

shape when viewed normal to the best plane of the central four-membered ring.

Derived parameters for the methanesulfonyl (mesyl) groups are similar to each other and to those reported previously for other compounds (Harms, Sheldrick, Reichert & Tietze, 1986; Schlemper & Clark, 1985). Comparison of the structural parameters of (1) and the dimesyl portion of (2) offers no clue as to why the subsequent reaction of (2) with sodium malonate requires a temperature increase of approximately 50 K.

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#### References

ALMENNINGEN, A., BASTIANSEN, O. & SKANCKE, P. N. (1961). *Acta Chem. Scand.* **15**, 711–712.

BAKER, A. D., SCHARFMAN, R. & STEIN, C. A. (1983). *Tetrahedron Lett.* **24**, 2957–2960.

BUCHTA, E. & MERK, W. (1966). *Justus Liebigs Ann. Chem.* **694**, 1–8.

Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.

HARMS, K., SHELDRIK, G. M., REICHERT, U. & TIETZE, L.-F. (1986). *Acta Cryst.* **C42**, 1662–1663.

HULSHOF, L. A., VOS, A. & WYNBERG, H. (1972). *J. Org. Chem.* **37**, 1767–1770.

HULSHOF, L. A., WYNBERG, H., VAN DIJK, B. & DE BOER, J. L. (1976). *J. Am. Chem. Soc.* **98**, 2733–2740.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.

RENDELL, A. P. L., BACSKAY, G. B. & HUSH, N. S. (1988). *J. Am. Chem. Soc.* **110**, 8343–8354.

SCHLEMPER, E. O. & CLARK, G. R. (1985). *Acta Cryst.* **C41**, 130–132.

STEIN, C. A. & TAUBE, H. (1981). *J. Am. Chem. Soc.* **103**, 693–695.

*Acta Cryst.* (1990). **C46**, 2405–2407

## A 1,20-Cyclo Derivative from Atisine\*

BY M. PRZYBYLSKA AND F. R. AHMED

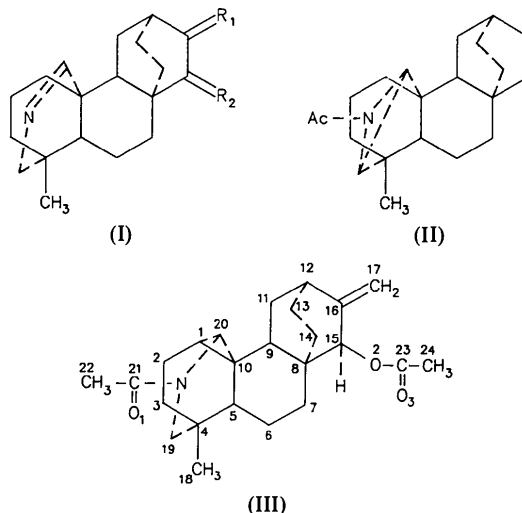
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**Abstract.** *N*-Acetyl-1,20-cyclo-16,17-didehydroatidan-15 $\beta$ -yl acetate, C<sub>24</sub>H<sub>33</sub>NO<sub>3</sub>, *M<sub>r</sub>* = 383.53, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 12.555 (2), *b* = 22.301 (4), *c* = 7.387 (2) Å, *V* = 2068.3 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.219, *D<sub>x</sub>* = 1.231 Mg m<sup>-3</sup>, λ(Cu Kα<sub>1</sub>) = 1.54056 Å, μ = 0.597 mm<sup>-1</sup>, *F*(000) = 832, *T* = 293 K, *R* = 0.060 for 1625 observed reflexions with *I* ≥ 2.0σ(*I*). The presence of a three-membered ring leads to considerable distortion of two adjoining six-membered rings. Weak hydrogen bonds of the type C—H⋯O=C link the molecules into chains parallel to *c*.

**Introduction.** An unusual reaction of a series of azomethines derived from atisine and ajaonine was discovered some time ago (Edwards, 1961). Those observations were confirmed later by Pelletier & Parthasarathy (1965). The azomethine with the least substituents, (I): *R*<sub>1</sub> = *R*<sub>2</sub> = H<sub>2</sub>, when heated with an acetic acid–acetic anhydride mixture gave a saturated *N*-acetyl derivative. It was suggested (Edwards, 1961) that this had structure (II); however, the <sup>13</sup>C NMR spectrum of this product did not fit this structure. An alternative formula, (III): *R*<sub>1</sub> = CH<sub>2</sub>; *R*<sub>2</sub> = β-OAc,

α-H, was later suggested by R. J. Kolt in these laboratories for the acetylation product of the more-substituted azomethine, (I): *R*<sub>1</sub> = CH<sub>2</sub>; *R*<sub>2</sub> = OH, H. Confirmation of (III) came from this X-ray analysis. A full account of the chemical and spectroscopic work carried out recently will be published (Edwards, Dvornik & Kolt, 1990).



\* Issued as NRCC No. 31887.

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ ), with e.s.d.'s in parentheses

	x	y	z	$B_{\text{eq}}$
O(1)	3708 (3)	1297 (1)	-4460 (6)	7.4
O(2)	5153 (2)	-1735 (1)	99 (5)	5.5
O(3)	4237 (4)	-2271 (2)	2133 (8)	10.4
N	4653 (3)	1119 (1)	-1908 (6)	4.7
C(1)	6137 (3)	406 (2)	-2936 (9)	5.8
C(2)	6911 (4)	918 (2)	-2461 (10)	7.3
C(3)	6977 (4)	1054 (2)	-448 (9)	6.3
C(4)	5948 (3)	943 (2)	622 (8)	5.3
C(5)	5664 (3)	269 (2)	479 (8)	5.2
C(6)	4683 (4)	100 (2)	1607 (7)	5.7
C(7)	4432 (4)	-570 (2)	1395 (8)	5.8
C(8)	4307 (3)	-772 (2)	-520 (7)	4.3
C(9)	5270 (3)	-590 (2)	-1683 (7)	4.5
C(10)	5510 (3)	88 (2)	-1460 (7)	4.7
C(11)	5119 (4)	-819 (2)	-3643 (8)	5.6
C(12)	4070 (3)	-1161 (2)	-3838 (7)	4.9
C(13)	3159 (4)	-721 (2)	-3331 (9)	6.3
C(14)	3273 (3)	-527 (2)	-1376 (8)	5.4
C(15)	4178 (3)	-1460 (2)	-644 (8)	5.0
C(16)	4015 (3)	-1663 (2)	-2536 (7)	4.8
C(17)	3838 (4)	-2229 (2)	-2994 (9)	6.1
C(18)	6153 (5)	1139 (2)	2546 (9)	7.2
C(19)	5016 (3)	1310 (2)	-118 (7)	5.1
C(20)	4972 (3)	542 (2)	-2652 (7)	4.6
C(21)	3962 (3)	1440 (2)	-2935 (8)	5.4
C(22)	3507 (4)	2004 (2)	-2022 (9)	6.6
C(23)	5053 (5)	-2123 (2)	1426 (8)	6.5
C(24)	6134 (5)	-2354 (2)	2038 (11)	8.6

**Experimental.** Crystal density was measured by flotation in carbon tetrachloride and toluene mixture. X-ray measurements were carried out with a small crystal of dimensions  $0.22 \times 0.27 \times 0.29$  mm on an Enraf-Nonius CAD-4 diffractometer with Ni-filtered Cu radiation. Cell parameters were derived by least squares from  $\theta$  values of 13 reflexions with  $18 < \theta < 38^\circ$  and  $\alpha, \beta, \gamma$  constrained to  $90^\circ$ . Intensities were measured by  $\omega$ - $2\theta$  scans to  $2\theta = 130^\circ$ ;  $h 0 \rightarrow 14$ ,  $k 0 \rightarrow 26$ ,  $l 0 \rightarrow 8$ ;  $\Delta\omega = (1.0 + 0.14\tan\theta)^\circ$  extended by 25% at each side for the background; horizontal aperture width  $(5.0 + 0.4\tan\theta)$  mm;  $\omega$ -scan speed  $\leq 2.0^\circ \text{ min}^{-1}$ . Three standard reflexions were measured every hour of exposure time throughout the experiment. Out of 2039 independent reflexions 1625 were observed with  $I \geq 2.0\sigma(I)$ . Corrections for Lorentz and polarization, background, and scale, but not for absorption, were applied. The structure was determined by direct methods with the aid of MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier maps. H-atom positions were obtained from difference maps. Refinement by block-diagonal least squares,  $9 \times 9$  per atom, minimizing  $\sum w(|F_o| - |F_c|)^2$  with  $w^{-1} = 1 + (|F_o|/15)^2$ . Convergence was reached at  $R = 0.060$  for the observed reflexions,  $wR = 0.075$ , average shift  $= 0.09\sigma$  and maximum shift  $= 0.49\sigma$ . Since most of the H atoms did not refine well, it was necessary to fix their original coordinates and  $B$

values. The residual electron density in the final difference map was within  $-0.20$  to  $+0.16 e \text{\AA}^{-3}$ . Reflexions 012 and 141, which appeared to be poorly measured, were excluded from later stages of refinement. Scattering-factor curves were from *International Tables for X-ray Crystallography* (1974, Vol. IV) and from Stewart, Davidson & Simpson (1965) for the H atoms. Computations were carried out with the NRC programs (Ahmed, Hall, Pippy & Huber, 1973). The final atomic coordinates are presented in Table 1.\*

**Discussion.** A parallel projection of the molecule of *N*-acetyl-1,20-cyclo-16,17-didehydroatidan-15 $\beta$ -yl acetate is shown in Fig. 1 (Johnson, 1976). The absolute configuration corresponds to that of atisine and analogous compounds (ApSimon & Edwards, 1962).

The bond lengths and valence angles, not corrected for thermal vibration, are presented in Table 2. The C(16)=C(17) double bond is of length  $1.326(7) \text{\AA}$  and its two adjoining bonds, with  $sp^3$ - $sp^2$  character, have lengths C(12)-C(16) =  $1.478(7)$  and C(15)-C(16) =  $1.483(8) \text{\AA}$ . The remaining C-C bond lengths are in the range  $1.493(8)$ - $1.553(6) \text{\AA}$ , as is usually observed for this type of compound. Two of the C-N bond lengths are normal [ $1.455(5)$  and  $1.462(7) \text{\AA}$ ], but N-C(21) is considerably shorter [ $1.357(6) \text{\AA}$ ] due to its proximity to the carbonyl group. The C-H lengths are  $0.98$  to  $1.15 \text{\AA}$ .

The valence angles show considerable deviations from tetrahedral values, especially in the neighbour-

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53131 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

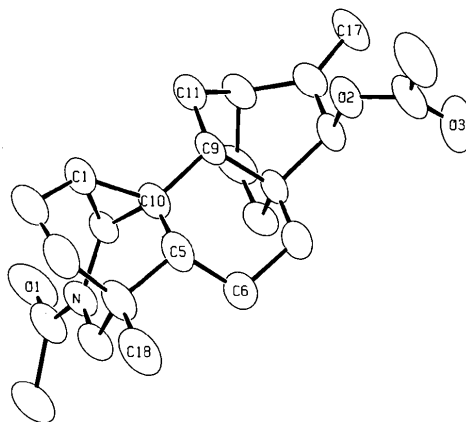


Fig. 1. ORTEP plot showing 40% probability thermal ellipsoids.

Table 2. Interatomic distances (Å) and valence angles (°)

O(1)—C(21)	1.213 (7)	C(6)—C(7)	1.535 (6)
O(2)—C(15)	1.475 (5)	C(7)—C(8)	1.493 (8)
O(2)—C(23)	1.314 (6)	C(8)—C(9)	1.538 (6)
O(3)—C(23)	1.196 (8)	C(8)—C(14)	1.544 (6)
N—C(19)	1.462 (7)	C(8)—C(15)	1.546 (6)
N—C(20)	1.455 (5)	C(9)—C(10)	1.551 (6)
N—C(21)	1.357 (6)	C(9)—C(11)	1.547 (8)
C(1)—C(2)	1.540 (7)	C(10)—C(20)	1.502 (7)
C(1)—C(10)	1.520 (7)	C(11)—C(12)	1.529 (6)
C(1)—C(20)	1.508 (5)	C(12)—C(13)	1.553 (6)
C(2)—C(3)	1.520 (10)	C(12)—C(16)	1.478 (7)
C(3)—C(4)	1.535 (7)	C(13)—C(14)	1.514 (9)
C(4)—C(5)	1.548 (6)	C(15)—C(16)	1.483 (8)
C(4)—C(18)	1.509 (9)	C(16)—C(17)	1.326 (7)
C(4)—C(19)	1.529 (6)	C(21)—C(22)	1.537 (7)
C(5)—C(6)	1.534 (7)	C(23)—C(24)	1.520 (9)
C(5)—C(10)	1.501 (8)		
C(15)—O(2)—C(23)	118.2 (4)	C(1)—C(10)—C(5)	119.5 (4)
C(19)—N—C(20)	120.9 (4)	C(1)—C(10)—C(9)	118.6 (4)
C(19)—N—C(21)	123.5 (4)	C(1)—C(10)—C(20)	59.9 (3)
C(20)—N—C(21)	115.6 (4)	C(5)—C(10)—C(9)	112.9 (4)
C(2)—C(1)—C(10)	120.6 (4)	C(5)—C(10)—C(20)	115.9 (4)
C(2)—C(1)—C(20)	115.5 (4)	C(9)—C(10)—C(20)	120.5 (4)
C(10)—C(1)—C(20)	59.5 (3)	C(9)—C(11)—C(12)	111.0 (4)
C(1)—C(2)—C(3)	113.9 (5)	C(11)—C(12)—C(13)	107.3 (4)
C(2)—C(3)—C(4)	115.2 (4)	C(11)—C(12)—C(16)	110.9 (4)
C(3)—C(4)—C(5)	108.4 (4)	C(13)—C(12)—C(16)	106.7 (4)
C(3)—C(4)—C(18)	107.1 (4)	C(12)—C(13)—C(14)	109.9 (4)
C(3)—C(4)—C(19)	112.0 (4)	C(8)—C(14)—C(13)	111.7 (4)
C(5)—C(4)—C(18)	112.6 (4)	O(2)—C(15)—C(8)	107.7 (4)
C(5)—C(4)—C(19)	108.6 (4)	O(2)—C(15)—C(16)	109.8 (4)
C(18)—C(4)—C(19)	108.2 (4)	C(8)—C(15)—C(16)	111.9 (4)
C(4)—C(5)—C(6)	112.7 (4)	C(12)—C(16)—C(15)	112.1 (4)
C(4)—C(5)—C(10)	110.9 (4)	C(12)—C(16)—C(17)	124.3 (4)
C(6)—C(5)—C(10)	110.4 (4)	C(15)—C(16)—C(17)	123.7 (4)
C(5)—C(6)—C(7)	110.4 (4)	N—C(19)—C(4)	114.0 (4)
C(6)—C(7)—C(8)	114.3 (4)	N—C(20)—C(1)	119.8 (4)
C(7)—C(8)—C(9)	111.5 (4)	N—C(20)—C(10)	119.9 (4)
C(7)—C(8)—C(14)	111.7 (4)	C(1)—C(20)—C(10)	60.7 (3)
C(7)—C(8)—C(15)	111.5 (4)	O(1)—C(21)—N	123.3 (4)
C(9)—C(8)—C(14)	109.8 (4)	O(1)—C(21)—C(22)	121.7 (4)
C(9)—C(8)—C(15)	108.1 (4)	N—C(21)—C(22)	115.1 (4)
C(14)—C(8)—C(15)	103.8 (4)	O(2)—C(23)—O(3)	126.1 (5)
C(8)—C(9)—C(10)	110.5 (4)	O(2)—C(23)—C(24)	111.1 (5)
C(8)—C(9)—C(11)	109.8 (4)	O(3)—C(23)—C(24)	122.8 (5)
C(10)—C(9)—C(11)	116.4 (4)		

hood of the three-membered ring where they are 59.5 (3)–120.6 (4)°. As expected, the planar conformation is maintained at each of the  $sp^2$  atoms: C(16), C(21) and C(23). The N atom, which is part of the amide group, is also planar with  $sp^2$  hybridization.

Torsion angles are given in Table 3. Ring *A* is a sofa at C(4) with the remaining five atoms almost coplanar. The asymmetry parameter is  $\Delta C_s[C(4)] = 1.4^\circ$  (Duax, Weeks & Rohrer, 1976). Ring *B* is of a slightly flattened chair form, as the torsion angles have absolute values from 51.3 (5) to 56.7 (5)°. Ring *E* has the half-chair conformation, with C(4) and C(5) situated above and below the plane of the other four atoms. The asymmetry parameters are  $\Delta C_2[C(4)—C(5)] = 13.7^\circ$  and  $\Delta C_s[C(4)] = 16.2^\circ$ . The average deviation of the torsion angles in the *C*, *D* and *C/D* rings in the bicyclo[2.2.2]octane system from the ideal boat value of 0 and  $\pm 60^\circ$  is 2.8° and the maximum is 5.5°.

Table 3. Torsion angles (°)

Ring A		Ring B	
C(10)—C(1)—C(2)—C(3)	0.6 (7)	C(10)—C(5)—C(6)—C(7)	54.7 (5)
C(1)—C(2)—C(3)—C(4)	-31.4 (7)	C(5)—C(6)—C(7)—C(8)	-54.2 (6)
C(2)—C(3)—C(4)—C(5)	61.7 (6)	C(6)—C(7)—C(8)—C(9)	52.8 (5)
C(3)—C(4)—C(5)—C(10)	-59.4 (5)	C(7)—C(8)—C(9)—C(10)	-51.3 (5)
C(4)—C(5)—C(10)—C(1)	30.9 (6)	C(8)—C(9)—C(10)—C(5)	54.8 (5)
C(5)—C(10)—C(1)—C(2)	-1.1 (7)	C(9)—C(10)—C(5)—C(6)	-56.7 (5)
Ring C		Ring D	
C(14)—C(8)—C(9)—C(11)	-56.8 (5)	C(16)—C(12)—C(13)—C(14)	56.4 (5)
C(8)—C(9)—C(11)—C(12)	-0.5 (5)	C(12)—C(13)—C(14)—C(8)	5.4 (6)
C(9)—C(11)—C(12)—C(13)	59.7 (5)	C(13)—C(14)—C(8)—C(15)	-61.0 (5)
C(11)—C(12)—C(13)—C(14)	-62.5 (5)	C(14)—C(8)—C(15)—C(16)	57.6 (5)
C(12)—C(13)—C(14)—C(8)	5.4 (6)	C(8)—C(15)—C(16)—C(12)	2.8 (5)
C(13)—C(14)—C(8)—C(9)	54.5 (5)	C(15)—C(16)—C(12)—C(13)	-61.3 (5)
Ring C/D		Ring E	
C(15)—C(8)—C(9)—C(11)	55.9 (5)	C(19)—C(4)—C(5)—C(10)	62.5 (5)
C(8)—C(9)—C(11)—C(12)	-0.5 (5)	C(4)—C(5)—C(10)—C(20)	-37.6 (5)
C(9)—C(11)—C(12)—C(16)	-56.5 (5)	C(5)—C(10)—C(20)—N	1.0 (6)
C(11)—C(12)—C(16)—C(15)	55.2 (5)	C(10)—C(20)—N—C(19)	11.3 (6)
C(12)—C(16)—C(15)—C(8)	2.8 (5)	C(20)—N—C(19)—C(4)	15.1 (6)
C(16)—C(15)—C(8)—C(9)	-59.0 (5)	N—C(19)—C(4)—C(5)	-50.9 (5)
Side groups			
C(19)—N—C(21)—C(22)	-4.7 (6)		
C(20)—N—C(21)—O(1)	-7.9 (7)		
C(16)—C(15)—O(2)—C(23)	-113.4 (5)		
C(15)—O(2)—C(23)—O(3)	-1.6 (8)		

The short intermolecular approach of 2.31 Å between O(1) of the carbonyl group and H(14,1) indicates the existence of a weak hydrogen bond with C(14)—H(14,1)···O(1) = 151° (Taylor & Kennard, 1982). The shortest five H···H contacts vary from 2.25 to 2.36 Å. There are no other intermolecular distances shorter than the sums of the appropriate van der Waals radii.

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## References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). *NRC Crystallographic Programs for the IBM360 System. Accession Nos. 133–147. J. Appl. Cryst.* **6**, 309–346.
- APSIMON, J. W. & EDWARDS, O. E. (1962). *Can. J. Chem.* **40**, 896–902.
- DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. ELIEL & N. ALLINGER, pp. 271–283. New York: John Wiley.
- EDWARDS, O. E. (1961). *Chem. Can.* **13**, 40–43 (Merck Award Lecture).
- EDWARDS, O. E., DVORNIK, D. & KOLT, R. J. (1990). *Can. J. Chem.* In preparation.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- PELLETIER, S. W. & PARTHASARATHY, P. C. (1965). *J. Am. Chem. Soc.* **87**, 777–798.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.