

Les molécules s'associent par un réseau de liaisons hydrogène présenté par la Fig. 2 et le Tableau 8. Les molécules déduites l'une de l'autre par translation des vecteurs **a** ou **c** sont liées par ponts hydrogène tandis que les molécules se déduisant les unes des autres par action d'axe binaire hélicoïdal parallèle à **b** ne participent qu'à des interactions de van der Waals.

Tableau 8. Réseau des liaisons hydrogène auquel participe la molécule dont les coordonnées figurent dans le Tableau 2

Atome O(1)			
O(1)—H(O1)···O(10)	(<i>x</i> −1, <i>y</i> , <i>z</i>)	2,725 (3) Å	1,76 (4) Å
O(1)···H(N)—N	(<i>x</i> , <i>y</i> , <i>z</i> +1)		
Atome N			
N—H(N)···O(1)	(<i>x</i> , <i>y</i> , <i>z</i> −1)	2,863 (3) Å	1,92 (4) Å
Atome O(10)			
O(10)···H(O1)—O(1)	(<i>x</i> +1, <i>y</i> , <i>z</i>)		

Les intensités de ce composé ont été collectées sur le diffractomètre du Laboratoire de Cristallographie dirigé par Mme C. Pascard à l'Institut des Substances Naturelles de Gif sur Yvette. Nous la remercions ainsi que ses collaborateurs pour leur aide efficace et sympathique.

Références

- BEAU, J. M. & SINAÏ, P. (1975). *Carbohydr. Res.* Sous presse.
 BENTLEY, T. (1972). *Ann. Rev. Biochem.* pp. 953–996.
 BERMAN, H. M., CHU, S. S. C. & JEFFREY, G. A. (1967). *Science*, **157**, 1576–1577.
 FRIES, D. C., RAO, S. T. & SUNDARALINGAM, M. (1971). *Acta Cryst.* **B27**, 994–1005.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* **B24**, 91–96.
 JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
 JOHNSON, L. N. (1966). *Acta Cryst.* **21**, 885–891.
 KUHN, R. & KRÜGER, G. (1956). *Chem. Ber.* **89**, 1473–1486.
 MARSH, R. E. & DONOHUE, J. (1967). *Advanc. Protein Chem.* **22**, 235–255.
 MORGAN, W. J. T. & ELSON, L. A. (1933). *Biochem. J.* **27**, 1824–1828.
 NEUMAN, A., GILLIER-PANDRAUD, H., LONGCHAMON, F. & RABINOVICH, D. (1975). *Acta Cryst.* **B31**, 474–477.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). *The X-RAY System*. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland.
 TIPPER, D. J. (1968). *Biochemistry*, **7**, 1441–1449.

Acta Cryst. (1976). **B32**, 24

The Conformations of Tetracyclic Diterpenes. III.* The Crystal and Molecular Structure of Methyl *ent*-16β-*p*-Bromobenzyloxy-17(16→12)*abeo*-atisan-19-oate, a Product of the Formolysis of Methyl 12α-Toluene-*p*-sulphonyloxy-*ent*-beyeran-19-oate

BY GEORGE FERGUSON AND WAYNE C. MARSH

Department of Chemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

(Received 8 May 1975; accepted 12 May 1975)

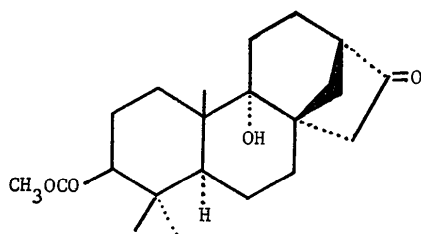
Crystals of the rearrangement product are monoclinic; $a = 7.195$ (1), $b = 10.623$ (2), $c = 16.978$ (2) Å, $\beta = 96.78$ (1)°, $Z = 2$, space group $P2_1$. The structure was solved by Patterson and Fourier methods and refined by least-squares procedures to $R = 0.069$ for 1274 observed reflexions. The flattened chair conformations of rings *A* and *B* as well as the observed conformation of the bicyclo[2,2,2]octyl system are largely explicable in terms of intramolecular steric interactions.

Introduction

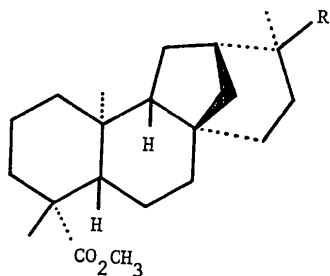
We have previously described the structures of two tetracyclic diterpenes containing a bicyclo[3,2,1]octane moiety: 3-acetoxy-9-hydroxy-17-norkauran-16-one (I) (Ferguson & Marsh, 1975*a*) and a derivative (II, R = OCOC₆H₄Br) of an acetolysis product (II, R = OCOCH₃) of the tosylate of 12α-beyeranol (III) (Ferguson & Marsh, 1975*b*).

When the solvolysis of the tosylate (III) was carried out in buffered formic acid the carbonium ion rearrangement proceeded by a different path yielding a new product having the suggested structure (IV, R = OCOH) (McAlees, McCrindle & Murphy, 1975). We now report the X-ray analysis of the heavy-atom derivative (IV, R = OCOC₆H₄Br) which was undertaken to confirm the postulated structure and to examine the conformations of the molecule in general and the bicyclo[2,2,2]octane system in particular.

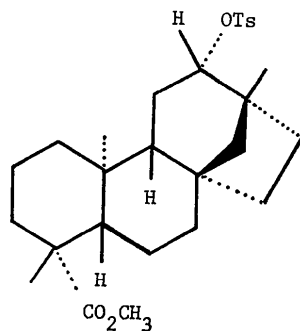
* Part II: *Acta Cryst.* **B31**, 2228–2232.



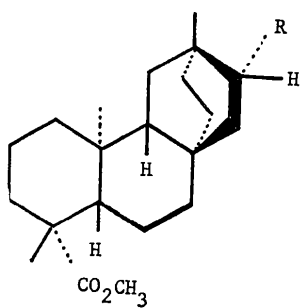
(I)



(II)



(III)



(IV)

Experimental

The heavy-atom derivative (IV, $\text{R} = \text{OCOC}_6\text{H}_4\text{Br}$) crystallized as irregularly shaped colourless prisms elongated along \mathbf{a} . Preliminary cell parameters and space-group data were determined from photographs; accurate cell parameters and orientation matrix were obtained by a least-squares procedure applied to 12 general reflexions measured on a diffractometer.

Crystal data

$\text{C}_{28}\text{H}_{37}\text{BrO}_4$, $M = 517.51$. Monoclinic, $a = 7.195$ (1), $b = 10.623$ (2), $c = 16.978$ (2) Å, $\beta = 96.78$ (1)°, $U = 1288.6$ Å³, $D_c = 1.33$ g cm⁻³, $Z = 2$, $F(000) = 544$. $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 17.2$ cm⁻¹. Systematic absences $0k0$ when k is odd. Space group $P2_1(C_2^2)$ or $P2_1/m(C_{2h}^2)$. $P2_1$ from structure analysis.

The intensities of all reflexions with $2\theta(\text{Mo } K\alpha) < 50^\circ$ were measured on a PDP8-I controlled Hilger and Watts four-circle diffractometer with a scintillation counter and graphite monochromator. A θ/ω step scan was employed with 0.01° steps, 1 s per step counting time, and a scan width of 0.7° in θ . Background counts of 17.5 s were made at the beginning and end of each scan. The intensities of two standard reflexions were measured after every 100 reflexions; the maximum variation was $\pm 1.4\%$. Of the 2409 unique data, 1274 had a net count $> 3\sigma(I)$ above background, where $\sigma(I) = [S + 4(B_1 + B_2) + (0.07S)^2]^{1/2}$ with S the scan count and B_1 and B_2 the background counts. The remaining 1135 data $< 3\sigma(I)$ above background were taken as unobserved.

Structure analysis

The positions of the Br and the remaining atoms of the *p*-bromobenzoate group were deduced from a sharpened Patterson synthesis. With the y coordinate of Br set at $\frac{1}{4}$ to fix the origin in space group $P2_1$ ($P2_1/m$ was eliminated because of the known optical activity), these ten atomic positions were used as input into the recycling procedure of Karle (1968). Three iterations of tangent refinement followed by an E map based on the refined phases were sufficient to locate all non-hydrogen atoms. The enantiomorph chosen corresponded to the known absolute configuration (McAlees, McCrindle & Murphy, 1975). Initial refinement by full-matrix least-squares methods with all atoms isotropic reduced R from 0.25 to 0.154. Subsequent refinement by anisotropic block-diagonal least-squares methods gave $R = 0.084$. Finally the H atoms were included in the structure factors in calculated positions with isotropic B values of 7.0 Å², but not in the refinement; the final R was 0.069 for the 1274 observed reflexions and 0.098 for all 2409 data. The scattering factors for Br, O, and C, including corrections for the anomalous scattering of Br, were taken from *International Tables for X-ray Crystallography* (1962), and those for H from Stewart, Davidson & Simpson (1965). The weighting scheme was $\omega = 0$ for the unobserved reflexions and $\omega = 1/\sigma(F_o)^2$ for the observed reflexions; the relative validity of the weighting scheme, judged by the variation of $\omega\Delta^2$ over ranges of $\sin \theta/\lambda$ and $|F_o|$, was satisfactory. The final weighted $R([\sum \omega(F_o - F_c)^2 / \sum \omega F_o^2]^{1/2})$ was 0.073. A final difference synthesis showed maximum fluctuations of ± 0.2 e Å⁻³ except in the neighbourhood of the Br atom where ripples of ± 0.9 e Å⁻³ were present. The final coordinates and thermal parameters are listed in Table 1. Table 2 contains the

bond lengths and angles.* A stereo view of the molecule produced by *ORTEP* (Johnson, 1965) illustrating

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31118 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the ellipsoids of thermal motion is shown in Fig. 1. The thermal motion was analysed in terms of the rigid body modes of translation, libration, and screw motion (Schomaker & Trueblood, 1968). The results indicated that the main skeleton of the molecule, C(1)–C(16) (Fig. 1), approximated a rigid body fairly well; the r.m.s. standard deviation in the temperature factors, U_{ij} (Table 1), was 0.0070 Å² while the r.m.s. ΔU_{ij} was

Table 1. *Positional and thermal parameters*

(a) Fractional coordinates ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z		x	y	z
Br	12567 (2)	$\frac{1}{4}$ *	1133 (1)	C(13)	7230 (15)	1417 (11)	5104 (5)
O(1)	5773 (10)	2001 (9)	3644 (4)	C(14)	6301 (14)	2626 (17)	5401 (5)
O(2)	8370 (10)	1701 (7)	4476 (3)	C(15)	8982 (15)	2975 (11)	6427 (6)
O(3)	6506 (12)	2529 (13)	9929 (4)	C(16)	9974 (15)	1792 (13)	6148 (6)
O(4)	7319 (12)	4069 (9)	9171 (4)	C(17)	9551 (22)	−305 (14)	5501 (7)
C(1)	5061 (18)	476 (12)	7854 (7)	C(18)	3275 (19)	4078 (17)	8769 (8)
C(2)	4559 (18)	510 (13)	8707 (6)	C(19)	6242 (16)	3121 (13)	9322 (6)
C(3)	3524 (18)	1696 (16)	8848 (6)	C(20)	8158 (15)	1611 (13)	8094 (6)
C(4)	4593 (15)	2946 (12)	8690 (5)	C(21)	8926 (16)	4365 (13)	9742 (6)
C(5)	5103 (14)	2845 (10)	7809 (6)	C(22)	7455 (14)	1951 (10)	3744 (6)
C(6)	5959 (18)	4041 (12)	7497 (6)	C(23)	8665 (14)	2031 (9)	3129 (5)
C(7)	5766 (17)	3931 (11)	6571 (5)	C(24)	10600 (16)	1940 (12)	3287 (5)
C(8)	6817 (13)	2813 (10)	6308 (6)	C(25)	11760 (15)	2046 (11)	2700 (5)
C(9)	6249 (14)	1586 (10)	6709 (5)	C(26)	10938 (15)	2278 (14)	1942 (5)
C(10)	6162 (13)	1646 (11)	7621 (6)	C(27)	9070 (13)	2341 (16)	1756 (5)
C(11)	7278 (19)	449 (11)	6406 (6)	C(28)	7917 (14)	2216 (12)	2359 (5)
C(12)	8537 (16)	842 (11)	5789 (6)				

* Held invariant to fix the origin in space group $P2_1$.

(b) Anisotropic thermal parameters (Å² × 10²) in the expression

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$$

with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	7.84 (6)	8.70 (7)	5.05 (5)	−0.67 (9)	2.15 (5)	−0.14 (9)
O(1)	5.3 (4)	12.6 (9)	5.1 (4)	−1.5 (5)	0.6 (4)	0.7 (4)
O(2)	6.2 (4)	6.4 (5)	2.4 (3)	−0.5 (4)	0.5 (3)	0.5 (3)
O(3)	11.0 (6)	12.2 (7)	4.4 (3)	−0.9 (9)	0.9 (4)	1.7 (7)
O(4)	8.0 (6)	7.5 (6)	5.1 (4)	0.5 (5)	1.3 (4)	0.2 (4)
C(1)	8.7 (9)	6.1 (9)	5.7 (7)	−2.0 (7)	1.9 (6)	0.3 (6)
C(2)	8.8 (9)	7.2 (10)	6.9 (8)	−3.0 (8)	3.4 (7)	0.9 (7)
C(3)	7.8 (9)	12.2 (11)	5.0 (6)	−1.5 (9)	3.7 (6)	1.3 (8)
C(4)	6.5 (7)	7.2 (12)	4.3 (5)	1.3 (7)	2.5 (5)	1.0 (5)
C(5)	5.3 (6)	5.9 (9)	3.9 (5)	0.4 (6)	1.3 (4)	1.0 (5)
C(6)	8.3 (8)	5.1 (8)	5.6 (6)	1.4 (7)	2.9 (6)	0.8 (6)
C(7)	8.0 (8)	4.6 (7)	4.7 (5)	1.5 (7)	2.1 (6)	0.4 (5)
C(8)	4.6 (5)	3.7 (8)	3.9 (4)	−0.3 (5)	1.0 (4)	0.2 (4)
C(9)	5.3 (6)	3.3 (6)	4.8 (5)	−0.7 (6)	2.0 (5)	0.6 (5)
C(10)	4.7 (6)	4.8 (7)	3.6 (5)	0.8 (6)	1.1 (4)	0.9 (5)
C(11)	10.8 (10)	4.5 (8)	4.8 (6)	1.9 (7)	3.0 (7)	1.1 (6)
C(12)	8.0 (8)	3.2 (7)	4.8 (6)	1.0 (7)	2.7 (6)	0.8 (5)
C(13)	6.4 (7)	5.2 (8)	3.2 (5)	−0.7 (6)	1.8 (5)	−0.1 (5)
C(14)	7.1 (6)	6.7 (8)	3.8 (4)	0.3 (9)	1.7 (4)	−0.6 (8)
C(15)	6.2 (7)	6.2 (9)	3.6 (5)	0.2 (6)	1.3 (5)	1.1 (5)
C(16)	5.2 (6)	8.4 (9)	3.9 (5)	1.7 (7)	0.4 (5)	1.6 (6)
C(17)	12.0 (13)	7.8 (9)	6.3 (7)	2.7 (9)	3.4 (8)	1.0 (7)
C(18)	6.3 (8)	10.6 (12)	9.0 (9)	2.4 (9)	4.5 (7)	0.1 (9)
C(19)	7.0 (7)	7.4 (9)	3.9 (5)	1.5 (7)	2.6 (5)	0.6 (5)
C(20)	5.2 (7)	7.6 (9)	4.7 (6)	1.2 (7)	1.8 (5)	1.0 (7)
C(21)	5.4 (7)	9.6 (9)	5.1 (6)	0.8 (7)	0.7 (5)	−0.5 (6)
C(22)	5.5 (6)	4.5 (6)	4.5 (6)	−1.4 (5)	0.9 (5)	−1.0 (5)
C(23)	5.1 (6)	3.0 (8)	3.5 (4)	−0.2 (5)	1.0 (4)	−0.3 (4)
C(24)	7.7 (7)	4.9 (8)	3.3 (5)	0.8 (7)	0.2 (5)	−0.1 (5)
C(25)	6.1 (6)	5.2 (9)	3.7 (5)	0.8 (6)	1.0 (5)	−0.3 (5)
C(26)	7.4 (7)	4.2 (9)	4.2 (5)	−0.6 (8)	2.5 (5)	−0.7 (7)
C(27)	5.2 (5)	6.7 (9)	3.9 (4)	−2.2 (8)	0.7 (4)	−0.5 (8)
C(28)	5.5 (6)	4.5 (10)	4.0 (5)	−1.5 (7)	0.3 (4)	−0.1 (6)

0.0063 Å². The results of the analysis further suggest that the translational tensor is roughly isotropic with the librational tensor somewhat less so. The appropriate bond distances and angles were corrected for libration (Cruickshank, 1956, 1961); however there were no significant changes to those values listed in Table 2 and the corrected values are not given.

Discussion

To some extent the accuracy of the analysis was frustrated by the poor quality of the crystals and by the

fairly high thermal motion of many of the atoms. With few exceptions the bond distances (Table 2) agree within experimental error with expected values (Sutton, 1965). The worst agreement is for C(4)–C(5) where the observed length, 1.59 (1) Å, is 0.05 Å larger than a standard C_{sp3}–C_{sp3} bond; neither atom has abnormally large or anisotropic thermal parameters. In view of this and similar discrepancies the analysis does not seem sufficiently accurate to justify any detailed discussion of the bond lengths.

The gross features of the conformations of the various parts of the molecule, in particular the bicyclo[2,2,2]octyl system, are a function of the intra-annular torsion angles listed in Table 3. Ring *A* has a chair conformation slightly flattened at the junction to ring *B* [Fig. 2(a)]. There are short trans-annular contacts between C(20) and the acetoxy side chain on C(4) [Table 4(a)]; in other structures where similar ring *A* flattening was observed (Ferguson, Macaulay, Midgley, Robertson & Whalley, 1970; Rendle, 1972; Ferguson & Marsh, 1975a) it has been attributed to a rotation about C(4)–C(5) to relieve this cross-ring steric interaction. In contrast, however, the structure of II (R = OCOC₆H₄Br) (Ferguson & Marsh, 1975b) also had similar steric interactions, but ring *A* had a virtually ideal chair conformation. It would seem then that the complete explanation of such occasional ring *A* flattening must include more than intramolecular effects alone; most likely intermolecular forces as well as perhaps various conformational transmission effects.

Table 2. Bond lengths and angles

(a) Bond lengths (Å) with estimated standard deviations in parentheses

C(1)–C(2)	1.53 (2)	C(12)–C(16)	1.52 (2)
C(1)–C(10)	1.55 (2)	C(12)–C(17)	1.53 (2)
C(2)–C(3)	1.50 (2)	C(13)–O(2)	1.45 (1)
C(3)–C(4)	1.57 (2)	C(13)–C(14)	1.56 (2)
C(4)–C(5)	1.59 (1)	C(15)–C(16)	1.55 (2)
C(4)–C(18)	1.55 (2)	C(19)–O(3)	1.20 (1)
C(4)–C(19)	1.51 (1)	C(19)–O(4)	1.31 (2)
C(5)–C(6)	1.53 (2)	C(21)–O(4)	1.45 (1)
C(5)–C(10)	1.54 (2)	C(22)–O(1)	1.20 (1)
C(6)–C(7)	1.57 (1)	C(22)–O(2)	1.36 (1)
C(7)–C(8)	1.51 (2)	C(22)–C(23)	1.44 (1)
C(8)–C(9)	1.55 (1)	C(23)–C(24)	1.39 (2)
C(8)–C(14)	1.55 (1)	C(23)–C(28)	1.37 (1)
C(8)–C(15)	1.56 (1)	C(24)–C(25)	1.38 (1)
C(9)–C(10)	1.56 (1)	C(25)–C(26)	1.37 (1)
C(9)–C(11)	1.54 (2)	C(26)–Br	1.923 (9)
C(10)–C(20)	1.56 (1)	C(26)–C(27)	1.35 (1)
C(11)–C(12)	1.52 (2)	C(27)–C(28)	1.40 (1)
C(12)–C(13)	1.54 (1)		

(b) Valency angles (°) with estimated standard deviations in parentheses

C(13)O(2)C(22)	117.1 (7)	C(9)C(10)C(20)	111.6 (8)
C(19)O(4)C(21)	118.4 (9)	C(9)C(11)C(12)	111.4 (10)
C(2)C(1)C(10)	114.0 (10)	C(1)C(12)C(13)	105.6 (9)
C(1)C(2)C(3)	110.3 (10)	C(11)C(12)C(16)	109.7 (9)
C(2)C(3)C(4)	114.9 (11)	C(11)C(12)C(17)	110.3 (10)
C(3)C(4)C(5)	106.0 (9)	C(13)C(12)C(16)	111.5 (10)
C(3)C(4)C(18)	108.9 (10)	C(13)C(12)C(17)	110.4 (9)
C(3)C(4)C(19)	109.9 (9)	C(16)C(12)C(17)	109.3 (10)
C(5)C(4)C(18)	110.3 (9)	O(2)C(13)C(12)	106.9 (8)
C(5)C(4)C(19)	115.3 (9)	O(2)C(13)C(14)	111.6 (9)
C(18)C(4)C(19)	106.3 (10)	C(12)C(13)C(14)	109.3 (8)
C(4)C(5)C(6)	114.7 (9)	C(8)C(14)C(13)	111.4 (9)
C(4)C(5)C(10)	115.3 (8)	C(12)C(16)C(15)	110.2 (9)
C(6)C(5)C(10)	112.7 (9)	O(3)C(19)O(4)	121.7 (10)
C(5)C(6)C(7)	107.1 (9)	O(3)C(19)C(4)	125.3 (12)
C(6)C(7)C(8)	111.8 (9)	O(4)C(19)C(4)	112.7 (9)
C(7)C(8)C(9)	111.3 (8)	O(1)C(22)O(2)	120.5 (9)
C(7)C(8)C(14)	109.1 (9)	O(1)C(22)C(23)	125.4 (9)
C(7)C(8)C(15)	113.8 (9)	O(2)C(22)C(23)	113.9 (8)
C(9)C(8)C(14)	106.6 (9)	O(22)C(23)C(24)	122.3 (8)
C(9)C(8)C(15)	110.3 (8)	C(22)C(23)C(28)	119.9 (9)
C(14)C(8)C(15)	105.3 (8)	C(24)C(23)C(28)	117.8 (9)
C(8)C(9)C(10)	116.6 (8)	C(23)C(24)C(25)	122.3 (8)
C(8)C(9)C(11)	110.5 (9)	C(24)C(25)C(26)	117.5 (9)
C(10)C(9)C(11)	116.3 (8)	C(25)C(26)C(27)	122.4 (9)
C(1)C(10)C(5)	109.3 (8)	C(25)C(26)Br	117.4 (7)
C(1)C(10)C(9)	107.6 (8)	C(27)C(26)Br	120.2 (7)
C(1)C(10)C(20)	108.4 (9)	C(26)C(27)C(28)	119.1 (8)
C(5)C(10)C(9)	108.7 (8)	C(27)C(28)C(23)	120.9 (9)
C(5)C(10)C(20)	111.2 (9)		

Table 3. Intra-annular torsion angles (°)

(a) Ring <i>A</i>			
C(10)C(1)–C(2)C(3)	54.5	C(3)C(4)–C(5)C(10)	–53.4
C(1)C(2)–C(3)C(4)	–57.1	C(4)C(5)–C(10)C(1)	53.2
C(2)C(3)–C(4)C(5)	55.1	C(2)C(1)–C(10)C(5)	–52.2
(b) Ring <i>B</i>			
C(6)C(5)–C(10)C(9)	–55.3	C(6)C(7)–C(8)C(9)	53.2
C(10)C(5)–C(6)C(7)	63.3	C(7)C(8)–C(9)C(10)	–46.6
C(5)C(6)–C(7)C(8)	–61.6	C(8)C(9)–C(10)C(5)	46.3
(c) The bicyclo[2,2,2]octane moiety			
	BOC	BSO	Present structure
C(8)C(9)–C(11)C(12)*	–0.4	4.7	–0.9
C(8)C(15)–C(16)C(12)	–0.1	5.1	3.5
C(8)C(14)–C(13)C(12)	–0.6	5.4	–5.4
C(11)C(9)–C(8)C(15)	–59.6	–61.4	–54.9
C(11)C(9)–C(8)C(14)	59.0	54.0	58.9
C(16)C(15)–C(8)C(9)	59.4	55.1	53.7
C(16)C(15)–C(8)C(14)	–60.1	–59.3	–61.0
C(13)C(14)–C(8)C(9)	–58.2	–60.6	–55.3
C(13)C(14)–C(8)C(15)	60.6	53.9	62.0
C(9)C(11)–C(12)C(16)	60.0	57.3	59.3
C(9)C(11)–C(12)C(13)	–58.3	–62.5	–61.1
C(15)C(16)–C(12)C(11)	–59.5	–63.7	–60.2
C(15)C(16)–C(12)C(13)	59.6	56.0	56.5
C(14)C(13)–C(12)C(11)	59.0	57.1	63.9
C(14)C(13)–C(12)C(16)	–59.5	–61.8	–55.2
C(9)C(8)···C(12)C(11)	–0.2	2.8	–0.5
C(15)C(8)···C(12)C(16)	0.0	3.0	2.0
C(14)C(8)···C(12)C(13)	–0.3	3.1	–3.2

* The numbering scheme is that for the present structure.

Table 4. *Intra- and intermolecular contacts* (Å)

Superscripts refer to atoms at:

(1)	$1+x$	y	z	(4)	$2-x$	$\frac{1}{2}+y$	$1-z$
(2)	$1+x$	y	$-1+z$	(5)	$1-x$	$\frac{1}{2}+y$	$1-z$
(3)	x	y	$1+z$				

(a) Selected intramolecular contacts

C(20)···O(3)	3.60 (1)	C(20)···C(15)	3.30 (1)
C(20)···O(4)	3.28 (1)	C(20)···C(16)	3.70 (1)
C(20)···C(19)	3.70 (1)		

(b) Intermolecular contacts < 3.8 Å

C(24)···O(1) ¹	3.70 (1)	C(6)···C(25) ⁴	3.62 (2)
C(25)···O(1) ¹	3.13 (1)	C(21)···Br ⁴	3.75 (1)
C(21)···C(18) ¹	3.72 (2)	C(22)···C(17) ⁴	3.76 (2)
Br···O(3) ²	3.685 (8)	C(23)···C(17) ⁴	3.79 (2)
O(3)···C(27) ³	3.42 (1)	C(24)···C(17) ⁴	3.59 (2)
O(4)···Br ⁴	3.683 (9)	C(7)···O(1) ⁵	3.45 (2)
O(2)···C(17) ⁴	3.51 (2)		

Ring *B* also adopts a chair conformation the C(8)C(9)C(10) end of which is considerably flattened relative to the C(5)C(6)C(7) end [Table 3 and Fig. 2(b)]. There are short cross-ring contacts between C(20) and C(15) and C(16) [Table 4(a)] and these, together with the junction to the bicyclo[2,2,2]octyl system, most probably determine the observed conformation.

The most interesting single feature of this particular diterpene is the bicyclo[2,2,2]octyl moiety. In other derivatives of bicyclo[2,2,2]octane the conformation has ranged from essentially fully eclipsed D_{3h} in the 1,4-dicarboxylic acid derivative (Ermer & Dunitz, 1969) to a slightly staggered conformation with D_3 symmetry found for 1-*p*-bromobenzenesulphonyloxymethylbicyclo[2,2,2]octane (Cameron, Ferguson & Morris,

1968). Potential energy calculations on bicyclo[2,2,2]octane itself (Ermer & Dunitz, 1969) suggested

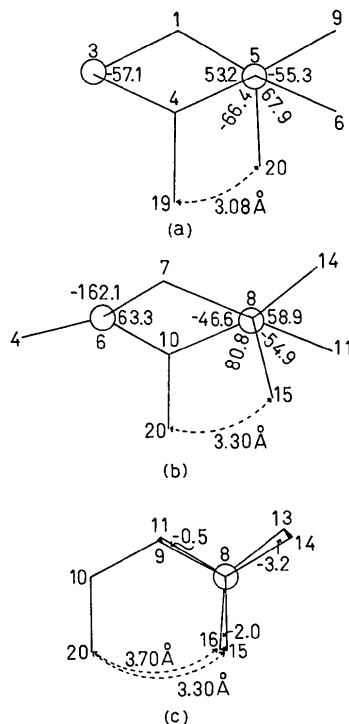


Fig. 2. Newman projections: (a) Along the C(5)–C(6) bond. (b) Along the C(8)–C(9) bond. (c) Along the C(8)···C(12) vector.

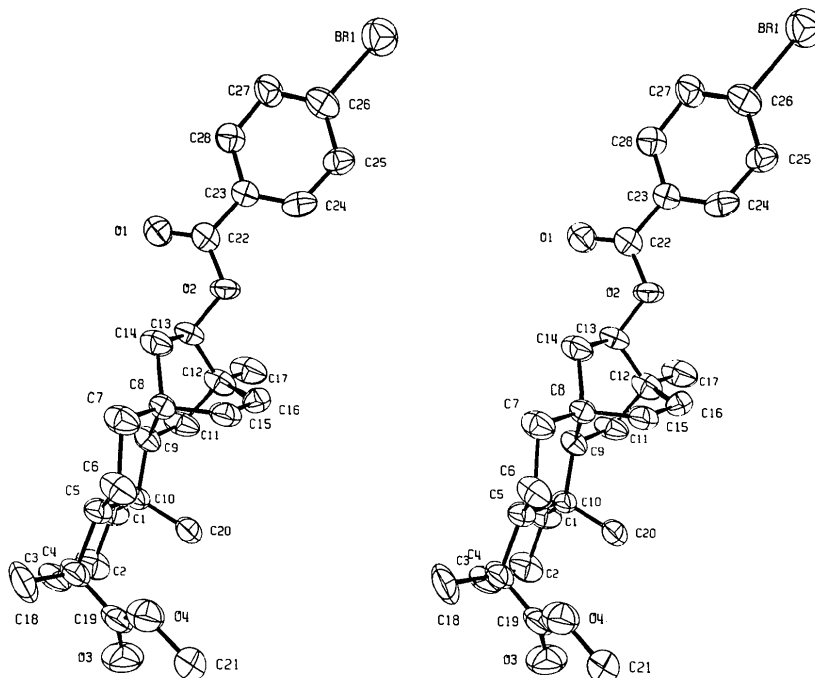


Fig. 1. Stereo diagram of (IV), R = OCOC₆H₄Br; the thermal ellipsoids shown are at the 50% probability level.

that the conformation of minimum energy may be slightly displaced from the eclipsed D_{3h} form, but that the barrier is only of the order of $0.1 \text{ kcal mol}^{-1}$. In the present structure the incorporation of the bicyclooctane into the fused ring system results in a conformation different from both those previously described. The observed conformation may be described by the torsion angles within the bicyclic moiety (Table 3) and by the Newman projection along the 1,4-axis [Fig. 2(c)]. Table 3 contains, in addition, the corresponding torsion angles for bicyclo[2,2,2]octane-1,4-carboxylic acid, BOC (Ermer & Dunitz, 1969), and 1-*p*-bromobenzenesulphonyloxymethylbicyclo[2,2,2]octane, BSO (Cameron, Ferguson & Morris, 1968). The observed conformation may be explained to a large extent by the severe intramolecular steric overcrowding [Table 4(a)]. There is a short contact (3.295 \AA) between C(20) and C(15) and also one (3.698 \AA) between C(20) and C(16). These result in a large increase in C(8)C(9)C(10) to 116.6° and somewhat smaller increases in C(15)C(8)C(9) and C(9)C(10)C(20) to 110.3° and 111.6° respectively; there are concomitant decreases in C(15)C(8)C(14) and C(14)C(8)C(9) to 105.3° and 106.6° respectively. At the other end of the bicyclooctane system, C(11)C(12)C(13) has decreased to 105.6° while C(13)C(12)C(16) has increased to 111.5° . As well as the various intramolecular steric effects the presence of the bulky *p*-bromobenzoate group on C(13) undoubtedly plays a part in deter-

mining the exact conformation of the bicyclo[2,2,2]octyl system. A stereo view of the molecular packing is shown in Fig. 3. There are no unusual intermolecular contacts; those less than 3.8 \AA [Table 4(b)] correspond to van der Waals interactions.

We acknowledge the National Research Council of Canada for financial support; also Professor R. McCrindle for the crystals and much helpful discussion. The computer programs used were locally modified versions of the X-RAY 72 system (University of Maryland, Technical Report TR-192, 1972) and programs supplied by the University of British Columbia.

References

- CAMERON, A. F., FERGUSON, G. & MORRIS, D. G. (1968). *J. Chem. Soc. (B)*, pp. 1249–1255.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747–753, 754–756.
 CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896–897.
 ERMER, O. & DUNITZ, J. D. (1969). *Helv. Chim. Acta*, **52**, 1861–1886.
 FERGUSON, G., MACAULEY, E., MIDGLEY, J. M., ROBERTSON, J. M. & WHALLEY, W. B. (1970). *J. Chem. Soc. (D)*, pp. 954–955.
 FERGUSON, G. & MARSH, W. C. (1975a). *Acta Cryst.* **B31**, 1684–1689.

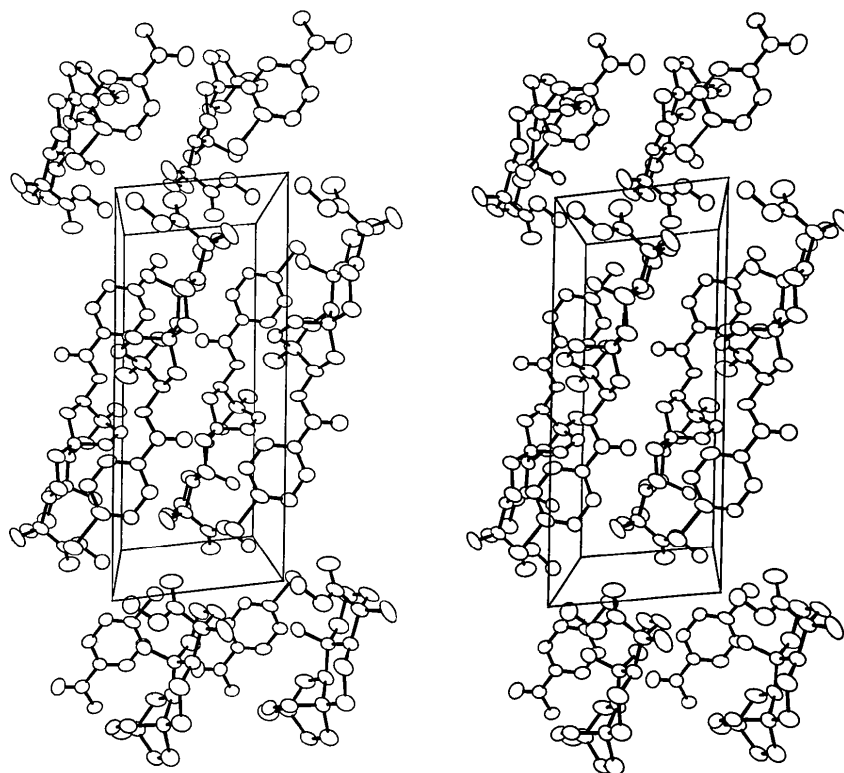


Fig. 3. Stereo diagram of the molecular packing. The origin is at the top left hand corner with y pointing towards the viewer, $x \rightarrow$ and $z \downarrow$.

- FERGUSON, G. & MARSH, W. C. (1975*b*). *Acta Cryst.* B31, 2228–2232.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KARLE, J. (1968). *Acta Cryst.* B24, 182–186.
- MCALEES, A. J., MCCRINDLE, R. & MURPHY, S. T. (1975). *J. Chem. Soc. Perkin I*. In the press.
- RENDLE, D. F. (1972). Ph. D. Thesis, Univ. of Guelph, Guelph, Ontario, Canada.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3178–3187.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Special Publication No. 18. London: The Chemical Society.

Acta Cryst. (1976). B32, 30

The Crystal and Molecular Structure of Chloropyridine-*N,N'*-tetramethylenebis(salicylaldiminato)rhodium(III)

BY BRYAN M. GATEHOUSE, BERNHARD E. REICHERT* AND BRUCE O. WEST

Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168

(Received 9 May 1975; accepted 12 May 1975)

The structure of the title compound has been determined by single-crystal X-ray analysis and refined by least-squares methods to an *R* of 0.060 with 3207 counter intensities. The crystals are monoclinic, space group $P2_1/c$, with $Z=4$ and $a=8.893$, $b=11.519$, $c=22.087$ Å, $\beta=104.17^\circ$. The molecule has the pyridine and Cl ligands 91° apart with the Schiff-base twisted into a *cis-β*-configuration.

Introduction

While the *cis-β* configuration of a tetradentate Schiff-base ligand (Fig. 1) has been crystallographically demonstrated in several compounds where this arrangement is forced by a bidentate ligand occupying the other two sites in the coordination octahedron of a metal (Calligaris, Nardin & Randaccio, 1970; Bailey, Higson & McKenzie, 1972; Calligaris, Manzini, Nardin & Randaccio, 1972), there has been no previous report of an X-ray structure for a compound with a tetradentate Schiff-base and two monodentate ligands in which a *cis-β* configuration is adopted. Such a structure was proposed (van den Bergen, Cozens & Murray, 1970) for $\text{Me}_2\text{SnSalen}$ [$\text{Salen}^{2-} = N,N'$ -ethylenebis(salicylaldiminato)dianion] on the basis of the ^1H n.m.r. spectrum, but an X-ray determination (Calligaris, Nardin & Randaccio, 1972*a*) showed the molecule to have the methyl groups *trans* with an essentially planar ligand. A more recent ^1H n.m.r. and infrared spectroscopic study has suggested that $\text{Me}_2\text{SnSalen}$ exists in two forms both in solution and in the solid state, one having the methyl groups *trans* and the other having them *cis* (Kawakami, Miya-Uchi & Tanaka, 1974), although this awaits confirmation.

The recently reported Rh complex RhSalbnPyCl [$\text{Salbn}^{2-} = N,N'$ -tetramethylenebis(salicylaldiminato)dianion] (Rogers & West, 1974*a*) was, on the basis of its ^1H n.m.r. spectrum, believed to have the Schiff-base

ligand twisted into a *cis-β* configuration with the pyridine and Cl also *cis* to one another (Rogers & West, 1974*b*). We report the structure of this compound which confirms the *cis-β* arrangement of the tetradentate ligand, and is the first X-ray determination to show such a configuration in the absence of a bidentate ligand.

Experimental

Crystals, grown by slow evaporation of a pyridine solution, were provided by Mr C. A. Rogers of this department. The orange-red compound crystallizes as elongated monoclinic prisms.

Crystal data

$\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_2\text{ClRh}$, $M=511.8$, monoclinic, $a=8.893$ (4), $b=11.519$ (6), $c=22.087$ (11) Å, $\beta=104.17^\circ$, $U=2192$ Å³, $D_m=1.55$ (1) g cm⁻³ (by flotation in a mixture of carbon tetrachloride and hexane), $Z=4$, $D_c=1.55$ g cm⁻³. $F(000)=1040$, $\mu=9.01$ cm⁻¹ for Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). Systematic absences indicate space group $P2_1/c$ (No. 14). The cell parameters were obtained with a Philips PW 1100 computer-controlled diffractometer by least-squares refinement of the reciprocal spacings for the $h00$, $0k0$, $00l$, $h0h$, $hh0$ and $0kk$ zones.

Intensity measurements

Intensities were collected on the diffractometer from a crystal $0.30 \times 0.25 \times 0.15$ mm with graphite-monochromated Mo $K\alpha$ radiation. A unique data set was collected out to 2θ (Mo $K\alpha$) = 56° by the ω -scan

* Present address: University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.