

Fig. 1. Stereoview of the molecule; 50% probability ellipsoids for non-hydrogen atoms.

$C(sp^2)-O = 1.32$ ,  $C(sp^2)=O = 1.19$ ,  $C(ar)-C(ar) = 1.37$ ,  $C-Cl = 1.74$  Å [where  $C(ar)$  is in an aromatic ring]; the ranges of the values of bond angles (and means) are: angles at  $C(sp^3) = 106-113$  (111), at  $C(ar) = 118-123$  (120), at  $O = 113-120$  (116), and for carboxyl groups,  $C-C=O = 125-128$  (126),  $C-C-O = 110-112$  (111),  $O-C=O = 123^\circ$ .

The molecules are held together in the crystal by van der Waals forces, with no very strong intermolecular attractions. The extremities of the molecule exhibit considerable thermal motion, particularly the *p*-chlorobenzoyl groups. The largest thermal parameter is  $U_{11} = 0.311$  Å<sup>2</sup> for Cl(1), corresponding to a large root-

mean-square displacement of  $0.56$  (1) Å; this might indicate some disorder in the position of that *p*-chlorobenzoyl group, although a description in terms of large thermal vibration seems not unreasonable. The high thermal parameters for Cl might be the reason for the difficulties encountered in interpretation of the Patterson function. The planes of the *p*-chlorobenzoyl groups lie close to (103), but otherwise none of the early models show any correspondence to the true structure.

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## 4-(2-Amino-4-oxo-2-imidazolin-5-ylidene)-2-bromo-4,5,6,7-tetrahydropyrrolo-[2,3-*c*]azepin-8-one Methanol Solvate: a New Bromo Compound from the Sponge *Acanthella Aurantiaca*

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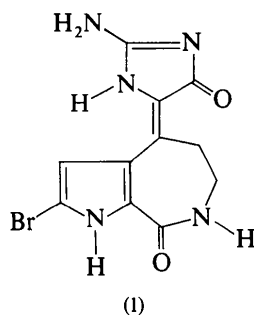
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**Abstract.** C<sub>11</sub>H<sub>10</sub>BrN<sub>5</sub>O<sub>2</sub>·CH<sub>4</sub>O,  $M_r = 356.07$ , monoclinic,  $P2_1/n$ ,  $a = 11.943$  (1),  $b = 16.252$  (2),  $c = 7.253$  (2) Å,  $\beta = 93.43$  (2)°,  $U = 1405.2$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.69$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu(\text{Cu } K\alpha) = 46.1$  cm<sup>-1</sup>. The structure was solved by the heavy-atom method and refined to an  $R$  value of 0.042 for 1997 independent observed reflexions. The molecule contains a seven-membered ring in an

approximate boat conformation. The packing is governed by a network of intermolecular hydrogen bonds, involving also the methanol O atom.

**Introduction.** The title compound (I) is a new metabolite containing Br; it was separated by chromatography from the butanolic extract of the Red Sea sponge *Acanthella Aurantiaca* (Cimino, De Rosa, De Stefano,

Mazzarella, Puliti & Sodano, 1982). This compound is moderately cytotoxic *in vitro* and was also found in the Mediterranean sponge *Axinella verrucosa*.



The single crystal used (0.04 × 0.06 × 0.2 mm) was obtained by slow evaporation from methanol. Intensity data were collected on an Enraf–Nonius CAD-4F PDP 11/34 diffractometer of the Centro di Metodologie Chimico-fisiche, Università di Napoli, using Ni-filtered Cu K $\alpha$  radiation and the  $\omega$ -2 $\theta$  scan technique ( $\theta \leq 70^\circ$ ). Two standard reflexions were recorded at regular intervals to monitor crystal and equipment stability. The unit-cell parameters were determined by least-squares refinement of the positions of 25 accurately centered reflexions. The intensities were corrected for Lorentz and polarization effects but no absorption corrections were made. The structure was solved using the heavy-atom and Fourier synthesis techniques. Refinement of the positional and isotropic

temperature factors was carried out by full-matrix least squares to an  $R$  value of 0.125. Anisotropic refinement of the temperature factors further reduced  $R$  to 0.054. A difference map then clearly showed all the H atoms at the expected positions. A final refinement of the non-hydrogen atoms was then carried out with weights obtained from counting statistics. The H atoms were included in the refinement with fixed isotropic thermal parameters equal to the  $B_{eq}$  values of the parent atoms. The final  $R$  was 0.042 for the 1997 observed reflexions [ $I \geq 2.5\sigma(I)$ ].\* The scattering-factor coefficients for all atoms were taken from Cromer & Waber (1974). Atomic fractional coordinates and equivalent isotropic temperature factors are given in Table 1.

**Discussion.** The structure established by this analysis is closely related to that proposed on spectroscopic grounds for the 'yellow compound' recently isolated from a Great Barrier Reef sponge (Sharma, Buyer & Pomerantz, 1980), from which it differs only in the presence of the Br atom bonded to C(1). The molecule contains a pyrroloazepine group connected through a double bond with an aminooxodihydroimidazole ring. Bond lengths and bond angles involving the non-hydrogen atoms are given in Table 2.

A comparison of the endocyclic torsion angles for the azepine group (Fig. 1) reveals that the ring adopts a distorted boat conformation with an approximate mirror plane passing through C(6) and the midpoint of the C(3)–C(4) bond. N(2), C(5), C(7) and C(8) lie in

Table 1. Positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\times 10^2$ )

$$B_{eq} = 4[(B_{11}B_{22}B_{33})/(\alpha^*b^*c^*)]^{1/3}.$$

	$x$	$y$	$z$	$B_{eq}$ ( $\text{\AA}^2$ )
Br(1)	5308 (1)	3495 (1)	1023 (1)	406 (2)
O(1)	843 (2)	2726 (2)	1395 (4)	327 (13)
O(2)	2683 (2)	-710 (2)	5796 (4)	276 (12)
N(1)	3159 (3)	2787 (2)	1046 (4)	236 (13)
N(2)	898 (3)	1344 (2)	1073 (5)	256 (14)
N(3)	4036 (3)	-75 (2)	7694 (4)	218 (12)
N(4)	4427 (3)	988 (2)	5847 (4)	214 (12)
N(5)	5414 (3)	894 (2)	8684 (4)	271 (14)
C(1)	4266 (3)	2678 (2)	1507 (5)	234 (15)
C(2)	4444 (3)	1916 (2)	2284 (5)	211 (14)
C(3)	3369 (3)	1533 (2)	2288 (5)	192 (13)
C(4)	2595 (3)	2084 (2)	1486 (5)	203 (14)
C(5)	1382 (3)	2071 (2)	1308 (5)	221 (14)
C(6)	1505 (3)	597 (2)	694 (6)	258 (16)
C(7)	2126 (3)	232 (2)	2400 (6)	238 (16)
C(8)	3065 (3)	762 (2)	3228 (5)	184 (14)
C(9)	3581 (3)	555 (2)	4858 (5)	179 (14)
C(10)	3371 (3)	-152 (2)	6121 (5)	214 (15)
C(11)	4653 (3)	608 (2)	7478 (5)	197 (14)
Solvent molecule				
O(3)	-1548 (3)	1270 (2)	1255 (5)	427 (15)
C(12)	-2104 (5)	2022 (3)	1021 (7)	479 (24)

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36823 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Br(1)–C(1)	1.868 (3)	N(5)–C(11)	1.308 (4)
O(1)–C(5)	1.248 (4)	C(1)–C(2)	1.371 (4)
O(2)–C(10)	1.237 (4)	C(2)–C(3)	1.427 (4)
N(1)–C(1)	1.356 (4)	C(3)–C(4)	1.390 (4)
N(1)–C(4)	1.373 (4)	C(3)–C(8)	1.483 (4)
N(2)–C(5)	1.321 (4)	C(4)–C(5)	1.446 (5)
N(2)–C(6)	1.449 (4)	C(6)–C(7)	1.524 (5)
N(3)–C(10)	1.357 (4)	C(7)–C(8)	1.509 (4)
N(3)–C(11)	1.346 (4)	C(8)–C(9)	1.342 (4)
N(4)–C(9)	1.394 (4)	C(9)–C(10)	1.500 (4)
N(4)–C(11)	1.348 (4)	O(3)–C(12)	1.396 (5)
C(1)–N(1)–C(4)	108.6 (3)	N(2)–C(5)–C(4)	117.0 (3)
C(5)–N(2)–C(6)	123.6 (3)	N(2)–C(6)–C(7)	113.4 (3)
C(10)–N(3)–C(11)	106.0 (2)	C(6)–C(7)–C(8)	114.5 (3)
C(9)–N(4)–C(11)	108.8 (2)	C(3)–C(8)–C(7)	119.7 (3)
Br(1)–C(1)–N(1)	120.7 (2)	C(3)–C(8)–C(9)	120.2 (3)
Br(1)–C(1)–C(2)	129.1 (3)	C(7)–C(8)–C(9)	120.0 (3)
N(1)–C(1)–C(2)	110.2 (3)	N(4)–C(9)–C(8)	127.4 (3)
C(1)–C(2)–C(3)	106.1 (3)	N(4)–C(9)–C(10)	102.4 (2)
C(2)–C(3)–C(4)	107.1 (3)	C(8)–C(9)–C(10)	130.1 (3)
C(2)–C(3)–C(8)	127.9 (3)	O(2)–C(10)–N(3)	125.2 (3)
C(4)–C(3)–C(8)	124.2 (3)	O(2)–C(10)–C(9)	125.4 (3)
N(1)–C(4)–C(3)	108.0 (3)	N(3)–C(10)–C(9)	109.4 (3)
N(1)–C(4)–C(5)	119.7 (3)	N(3)–C(11)–N(5)	113.4 (3)
C(3)–C(4)–C(5)	131.7 (3)	N(3)–C(11)–N(5)	125.3 (3)
O(1)–C(5)–N(2)	123.0 (3)	N(4)–C(11)–N(5)	121.3 (3)
O(1)–C(5)–C(4)	120.0 (3)		

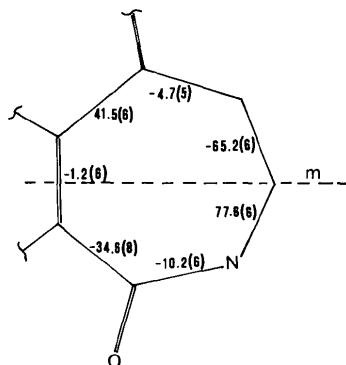


Fig. 1. Endocyclic torsion angles ( $^{\circ}$ ) of the seven-membered ring.

the plane and C(3), C(4) and C(6) are 0.667 (4), 0.638 (4) and 0.690 (4) Å out of it respectively. The puckering parameters according to Cremer & Pople (1975) are  $q_2 = 0.800$  (8) Å,  $\varphi_2 = -2.2$  (3) $^{\circ}$  and  $q_3 = 0.208$  (4) Å,  $\varphi_3 = -11.6$  (1) $^{\circ}$  for the sequence C(6), C(7), C(8), C(3), C(4), C(5), N(2). The deviation from ideal  $C_s$  symmetry described by the asymmetry parameter  $\Delta C_s$  (Duax, Weeks & Rohrer, 1976) is 10.3 (4) $^{\circ}$ . The *cis* amide group has dimensions close to those of the 'standard' *cis* peptide unit (Ramachandran & Sasisekharan, 1968) and its deviation from planarity is essentially due to a rotation around the C(5)–N(2) bond [ $\omega = -10.2$  (6) $^{\circ}$ ]. The pyrrole ring is planar within the e.s.d.'s, whereas in the imidazole ring C(9) is

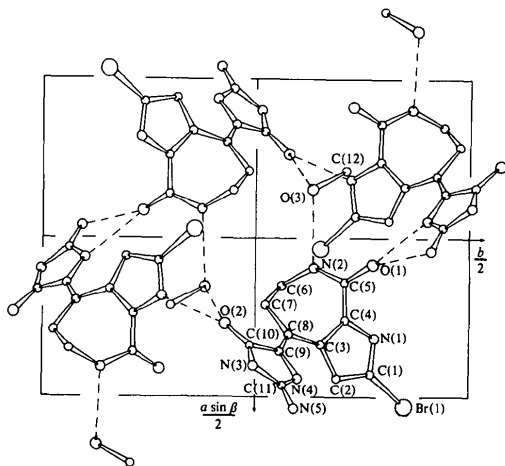


Fig. 2. Packing arrangement with the hydrogen-bonding scheme (dashed lines).

Table 3. Intermolecular hydrogen bonds

$D-H \cdots A$	$D \cdots A$ (Å)	$D-H$ (Å)	$H \cdots A$ (Å)	$\angle D-H \cdots A$ ( $^{\circ}$ )
$N(4)-H \cdots O(1)^i$	2.703 (3)	0.82 (4)	2.00 (4)	144 (4)
$N(5)-H \cdots O(1)^i$	2.855 (4)	0.80 (4)	2.17 (4)	144 (3)
$N(1)-H \cdots O(2)^{ii}$	2.934 (3)	0.87 (4)	2.09 (5)	163 (4)
$O(3)-H \cdots O(2)^{iii}$	2.755 (4)	0.86 (5)	1.90 (5)	173 (5)
$N(2)-H \cdots O(3)$	2.935 (4)	0.78 (3)	2.16 (3)	179 (4)

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

slightly but significantly displaced out of the best plane passing through the remaining atoms [0.031 (4) Å]. The dihedral angle between the five-membered rings is 43.7 (1) $^{\circ}$ . The tilting of these two rings which is achieved through the rotation about the C(3)–C(8) bond of the azepine ring partially increases the short intramolecular contact  $N(4) \cdots C(2)$  to 2.993 (4) Å.

The packing arrangement is shown in Fig. 2 with the numbering scheme used. The molecules are held in the extended crystal structure by hydrogen bonds (Table 3), in which the methanolic O participates extensively connecting pairs of centrosymmetrically related molecules. Both carbonyl O atoms act as acceptors for two hydrogen bonds.

All the other intermolecular contacts fall in the normal range with the exception of the close interaction between two aminooxodihydroimidazole rings related by a center of symmetry. The two rings are parallel with a mean interplanar distance of 3.33 Å. In the direction normal to the ring plane there is partial overlap between the two rings which indicates that a possible  $\pi$ – $\pi$  intermolecular interaction is favored.

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