 (3) | C9—C10—C13 | 119,5 (3) |
| C2—O3—C4 | 118,5 (3) | C12—C10—C13 | 106,2 (3) |
| O3—C4—C5 | 118,4 (3) | C1—C11—C9 | 86,3 (3) |
| O3—C4—O4 | 117,9 (4) | C5—C2′—C3′ | 110,0 (3) |
| C5—C4—O4 | 123,0 (4) | C5—C2′—C21 | 112,6 (4) |
| C4—C5—N6 | 115,5 (3) | C3′—C2′—C21 | 111,5 (4) |
| C4—C5—C2′ | 111,2 (3) | C2′—C3′—C4′ | 114,2 (4) |
| C4—C5—C6′ | 104,1 (3) | C3′—C4′—C5′ | 109,2 (4) |
| N6—C5—C2′ | 111,1 (4) | C3′—C4′—C22 | 112,5 (4) |
| N6—C5—C6′ | 105,3 (4) | C5′—C4′—C22 | 114,0 (4) |
| C2′—C5—C6′ | 109,1 (3) | C4′—C5′—C6′ | 111,1 (3) |
| C5—N6—C7 | 120,7 (4) | C4′—C5′—C23 | 114,3 (4) |
| C2—C7—N6 | 125,3 (3) | C6′—C5′—C23 | 109,9 (4) |
| C2—C7—C8 | 114,5 (3) | C5—C6′—C5′ | 113,6 (3) |
| N6—C7—C8 | 119,2 (3) | | |
| C1—C2—C7—C8 | 33,4 (3) | C2—C7—N6—C5 | 1,5 (3) |
| C2—C7—C8—C9 | −37,0 (3) | C7—N6—C5—C4 | 4,5 (3) |
| C7—C8—C9—C10 | 68,7 (4) | N6—C5—C4—O3 | 13,4 (3) |
| C8—C9—C10—C1 | −80,3 (4) | C5—C4—O3—C2 | −36,9 (4) |
| C9—C10—C1—C2 | 79,0 (4) | C4—O3—C2—C7 | 39,7 (3) |
| C10—C1—C2—C7 | −61,8 (3) | C6′—C5—C2′—C3′ | 54,6 (4) |
| C7—C8—C9—C11 | −25,2 (3) | C5—C2′—C3′—C4′ | −58,1 (4) |
| C8—C9—C11—C1 | 82,3 (4) | C2′—C3′—C4′—C5′ | 56,5 (4) |
| C9—C11—C1—C2 | −86,8 (4) | C3′—C4′—C5′—C6′ | −53,3 (4) |
| C11—C1—C2—C7 | 32,5 (3) | C4′—C5′—C6′—C5 | 55,3 (4) |
| O3—C2—C7—N6 | −22,3 (3) | C5′—C6′—C5—C2′ | −55,4 (4) |

Collection des données: *CAD*-4 *Software* (Enraf-Nonius, 1989). Réduction des données: *NONIUS* (Riche, 1989). Programme(s) pour la solution de la structure: *SHELXS*86 (Sheldrick, 1985). Programme(s) pour l'affinement de la structure: *SHELX*76 (Sheldrick, 1976). Les dessins ont été obtenus à l'aide de *R3M* (Riche, 1983); *ORTEP* (Johnson, 1965). Programme(s) pour la préparation du manuscrit: *ACTACIF* (Riche, 1992).

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Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope et des coordonnées des atomes d'hydrogène ont été déposées au dépôt d'archives de l'UICr (Référence: PA1094). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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# 1-(2,4-Dimethoxy-1,3,5-triazin-6-yloxy)-pyrrolidine-2,5-dione, $C_9H_{10}N_4O_5$

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## Abstract

The title structure displays the characteristic features of the methoxy-*s*-triazines. The two rings are approximately perpendicular. Parallel triazine rings

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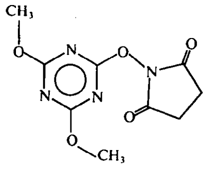
of two symmetry-related molecules are separated by about 3.4 Å and show partial stacking.

## Comment

The structure of the title compound, (I), has been determined as a part of our studies of 1,3,5-triazines (Główka & Iwanicka, 1989, 1991*a*,*b*; Główka, Iwanicka & Kamiński, 1990). Fig. 1 shows a view of the molecule.



(I)

The dimensions of the 2,4-dimethoxy-1,3,5-triazine fragment are in good agreement with those in the other *s*-triazine structures (Iwanicka, 1991). The study confirms the most characteristic feature of the methoxy-*s*-triazine system, *i.e.* the coplanar positions of the methoxy groups resulting from conjugation of the lone electron pairs at the O atoms with the triazine ring $\pi$ system. The appropriate N—C—O—C torsion angles are −6.2 (2) and −0.6 (3)°. The triazine ring is approximately perpendicular to the pyrrolidine ring plane with an interplanar angle of about 82°. Surprisingly, no other X-ray study of an *N*-aryloxypyrrolidine has been reported so far (*Cambridge Structural Database*, 1992). Thus we compared the geometry of the N—O—C link between the two rings with that of the diphthalimide phthalate structure (Bats & Teuber, 1985) and found that they agreed exceptionally well. The pairs of molecules related by centres of symmetry show partial stacking of parallel 2-methoxy-1,3,5-triazine systems (Fig. 2). The distance between approximately parallel *s*-triazine rings is about 3.4 Å.

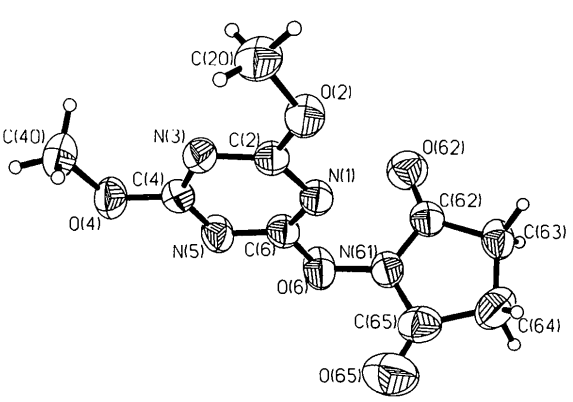


Fig. 1. A view of the molecule with the atomic labelling scheme. Anisotropic displacement parameters are at the 50% probability level and H atoms are shown as spheres or arbitrary radii.

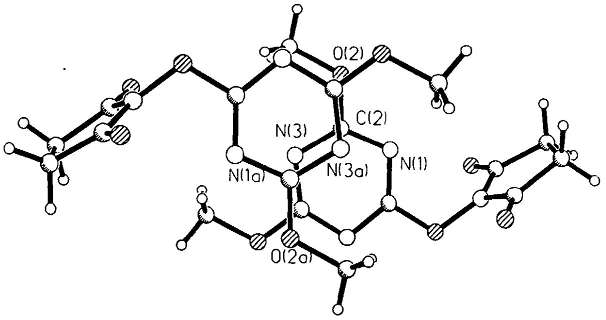


Fig. 2. Stacking of 2-methoxy-1,3,5-triazine fragments. The molecules shown are related by the centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$.

## Experimental

*Crystal data*

$C_9H_{10}N_4O_5$
$M_r = 254.18$
Monoclinic
$P2_1/n$
$a = 8.893\ (1)$ Å
$b = 10.681\ (2)$ Å
$c = 11.941\ (2)$ Å
$\beta = 94.33\ (1)°$
$V = 1130.99$ Å$^3$
$Z = 4$
$D_x = 1.492$ Mg m$^{-3}$

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}18°$
$\mu = 1.02$ mm$^{-1}$
$T = 293$ K
Prism
0.18 × 0.15 × 0.08 mm
White, transparent
Crystal source: toluene solution

*Data collection*

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2705 measured reflections
2156 independent reflections
1731 observed reflections $[F_o \geq 6\sigma(F_o)]$
$R_{\rm int} = 0.069$

$\theta_{\rm max} = 77°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 15$
2 standard reflections monitored every 100 reflections intensity variation: 2.5%

*Refinement*

Refinement on $F$
$R = 0.0438$
$wR = 0.0562$
$S = 1.039$
1731 reflections
204 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.00445F_o^2]$

$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.184$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.284$ e Å$^{-3}$
Extinction correction: Larson (1967)
Extinction coefficient: 0.018 (3)
Atomic scattering factors from *SHELXTL* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{\rm eq}$ |
|---|---|---|---|---|
| N(1) | −0.0093 (2) | 0.7120 (1) | 0.4067 (1) | 3.63 (4) |
| C(2) | −0.1131 (2) | 0.6250 (2) | 0.4238 (1) | 3.33 (4) |

| | | | | |
|---|---|---|---|---|
| O(2) | −0.2099 (2) | 0.6585 (1) | 0.4961 (1) | 4.52 (4) |
| N(3) | −0.1255 (2) | 0.5132 (1) | 0.3752 (1) | 3.69 (3) |
| C(4) | −0.0230 (2) | 0.4923 (2) | 0.3019 (2) | 3.68 (4) |
| O(4) | −0.0230 (2) | 0.3836 (1) | 0.2482 (1) | 4.84 (4) |
| N(5) | 0.0847 (2) | 0.5710 (2) | 0.2736 (1) | 4.20 (4) |
| C(6) | 0.0815 (2) | 0.6769 (2) | 0.3308 (2) | 3.64 (4) |
| O(6) | 0.1922 (2) | 0.7574 (1) | 0.3013 (1) | 4.87 (4) |
| C(20) | −0.3366 (3) | 0.5766 (3) | 0.5114 (2) | 4.96 (6) |
| C(40) | −0.1362 (3) | 0.2932 (2) | 0.2749 (3) | 5.47 (7) |
| N(61) | 0.1964 (2) | 0.8680 (1) | 0.3617 (2) | 4.11 (4) |
| C(62) | 0.1031 (2) | 0.9674 (2) | 0.3307 (2) | 3.96 (4) |
| O(62) | 0.0052 (2) | 0.9650 (2) | 0.2557 (1) | 5.66 (5) |
| C(63) | 0.1486 (2) | 1.0710 (2) | 0.4100 (2) | 4.52 (5) |
| C(64) | 0.2723 (3) | 1.0190 (3) | 0.4898 (2) | 5.79 (7) |
| C(65) | 0.2956 (2) | 0.8853 (2) | 0.4546 (2) | 4.96 (5) |
| O(65) | 0.3776 (2) | 0.8060 (2) | 0.4949 (2) | 7.73 (7) |

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| C(2)—O(2) | 1.314 (2) | C(6)—O(6) | 1.373 (2) |
| C(4)—O(4) | 1.326 (2) | C(6)—N(61) | 1.383 (2) |
| C(2)—O(2)—C(20) | 118.2 (2) | C(6)—O(6)—N(61) | 113.2 (2) |
| C(4)—O(4)—C(40) | 116.9 (2) | | |
| N(1)—C(6)—O(6)—N(61) | 2.4 (2) | N(3)—C(2)—O(2)—C(20) | −6.2 (2) |
| C(6)—O(6)—N(61)—C(62) | −83.9 (2) | N(3)—C(4)—O(4)—C(40) | −0.6 (3) |

Structure solution and refinement were performed using the *SHELXTL* (Sheldrick, 1990) program package on a PS-2 computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VS1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Geneserine Hydrochloride

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## Abstract

An experimental procedure to obtain single crystals of geneserine hydrochlorode, 1,2,3,3a,8,8a-hexahydro-1,3a,8-trimethylpyrrolo[2,3-*b*]indol-5-ol methylcarbamate *N*-oxide hydrochloride (IUPAC system: 5-methylcarbamoyloxy-1,2,3,3a,8,8a-hexahydro-1-hydroxy-1,3a,8-trimethylpyrrolo[2,3-*b*]indol-1-ium chloride), is described. The structure of the compound has been determined by X-ray diffraction: it crystallizes in the triclinic space group *P*1 and the unit cell contains two independent $C_{15}H_{22}N_3O_3^+$ cations, two independent $Cl^-$ anions and a single water molecule. The conformations of the two cations are described; a comparison of their geometries shows no significant differences. The crystal packing is characterized by a network of hydrogen bonds giving stacks of corrugated layers.

## Comment

Geneserine {(−)-2,3,4,4a,9,9a-hexahydro-2,4a*α*,9*α*-trimethyl-1,2-oxazino[6,5-*b*]indol-6-ol methylcarbamate ester} (I) is an alkaloid which was first isolated from the basic extracts of Calabar bean seeds (Polonovsky, 1915) and later obtained from physostigmine by oxidation with $H_2O_2$ (Polonovsky, 1917). The structure for geneserine with a *cis*-fused tetrahydro-1,2-oxazine ring [instead of the *N*-oxide structure postulated by Polonovsky (1925)] was established unambiguously by Hootele′ (1969) and independently supported by $^1$H NMR analysis using nuclear Overhauser effect measurements (Robinson & Moorcroft, 1970). Since the absolute configuration at the indoline C4 was already known (Hill & Newkome, 1969; Pauling & Petcher, 1973), the absolute stereochemistry of the alkaloid was determined to be 4a*S*,9a*S*. Total synthesis of the racemic form of (I) was reported by Shisido, Hiroya, Komatsu, Fukumoto & Kametani (1986, 1987)

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