$C_{20}H_{14}Cl_2N_2O_4$

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(3R)-cis-4-Acetyl-cis-3-methylcarbamoyl-1,4-thiazinane 1-Oxide, C8H14N2O3S

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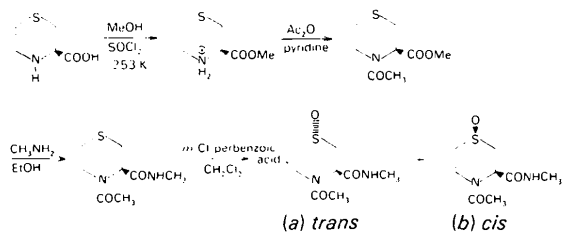*University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, B-2610 Wilrijk, Belgium*

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Abstract. $M_r = 218.3$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 8.576$ (2), $b = 15.845$ (4), $c = 7.263$ (3) Å, $V = 987.0$ (9) Å^3, $F(000) = 464$, $D_x = 1.469$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.310$ mm^{-1}, room temperature, $R = 0.047$ and $R_w = 0.045$ for 1172 reflections with $I > 2\sigma(I)$ out of 1284 independent measurements. The six-membered ring adopts a distorted chair conformation with the S=O bond and the methylcarbamoyl group in an axial orientation, and the N-acetyl substituent in an inclinal position. The planes of the latter groups are nearly perpendicular to each other.

Introduction. In continuation of a series of investigations on the conformation and geometry of derivatives of small cyclic peptides and amino acids we examined the title compound which was synthesized (Van der Auwera & Anteunis, 1984) from L-4-thiapipecolic acid in the sequence of reactions presented below.

(a) trans   (b) cis

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The final mixture was separated by column chromatography on silica using CHCl$_3$ to CHCl$_3$/MeOH (6:1) as eluent. Compound (*a*) is characterized by $\alpha_D^{18°C} = -61.4°$ ($c = 0.98$ g dm^{-3}; H$_2$O) and m.p. 434 K (softening at 431 K) and compound (*b*) by $\alpha_D^{18°C} = -100°$ ($c = 0.95$ g dm^{-3}; H$_2$O) and m.p. 461 K (softening at 447 K). The structure of compound (*b*) is reported here. NMR measurements on the title compound had revealed the relative positions of the N-acetyl and 3-methylcarbamoyl substituents as *cis* to the S=O bond in a distorted chair conformation. A further analysis of the NMR spectra, particularly a quantitative interpretation of vicinal coupling constants $^3J_{H,H}$ by the Karplus relation, requires background information about the ring torsion angles. Such information is expected from the X-ray determination of the compound in the crystalline state.

Experimental. Unit-cell dimensions determined from 25 high-order reflections. Intensity data collected up to a glancing angle $\theta = 27°$ ($0 \leq h \leq 10$; $0 \leq k \leq 20$; $0 \leq l \leq 9$) in the ω/θ scan mode; Mo radiation, graphite monochromator. Three intensity-control reflections measured every 120 min showed no crystal decay. Enraf–Nonius CAD-4 diffractometer. Crystal 0.15 × 0.15 × 0.2 mm. No absorption correction. The Patterson vector map gave the S position and a Fourier map, calculated on the S phases, revealed the remaining non-hydrogen atoms. After a few cycles of least-squares refinement (on *F*) (Enraf–Nonius *Structure Determination Package*, Frenz, 1978) a difference electron density map showed the positions of all H

atoms. All positional parameters were refined with anisotropic temperature parameters for non-H atoms and one isotropic temperature factor fixed to $B = 4 \text{ Å}^2$ for H atoms (overall B in the Wilson plot 3 Å^2). Reflections weighted individually with a weight based on counting statistics. Refinement converged to $R_w = 0.045$, $R = 0.047$ with $(\Delta/\sigma)_{max} = 0.05$. Max. peak in final difference Fourier map 0.2 e Å^{-3}. No extinction correction applied.

Discussion. Final values of the refined parameters are summarized in Table 1* while the numbering scheme of

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* Lists of H positions, anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39512 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the atoms is given in Fig. 1. CH distances range from 0.82 to 1.11 Å, with an average of 0.96 Å; other bond lengths and valence angles are listed in Table 2. A selection of torsion angles is given in Table 3. The sign distribution clearly shows that the six-membered ring has a chair conformation. Cremer & Pople (1975) ring parameters, with e.s.d.'s according to Norrestam (1981), are: $q_2 = 0.152$ (7), $q_3 = -0.603$ (7), $Q = 0.622$ (7) Å, $\varphi_2 = 215$ (3), $\theta_2 = 166$ (1)° for the sequences S, C(1), C(2), N(1), C(3), C(4). Although exact standard Cremer & Pople values for this type of ring are not known (Petit, Dillen & Geise, 1983) it is safe to say that the experimental values represent a distorted chair. The orientation of a substituent follows from the value of the angle (α) between the exocyclic valency and the plane of the ring (Cremer & Pople, 1975). An orientation is considered equatorial when
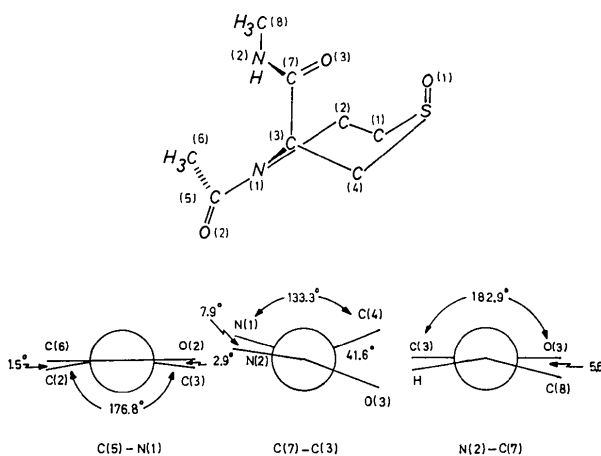
Table 1. *Positional parameters in fractions of the cell edges and isotropic temperature parameters* (Å^2)

The e.s.d.'s given in parentheses refer to the last significant digit. Isotropic temperature factors are calculated from the anisotropic temperature parameters assuming equal volume of the 50% probability region. B_{Iso} was calculated according to Lipson & Cochran (1968): $B_{Iso} = 8\pi^2(U^0_{11}U^0_{22}U^0_{33})^{1/3}$. All anisotropic thermal parameters were physically acceptable.

	x	y	z	B_{Iso}
S	−0.1803 (1)	−0.11199 (6)	−0.1893 (1)	3.01
O(1)	−0.2332 (3)	−0.1991 (2)	−0.1409 (4)	3.10
O(2)	0.2351 (3)	−0.0475 (2)	0.3071 (4)	3.73
O(3)	−0.2431 (3)	−0.1576 (2)	0.3345 (4)	3.91
N(1)	0.1124 (3)	−0.1173 (2)	0.0803 (4)	2.27
N(2)	−0.0267 (3)	−0.2354 (2)	0.3065 (4)	2.73
C(1)	0.0235 (5)	−0.1201 (2)	−0.2406 (5)	3.00
C(2)	0.1116 (5)	−0.1658 (2)	−0.0938 (5)	2.36
C(3)	−0.0379 (4)	−0.0974 (2)	0.1609 (5)	2.43
C(4)	−0.1513 (5)	−0.0565 (2)	0.0270 (6)	3.13
C(5)	0.2427 (4)	−0.0881 (2)	0.1610 (5)	2.66
C(6)	0.3977 (5)	−0.1059 (2)	0.0786 (6)	3.11
C(7)	−0.1119 (4)	−0.1682 (2)	0.2743 (5)	2.54
C(8)	−0.0746 (5)	−0.3021 (3)	0.4322 (6)	3.35

Fig. 1. Structural formula, conformation and numbering scheme of atoms of the title compound. Newman projections along C(5)—N(1), C(7)—C(3) and N(2)—C(7) show the arrangement of the substituents. (E.s.d.'s about 0.3°.)

Table 2. *Bond lengths* (Å) *and valence angles* (°) *with e.s.d.'s in parentheses*

The first column contains the values for the title compound, the second column, those for (3R,6R)-3-benzyl-1,4-diaza-8-thiabicyclo[4.4.0]decane-2,5-dione.

S=O(1)	1.495 (1)		N(2)—C(8)	1.456 (2)	1.433 (9)
S—C(1)	1.792 (2)	1.821 (8)	C(1)—C(2)	1.494 (2)	1.505 (12)
S—C(4)	1.817 (2)	1.855 (9)	C(3)—C(4)	1.520 (2)	1.521 (10)
N(1)—C(2)	1.480 (2)	1.474 (10)	C(3)—C(7)	1.529 (2)	1.476 (10)
N(1)—C(3)	1.451 (2)	1.459 (9)	C(5)—C(6)	1.485 (2)	1.462 (11)
N(1)—C(5)	1.344 (2)	1.373 (8)	C(5)—O(2)	1.242 (2)	1.220 (9)
N(1)—C(7)	1.313 (2)	1.337 (8)	C(7)—O(3)	1.219 (2)	1.227 (9)
O(1)—S—C(1)	106.2 (1)		N(1)—C(3)—C(7)	115.3 (1)	116.7 (8)
O(1)—S—C(4)	106.6 (1)		C(4)—C(3)—C(7)	113.1 (1)	105.5 (8)
C(1)—S—C(4)	94.6 (1)	97.0 (4)	S—C(4)—C(3)	115.8 (1)	114.2 (6)
C(2)—N(1)—C(3)	117.0 (1)	119.0 (8)	N(1)—C(5)—C(6)	120.2 (1)	115.1 (9)
C(2)—N(1)—C(5)	123.8 (1)	115.3 (8)	N(1)—C(5)—O(2)	120.5 (1)	122.3 (10)
C(3)—N(1)—C(5)	119.2 (1)	123.8 (9)	C(6)—C(5)—O(2)	119.3 (1)	122.4 (9)
C(7)—N(2)—C(8)	123.0 (1)	124.5 (8)	O(3)—C(7)—N(2)	124.1 (2)	121.5 (9)
S—C(1)—C(2)	112.3 (1)	110.3 (7)	O(3)—C(7)—C(3)	118.4 (1)	122.5 (9)
N(1)—C(2)—C(1)	111.1 (1)	113.7 (8)	N(2)—C(7)—C(3)	117.4 (1)	116.0 (9)
N(1)—C(3)—C(4)	113.7 (1)	109.7 (8)			

Table 3. *Selected torsion angles* (°) *in the title*
compound (e.s.d.'s about 0·3°)

C(1)–S–C(4)–C(3)	−51·7	C(4)–C(3)–C(7)–N(2)	141·2
S–C(4)–C(3)–N(1)	52·0	C(3)–C(7)–N(2)–C(8)	171·5
C(4)–C(3)–N(1)–C(2)	−51·2	C(2)–N(1)–C(5)–C(6)	−1·5
C(3)–N(1)–C(2)–C(1)	58·9		
N(1)–C(2)–C(1)–S	−66·4		
C(2)–C(1)–S–C(4)	58·5		

$0 \leq |\alpha| \leq 30°$, inclinal when $30 \leq |\alpha| \leq 60°$, and axial when $60 \leq |\alpha| \leq 90°$. The polar angles α for S–O(1), C(3)–C(7) and N(1)–C(5) are 94·8 (4), 68·9 (4) and 32·7 (4)°, respectively. Therefore, the S=O bond and the methylcarbamoyl substituent are axially oriented, whereas the acetyl group is inclinal.

N(1) is 0·022 (4) Å above the plane formed by C(2), C(3) and C(5), showing the near-planarity of the N(1) amide arrangement. The moiety N(1), C(5), C(6), O(2) is planar [largest deviation from the least-squares plane 0·008 (4) Å for C(5)] and is at a dihedral angle of 31·4 (3)° with the least-squares plane through the six-membered ring. The sp^2-hybridized C(7) is 0·015 (4) Å outside the plane given by C(3), C(7), O(3), N(2), which plane is at a dihedral angle of 109·4 (2)° with respect to the ring. The vicinal substituents, acetyl and methylcarbamoyl, are nearly perpendicular with a dihedral angle of 83·8 (2)° between their planes. The total geometry can best be seen from Fig. 1.

Another 4-thiapipecolic acid derivative is (3R,6R)-3-benzyl-1,4-diaza-8-thiabicyclo[4.4.0]decane-2,5-dione (Van Poucke & Lenstra, 1982). It may be regarded as structurally related to the title compound if we disregard the fact that the bonds N(1)–C(5) and C(3)–C(7) are *trans* oriented in the former and *cis* in the latter. Indeed bond lengths and valence angles compare favourably for the majority of values (see Table 2). Notable exceptions are the shorter C–S lengths in the title compound, which is normal since they are here adjacent to S=O. Also the bonds N(1)–C(5) and N(2)–C(7) are shorter, indicating that they have more amide character than in the bicyclic counterpart. The steric crowding in the title compound forces the angles at C(3) to be relatively large. For the same reason the least-puckered side of the six-membered ring is found at C(3) and C(4) and the most puckered side at C(1) and C(2).

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Structure of Trimethyl 8,13-Diphenyl-13-azatricyclo[8.2.1.0²,⁷]-trideca-2(7),3,5,11-tetraene-10,11,12-tricarboxylate, $C_{30}H_{27}NO_6$

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Abstract. $M_r = 497·55$, monoclinic, $P2_1/c$, $a = 15·074$ (3), $b = 9·839$ (1), $c = 18·545$ (3) Å, $\beta = 104·39$ (2)°, $V = 2664$ Å³, $Z = 4$, $D_x = 1·24$ Mg m⁻³, $\lambda(Cu\ K\alpha) = 1·5418$ Å, $\mu = 0·7$ mm⁻¹, $F(000) = 1048$, $T = 293$ K, final $R = 0·076$ for 2070 independent observed reflections. The dipolar cycloaddition of dimethyl acetylenedicarboxylate to the aziridine ring leads to only one diastereoisomeric pyrroline. Its