

Références

- BARTELL, L. S. (1960). *J. Chem. Phys.* **32**, 827–831.
 BAUGHMAN, R. H. (1974). *J. Polym. Sci.* **12**, 1511–1535.
 BROUTY, C., SPINAT, P. & WHULER, A. (1983). *Acta Cryst.* **C39**, 594–597.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 FISHER, D. A., ANDO, D. J., BLOOR, D. & HURSTHOUSE, M. B. (1979). *Acta Cryst.* **B35**, 2075–2079.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 GROSS, H., SIXL, H., KRÖHNKE, C. & ENKELMANN, V. (1980). *Chem. Phys.* **45**, 15–26.
 JOHNSON, C. K. (1965). *ORTEP*. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 PATEL, G. N., DUESLER, E. N., CURTIN, D. Y. & PAUL, I. C. (1980). *J. Am. Chem. Soc.* **102**, 461–466.
 WEGNER, G. (1972). *Makromol. Chem.* **154**, 35–48.
 WHULER, A., SPINAT, P. & BROUTY, C. (1984). *Acta Cryst.* **C40**, 693–696.

Acta Cryst. (1985). **C41**, 739–741

9 α ,10 α -Epoxy-5-methyl-19-nor-5 β -cholest-1-ene-3,6-dione, C₂₇H₄₀O₃

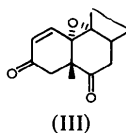
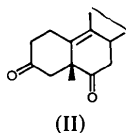
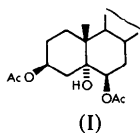
BY JAMES M. COXON, PATRICK D. QUAID AND PETER J. STEEL

Chemistry Department, University of Canterbury, Christchurch, New Zealand

(Received 24 October 1984; accepted 14 December 1984)

Abstract. $M_r = 412.6$, orthorhombic, $P2_12_12_1$, $a = 15.539$ (3), $b = 19.840$ (4), $c = 7.931$ (2) Å, $V = 2445$ Å³, $Z = 4$, $D_m = 1.13$ (1), $D_x = 1.12$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.66$ cm⁻¹, $F(000) = 904$, $T = 293$ K, final $R = 0.048$ for 1430 observed reflections. The structure determination establishes the configuration of the epoxy oxygen as 9 α ,10 α and locates the position of the double bond. The A–C rings are respectively in half-chair, half-boat and chair conformations whilst the D ring exists in a conformation intermediate between a 13 β -envelope and 13 β ,14 α -half-chair. The 17 β -side chain is in the most common extended conformation. Bond lengths and angles are normal.

Introduction. Westphalen's (1915) attempt to force acetylation of the tertiary hydroxyl group of (I) resulted in dehydration with rearrangement. Hydrolysis and oxidation of the product gave a non-conjugated diketone in which the position of the double bond was controversial but which is now well established to have structure (II) on the basis of chemical and spectroscopic studies (Coxon, Hoskins & Ridley, 1977).



During the course of other studies we epoxidized diketone (II) with *m*-chloroperbenzoic acid and obtained the expected, previously reported epoxide

(Shafiqullah, Ghaffari & Ali, 1980) along with a minor unsaturated epoxide (III), for which we now report a single-crystal X-ray structure analysis. The crystal structure is of interest for determination of the ring conformations in the uncommon 5 β ,9 α ,10 α steroid skeleton. A number of chemical and spectroscopic studies have attempted to deduce the conformations of Westphalen steroids (Glötter, Rabinsohn & Ozari, 1975) but to our knowledge no crystal structures have been reported.

Experimental. Colourless crystal, 0.63 × 0.17 × 0.15 mm, from petroleum ether. D_m by flotation (aqueous potassium iodide solution). Nicolet R3m automated four-circle diffractometer, graphite-monochromated Mo $K\alpha$, lattice parameters from 24 reflections in range $23 < 2\theta < 26^\circ$; $2\theta_{\text{max}} = 46^\circ$, standard reflections (no change) 800, 060, 002; 1979 unique reflections measured, 1430 with $I > 2\sigma(I)$ used in refinement, h 0–17, k 0–21, l 0–8, no absorption correction; structure solved by direct methods, blocked-cascade least-squares refinement, all non-H atoms anisotropic, H atoms included in calculated positions with isotropic thermal parameters equal to isotropic equivalent of their carrier atoms (C–H 0.96 Å); 271 parameters refined, function minimized $\sum w(|F_o| - |F_c|)^2$, $R = 0.048$, $wR = 0.046$, $w = [\sigma^2(F) + 0.00045F^2]^{-1}$, $S = 1.36$, max. (Δ/σ) value = 0.04 [$U_{12}C(20)$], av. $(\Delta/\sigma) = 0.01$, $\Delta\rho$ in final difference map = –0.18 to +0.15 e Å⁻³. All calculations on a Nova 4X computer using *SHELXTL* (Sheldrick, 1983), atomic scattering factors of *SHELXTL* used (*International Tables for X-ray Crystallography*, 1974).

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^*
O(3)	5642 (2)	7201 (2)	5406 (5)	98 (2)
O(6)	6147 (3)	9059 (1)	9553 (4)	92 (1)
O(9)	6940 (2)	9562 (1)	5106 (3)	52 (1)
C(1)	6000 (3)	8790 (2)	3547 (5)	68 (2)
C(2)	5981 (3)	8125 (2)	3702 (6)	77 (2)
C(3)	5872 (3)	7784 (2)	5314 (6)	68 (2)
C(4)	6064 (3)	8202 (2)	6831 (5)	63 (2)
C(5)	5773 (2)	8940 (2)	6675 (5)	44 (1)
C(6)	6068 (3)	9335 (2)	8222 (5)	53 (2)
C(7)	6264 (3)	10070 (2)	8036 (5)	49 (1)
C(8)	5970 (2)	10411 (2)	6411 (4)	44 (1)
C(9)	6167 (3)	9974 (2)	4884 (5)	42 (1)
C(10)	6096 (2)	9236 (2)	5043 (5)	46 (1)
C(11)	6065 (3)	10316 (2)	3197 (5)	59 (2)
C(12)	6420 (3)	11041 (2)	3095 (5)	57 (2)
C(13)	6131 (3)	11468 (2)	4578 (5)	49 (1)
C(14)	6403 (3)	11097 (2)	6181 (4)	45 (1)
C(15)	6304 (3)	11604 (2)	7621 (5)	63 (2)
C(16)	6531 (3)	12281 (2)	6754 (6)	70 (2)
C(17)	6626 (3)	12144 (2)	4852 (5)	51 (1)
C(18)	5149 (3)	11600 (2)	4507 (6)	67 (2)
C(19)	4778 (3)	8973 (2)	6676 (6)	68 (2)
C(20)	6379 (3)	12769 (2)	3762 (5)	59 (2)
C(21)	6428 (3)	12630 (2)	1863 (5)	74 (2)
C(22)	6915 (3)	13386 (2)	4204 (6)	71 (2)
C(23)	6512 (3)	14053 (2)	3702 (6)	67 (2)
C(24)	7052 (3)	14666 (2)	4151 (6)	70 (2)
C(25)	6636 (3)	15347 (2)	3797 (6)	62 (2)
C(26)	5871 (3)	15469 (2)	4916 (7)	87 (2)
C(27)	7279 (3)	15921 (2)	4016 (7)	92 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

O(3)—C(3)	1.212 (6)	O(6)—C(6)	1.195 (5)
O(9)—C(9)	1.463 (4)	O(9)—C(10)	1.462 (4)
C(1)—C(2)	1.325 (6)	C(1)—C(10)	1.487 (6)
C(2)—C(3)	1.457 (7)	C(3)—C(4)	1.491 (6)
C(4)—C(5)	1.539 (5)	C(5)—C(6)	1.525 (6)
C(5)—C(10)	1.507 (5)	C(5)—C(19)	1.548 (5)
C(6)—C(7)	1.499 (5)	C(7)—C(8)	1.525 (5)
C(8)—C(9)	1.520 (5)	C(8)—C(14)	1.530 (5)
C(9)—C(10)	1.473 (5)	C(9)—C(11)	1.508 (5)
C(11)—C(12)	1.543 (5)	C(12)—C(13)	1.518 (5)
C(13)—C(14)	1.527 (5)	C(13)—C(17)	1.561 (5)
C(13)—C(18)	1.550 (6)	C(14)—C(15)	1.530 (5)
C(15)—C(16)	1.549 (6)	C(16)—C(17)	1.539 (6)
C(17)—C(20)	1.559 (5)	C(20)—C(21)	1.533 (6)
C(20)—C(22)	1.521 (6)	C(22)—C(23)	1.518 (5)
C(23)—C(24)	1.520 (5)	C(24)—C(25)	1.524 (5)
C(25)—C(26)	1.503 (6)	C(25)—C(27)	1.525 (6)
C(9)—O(9)—C(10)	60.5 (2)	C(2)—C(1)—C(10)	121.3 (4)
C(1)—C(2)—C(3)	123.2 (4)	O(3)—C(3)—C(2)	122.1 (4)
O(3)—C(3)—C(4)	122.7 (4)	C(2)—C(3)—C(4)	115.2 (4)
C(3)—C(4)—C(5)	114.0 (4)	C(4)—C(5)—C(6)	109.6 (3)
C(4)—C(5)—C(10)	110.0 (3)	C(6)—C(5)—C(10)	113.0 (3)
C(4)—C(5)—C(19)	109.5 (3)	C(6)—C(5)—C(19)	106.2 (3)
C(10)—C(5)—C(19)	108.4 (3)	O(6)—C(6)—C(5)	120.4 (4)
O(6)—C(6)—C(7)	120.8 (4)	C(5)—C(6)—C(7)	118.7 (3)
C(6)—C(7)—C(8)	117.0 (3)	C(7)—C(8)—C(9)	111.1 (3)
C(7)—C(8)—C(14)	111.3 (3)	C(9)—C(8)—C(14)	108.9 (3)
O(9)—C(9)—C(8)	112.8 (3)	O(9)—C(9)—C(10)	59.7 (2)
C(8)—C(9)—C(10)	118.9 (3)	O(9)—C(9)—C(11)	116.3 (3)
C(8)—C(9)—C(11)	115.4 (3)	C(10)—C(9)—C(11)	121.0 (3)
O(9)—C(10)—C(1)	112.3 (3)	O(9)—C(10)—C(5)	116.2 (3)
C(1)—C(10)—C(5)	114.9 (3)	O(9)—C(10)—C(9)	59.8 (2)
C(1)—C(10)—C(9)	122.0 (3)	C(5)—C(10)—C(9)	119.0 (3)
C(9)—C(11)—C(12)	115.4 (3)	C(11)—C(12)—C(13)	112.0 (3)
C(12)—C(13)—C(14)	107.1 (3)	C(12)—C(13)—C(17)	116.3 (3)
C(14)—C(13)—C(17)	99.3 (3)	C(12)—C(13)—C(18)	110.9 (3)
C(14)—C(13)—C(18)	112.6 (3)	C(17)—C(13)—C(18)	110.2 (3)
C(8)—C(14)—C(13)	114.0 (3)	C(8)—C(14)—C(15)	116.9 (3)
C(13)—C(14)—C(15)	106.1 (3)	C(14)—C(15)—C(16)	102.4 (3)
C(15)—C(16)—C(17)	107.7 (3)	C(13)—C(17)—C(16)	103.9 (3)
C(13)—C(17)—C(20)	119.0 (3)	C(16)—C(17)—C(20)	112.3 (3)
C(17)—C(20)—C(21)	113.0 (3)	C(17)—C(20)—C(22)	112.2 (4)
C(21)—C(20)—C(22)	110.1 (4)	C(20)—C(22)—C(23)	114.6 (4)
C(22)—C(23)—C(24)	114.1 (4)	C(23)—C(24)—C(25)	115.5 (4)
C(24)—C(25)—C(26)	111.8 (4)	C(24)—C(25)—C(27)	111.3 (4)
C(26)—C(25)—C(27)	109.3 (4)		

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.* Bond lengths and angles are in Table 2. Fig. 1 shows a perspective view of the molecule and includes the atom labelling.

The structure determination unambiguously establishes the configuration of the epoxy oxygen as 9 α ,10 α , and locates the position of the double bond between C(1) and C(2).

Consideration of the signs and magnitudes of the intra-annular torsion angles (Fig. 2) and comparison with standard values (Bucourt, 1974) give the following ring conformations, ring *A*: 4 α ,5 β -half-chair with asymmetry parameter (Duax, Weeks & Rohrer, 1976) $\Delta C_2[C(1)-C(2)] = 6.8 (5)^\circ$; ring *B*: 5 β ,8 β -half-boat with $\Delta C_s[C(5)] = 8.7 (5)^\circ$ and $\Delta C_s[C(6)-C(7)] = 11.9 (5)^\circ$; ring *C*: chair with $\Delta C_2[C(9)-C(11)] = 2.2 (5)^\circ$; ring *D*: intermediate between a 13 β -envelope, $\Delta C_s[C(13)] = 10.4 (5)^\circ$ and a 13 β ,14 α -half-chair, $\Delta C_2[C(13)-C(14)] = 9.9 (5)^\circ$. This intermediate conformation for ring *D* is confirmed by the values of the pseudorotation parameters (Altona, Geise & Romers, 1968) $\psi_m = 45.9 (4)^\circ$ and $\Delta = 15.1 (4)^\circ$.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39977 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

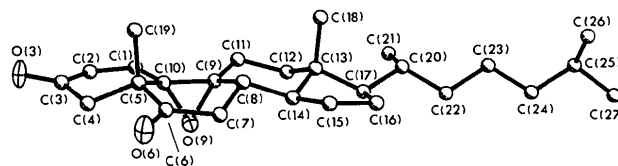


Fig. 1. Perspective view and atom labelling of the title compound. Hydrogen atoms are omitted for clarity.

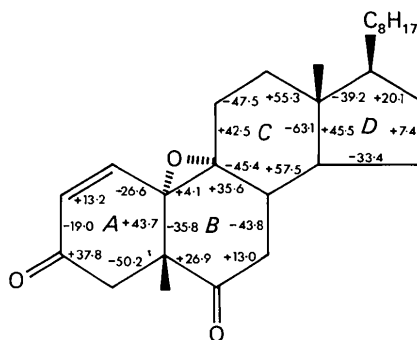


Fig. 2. Intra-annular torsional angles ($^\circ$, e.s.d.'s $\leq 0.5^\circ$) for the title compound.

These ring conformations are consistent with the *trans-syn-trans-anti-trans* ring junctions (Boeyens, Bull & Van Rooyen, 1980). For related Westphalen compounds chemical-reactivity studies were interpreted in terms of a half-chair conformation for ring *B* whilst NMR studies have shown this ring to be relatively flexible (Glötter *et al.*, 1975).

The 17β -side chain exists in the extended conformation which is the most common conformation in cholestane derivatives (Duax, Griffin, Rohrer & Weeks, 1980). All intermolecular contacts between non-H atoms are $>3.2 \text{ \AA}$.

We wish to acknowledge grants from the Research Committee of the New Zealand Universities Grants Committee.

References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.

BOEYENS, J. C. A., BULL, J. R. & VAN ROOYEN, P. H. (1980). *S. Afr. J. Chem.* **33**, 45–50.

BUCOURT, R. (1974). *Topics in Stereochemistry*, Vol. 8, edited by E. L. ELIEL & N. L. ALLINGER, pp. 159–224. New York: Wiley-Interscience.

COXON, J. M., HOSKINS, P. R. & RIDLEY, T. K. (1977). *Aust. J. Chem.* **30**, 1735–1742.

DUAX, W. L., GRIFFIN, J. F., ROHRER, D. C. & WEEKS, C. M. (1980). *Lipids*, **15**, 783–792.

DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by N. L. ALLINGER & E. L. ELIEL, pp. 271–383. New York: Wiley-Interscience.

GLOTTER, E., RABINSOHN, Y. & OZARI, Y. (1975). *J. Chem. Soc. Perkin Trans. 1*, pp. 2104–2108.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

SHAFIULLAH, GHAFARI, M. A. & ALI, H. (1980). *Tetrahedron*, **36**, 2263–2265.

SHELDRIK, G. M. (1983). *SHELXTL User Manual*, revision 4. Nicolet XRD Corporation, Cupertino, California.

WESTPHALEN, T. (1915). *Chem. Ber.* **48**, 1064–1069.

Acta Cryst. (1985). **C41**, 741–743

Structure of 1,4-Dinitrosopiperazine, $\text{C}_4\text{H}_8\text{N}_4\text{O}_2$

BY KIYOTANE SEKIDO, KOJUN OKAMOTO* AND SAKUTARO HIROKAWA

Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka City, 239 Japan

(Received 19 September 1984; accepted 14 December 1984)

Abstract. $M_r = 144.13$, orthorhombic, *Pbca*, $a = 9.495(4)$, $b = 6.570(3)$, $c = 10.521(7) \text{ \AA}$, $V = 656.3(9) \text{ \AA}^3$, $Z = 4$, $D_x = 1.459$, $D_m = 1.427 \text{ Mg m}^{-3}$, $\lambda = 0.7107 \text{ \AA}$, $\mu = 0.0877 \text{ mm}^{-1}$, $F(000) = 304$, $T = 293 \text{ K}$, final $R = 0.089$ for 959 independent reflections. The molecule is centrosymmetric, the piperazine ring having a chair form. The two nitroso groups are in the *anti* form. The N–O bond length is $1.202(4) \text{ \AA}$, and the N–N–O angle $113.4(3)^\circ$. The molecules are packed together to form infinite ribbons along the $[110]$ direction.

Introduction. As the piperazine system offers a rich selection of conformational questions, molecular shapes of this system have been investigated by NMR, dipole moment, and electron diffraction. Since piperazine derivatives are of interest due to their pharmacological activity and natural occurrence, we have studied the crystal structures of these derivatives by the X-ray method under a current program of this laboratory (Okamoto, Sekido, Itoh, Noguchi & Hirokawa, 1979;

Okamoto, Sekido, Ono, Noguchi & Hirokawa, 1982). 1,4-Dinitrosopiperazine (DNP) was chosen because it possesses several modes of conformational flexibility and it is a potent carcinogen in various animals. Lambert, Gosnell, Bailey & Henkin (1969) reported that the centrosymmetric *anti* form of DNP appeared to be present exclusively in the solid state, but a clear choice between a chair form and a boat form was not provided. The present work was undertaken to obtain the unambiguous structure of DNP.

Experimental. Colorless rectangular prismatic crystals (m.p. 430 K) obtained by slow evaporation from an ethanol solution. D_m measured by flotation in a mixture of toluene and tetrachloromethane. Crystal $0.5 \times 0.5 \times 0.6 \text{ mm}$. Rigaku AFC-III four-circle diffractometer, $\text{Mo K}\alpha$ radiation monochromatized by a graphite plate. X-ray intensity data measured by ω - 2θ scan, scan speed 4° min^{-1} in 2θ . Cell dimensions determined by least-squares method *RSLC-3* (UNICS, 1967) using 13 reflections with $25.0^\circ < \theta < 29.9^\circ$. Systematic absences $h = 2n + 1$ in $hk0$, $k = 2n + 1$ in $0kl$, and $l = 2n + 1$ in $h0l$. 959 independent reflections

* To whom correspondence should be addressed.