

## The Structure of 17 $\beta$ -Methylsparteine Diperchlorate

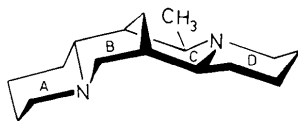
BY DANUTA PYŻAŁSKA, MARIAN GAWRON AND TERESA BOROWIAK

Department of Crystallography, Institute of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6,  
60-780 Poznań, Poland

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**Abstract.** C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>·2HClO<sub>4</sub>,  $M_r = 449.4$ , orthorhombic,  $P2_12_12_1$ ,  $a = 13.221(1)$ ,  $b = 18.555(3)$ ,  $c = 8.436(1)$  Å,  $Z = 4$ ,  $D_m = 1.42$ ,  $D_c = 1.44$  Mg m<sup>-3</sup>,  $V = 2069.6$  Å<sup>3</sup>;  $\mu(\text{Cu } K\alpha) = 3.24$  mm<sup>-1</sup>. From NMR and IR data, ring C was shown to adopt a boat conformation. The methyl group is in the equatorial position. The sparteine di-cation is hydrogen bonded by N–H...O bonds to two perchlorate anions with respective distances N(1)...O(1) 2.937 Å and N(16)...O(8) 2.969 Å.

**Introduction.** Protonation of sparteine leads to formation of a mono-cation which consists of a two-chair *trans*-quinolizidine A/B system and a two-chair *cis*-quinolizidine C/D system and which is stabilized by a N<sup>+</sup>–H...N hydrogen bond (Skolik & Wiewiórowski, 1970; Borowiak, Bokii & Struchkov, 1973). 17 $\beta$ -Methylsparteine on the other hand, does not form a mono-cation on protonation but easily transforms into the di-cation. This fact suggests that the skeleton of the 17 $\beta$ -methylsparteine di-cation is different from that of the sparteine mono-cation. According to chemical and physico-chemical evidence the bisquinolizidine ring system of 17 $\beta$ -methylsparteine diperchlorate was expected to have a chair–chair *trans*-quinolizidine A/B system and a boat–chair *trans*-quinolizidine C/D system (Wiewiórowski, Pieczonka & Skolik, 1977) (I).



An X-ray analysis of this compound was therefore undertaken in order to prove this hypothesis. It was also of interest to study the position of the methyl group and its influence on the conformation of the sparteine skeleton.

17 $\beta$ -Methylsparteine diperchlorate was recrystallized from a methanol solution. The space group and preliminary values of the unit-cell parameters were determined from precession photographs. Systematic absences:  $h00$  with  $h$  odd,  $0k0$  with  $k$  odd and  $00l$  with  $l$  odd, uniquely indicated the space group  $P2_12_12_1$ . The precise values of the unit-cell parameters were obtained by a least-squares fit of  $2\theta$ ,  $\omega$  and  $\chi$  settings for 15 diffractometer reflexions.

Using a crystal with dimensions  $0.16 \times 0.20 \times 0.35$  mm mounted on a Syntex  $P2_1$  diffractometer 1645 independent reflexions were collected to  $2\theta_{\text{max}} = 115^\circ$ . Cu  $K\alpha$  ( $\lambda = 1.54178$  Å) radiation (graphite monochromator) and  $\theta$ – $2\theta$  scan technique with variable scan rate ( $2$ – $29.30^\circ$  min<sup>-1</sup>) were applied. Two standard reflexions monitored every 30 reflexions showed no significant change in intensity during the data collection. 1479 reflexions with  $I > 1.96\sigma(I)$  were considered observed. Lorentz and polarization (but not absorption) corrections were applied to the intensity data.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971), using 245  $E^2$ 's down to 1.4. An  $E$  map calculated for the set of phases with best figures of merit revealed the positions of all non-hydrogen atoms except for the O atoms of the perchlorate groups. In order to find these atoms a difference Fourier map was calculated when  $R$  was 0.313. This  $\Delta F$  map showed all the perchlorate O atoms. The structure was refined with isotropic and then anisotropic thermal parameters to an  $R$  value of 0.095, using block-diagonal and full-matrix least-squares methods. 24 of the total 30 H atoms were located from two successive  $\Delta F$  maps and the positions of the remaining six H atoms were generated from the positions of the atoms to which they were bonded, tetrahedral angles being assumed. H atoms were assigned  $B$  values of 5 Å<sup>2</sup> and their parameters were

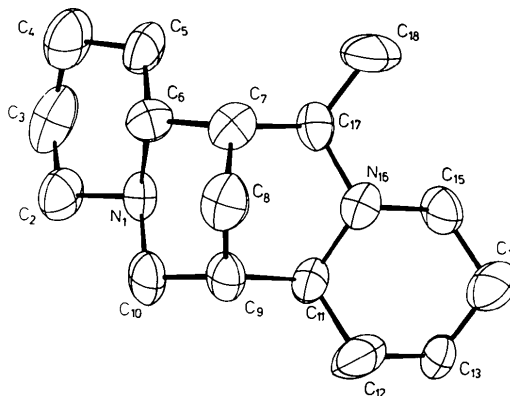


Fig. 1. View of the di-cation showing thermal ellipsoids.

included in the structure factor calculation, but were not refined. Full-matrix least-squares refinement converged at  $R = 0.060$  and  $R_w = 0.074$ , where  $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ ,  $R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$ .

Table 1. Final fractional atomic coordinates ( $\times 10^4$ ) with their e.s.d.'s in parentheses

	x	y	z
N(1)	742 (4)	1911 (3)	4136 (7)
C(2)	1014 (7)	2485 (5)	2949 (10)
C(3)	1254 (8)	2168 (6)	1358 (12)
C(4)	2091 (7)	1586 (6)	1457 (11)
C(5)	1792 (6)	1033 (5)	2669 (11)
C(6)	1604 (5)	1363 (4)	4258 (9)
C(7)	1368 (5)	827 (4)	5623 (10)
C(8)	1241 (6)	1241 (5)	7155 (9)
C(9)	308 (6)	1713 (4)	7009 (8)
C(10)	464 (6)	2269 (4)	5691 (10)
C(11)	-656 (5)	1237 (4)	6717 (9)
C(12)	-1427 (7)	1329 (5)	8020 (10)
C(13)	-2374 (7)	905 (5)	7620 (15)
C(14)	-2118 (5)	117 (5)	7468 (15)
C(15)	-1341 (6)	17 (4)	6140 (11)
N(16)	-366 (4)	449 (3)	6541 (7)
C(17)	418 (6)	337 (4)	5275 (9)
C(18)	712 (7)	-461 (5)	5183 (12)
Cl(1)	3154 (1)	3048 (1)	7518 (3)
Cl(2)	4661 (2)	606 (1)	5249 (3)
O(1)	3905 (4)	3614 (3)	7445 (8)
O(2)	3016 (6)	2769 (4)	6004 (8)
O(3)	3527 (6)	2488 (4)	8512 (10)
O(4)	2266 (5)	3320 (4)	8220 (11)
O(5)	5057 (18)	1014 (7)	4157 (19)
O(6)	3827 (8)	874 (10)	5850 (24)
O(7)	5291 (10)	628 (11)	6494 (18)
O(8)	4491 (15)	-30 (5)	4649 (13)
H(1)	119	1606	3757
H(21)	399	2873	2978
H(22)	1690	2739	3261
H(31)	1488	2643	636
H(32)	618	1881	862
H(41)	2143	1250	357
H(42)	2784	1802	1679
H(51)	2390	569	2647
H(52)	1066	857	2457
H(61)	2199	1627	4755
H(71)	1964	536	6071
H(81)	1853	1528	7379
H(82)	1275	941	8132
H(91)	396	1908	8274
H(101)	-189	2674	5284
H(102)	942	2683	5872
H(111)	-949	1434	5619
H(121)	-1785	1871	8050
H(122)	-1021	1228	9075
H(131)	-2773	886	6257
H(132)	-2779	846	8762
H(141)	-1627	-165	8554
H(142)	-2808	-289	7223
H(151)	-1513	187	4780
H(152)	-1023	-382	5936
H(161)	-50	314	7461
H(171)	144	446	4046
H(181)	300	-901	5130
H(182)	1233	-520	4777
H(183)	986	-608	6458

The function minimized in the least-squares calculations was  $\sum w(F_o - F_c)^2$ . The weighting scheme used was:

$$w = (F_o/F_{low})^2 \quad \text{if } F_o < F_{low},$$

$$w = 1 \quad \text{if } F_{low} \leq F_o \leq F_{high},$$

$$w = (F_{high}/F_o)^2 \quad \text{if } F_o > F_{high},$$

with  $F_{low} = 7$  and  $F_{high} = 21$ . Final positional parameters are given in Table 1.\*

**Discussion.** Fig. 1 shows the geometry of the di-cation and the labelling sequence of non-hydrogen atoms.

As was expected the sparteine skeleton consists of a chair-chair *trans*-quinolizidine *A/B* system and a boat-chair *trans*-quinolizidine *C/D* system. Bond distances and angles are listed in Tables 2 and 3.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33957 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Intramolecular distances (Å) with their e.s.d.'s

N(1)—C(2)	1.505 (10)	N(16)—C(15)	1.555 (10)
C(2)—C(3)	1.499 (13)	C(15)—C(14)	1.531 (13)
C(3)—C(4)	1.549 (14)	C(14)—C(13)	1.506 (13)
C(4)—C(5)	1.500 (14)	C(13)—C(12)	1.517 (12)
C(5)—C(6)	1.494 (12)	C(12)—C(11)	1.509 (11)
C(6)—C(7)	1.554 (11)	C(17)—C(18)	1.531 (11)
C(6)—N(1)	1.531 (9)	Cl(1)—O(1)	1.447 (5)
C(7)—C(8)	1.513 (12)	Cl(1)—O(2)	1.391 (7)
C(8)—C(9)	1.518 (11)	Cl(1)—O(3)	1.423 (8)
C(9)—C(10)	1.531 (11)	Cl(1)—O(4)	1.409 (7)
C(10)—N(1)	1.516 (10)	Cl(2)—O(5)	1.302 (17)
C(7)—C(17)	1.578 (10)	Cl(2)—O(6)	1.311 (14)
C(17)—N(16)	1.503 (9)	Cl(2)—O(7)	1.341 (14)
N(16)—C(11)	1.519 (9)	Cl(2)—O(8)	1.304 (11)
C(11)—C(9)	1.570 (11)		

Table 3. Bond angles ( $^\circ$ ) with their corresponding e.s.d.'s

N(1)—C(2)—C(3)	111.6 (7)	C(12)—C(13)—C(14)	109.7 (8)
C(2)—C(3)—C(4)	112.1 (8)	C(13)—C(14)—C(15)	109.3 (8)
C(3)—C(4)—C(5)	109.0 (8)	C(14)—C(15)—N(16)	109.6 (7)
C(4)—C(5)—C(6)	112.0 (7)	C(15)—N(16)—C(17)	110.2 (5)
C(5)—C(6)—N(1)	109.6 (6)	C(15)—N(16)—C(11)	107.9 (5)
C(5)—C(6)—C(7)	115.8 (7)	C(11)—N(16)—C(17)	112.2 (5)
C(7)—C(6)—N(1)	109.0 (6)	N(16)—C(17)—C(18)	110.2 (6)
C(6)—N(1)—C(2)	109.6 (6)	C(7)—C(17)—N(16)	109.6 (6)
C(6)—N(1)—C(10)	114.4 (6)	C(7)—C(17)—C(18)	111.4 (6)
C(2)—N(1)—C(10)	108.9 (6)	O(1)—Cl(1)—O(2)	108.8 (4)
C(6)—C(7)—C(8)	109.3 (6)	O(1)—Cl(1)—O(3)	108.5 (4)
C(8)—C(7)—C(17)	111.3 (6)	O(2)—Cl(1)—O(3)	108.4 (5)
C(6)—C(7)—C(17)	113.0 (6)	O(1)—Cl(1)—O(4)	109.3 (4)
C(7)—C(8)—C(9)	108.3 (7)	O(2)—Cl(1)—O(4)	114.2 (5)
C(8)—C(9)—C(10)	109.8 (6)	O(3)—Cl(1)—O(4)	107.6 (5)
C(8)—C(9)—C(11)	110.4 (6)	O(5)—Cl(2)—O(6)	113.0 (1.1)
C(10)—C(9)—C(11)	112.0 (6)	O(5)—Cl(2)—O(7)	106.7 (1.1)
N(1)—C(10)—C(9)	111.5 (6)	O(6)—Cl(2)—O(7)	102.0 (1.0)
C(9)—C(11)—N(16)	110.6 (6)	O(5)—Cl(2)—O(8)	108.7 (1.0)
C(9)—C(11)—C(12)	111.7 (6)	O(6)—Cl(2)—O(8)	110.4 (1.0)
C(12)—C(11)—N(16)	110.5 (6)	O(7)—Cl(2)—O(8)	116.0 (1.0)
C(11)—C(12)—C(13)	109.7 (7)		

Table 4. *Torsion angles* ( $^{\circ}$ )

Ring A	N(1)–C(2)–C(3)–C(4)	–54.7 (10)
	C(2)–C(3)–C(4)–C(5)	53.6 (10)
	C(3)–C(4)–C(5)–C(6)	–56.9 (9)
	C(4)–C(5)–C(6)–N(1)	60.6 (9)
	C(5)–C(6)–N(1)–C(2)	–58.8 (8)
	C(6)–N(1)–C(2)–C(3)	56.6 (8)
Ring B	N(1)–C(6)–C(7)–C(8)	–58.2 (7)
	C(6)–C(7)–C(8)–C(9)	65.6 (8)
	C(7)–C(8)–C(9)–C(10)	–63.4 (9)
	C(8)–C(9)–C(10)–N(1)	54.9 (7)
	C(9)–C(10)–N(1)–C(6)	–49.7 (8)
	C(10)–N(1)–C(6)–C(7)	50.8 (8)
Ring C	C(9)–C(11)–N(16)–C(17)	–54.6 (7)
	C(11)–N(16)–C(17)–C(7)	55.1 (7)
	N(16)–C(17)–C(7)–C(8)	2.6 (8)
	C(17)–C(7)–C(8)–C(9)	–60.0 (9)
	C(7)–C(8)–C(9)–C(11)	60.5 (7)
	C(8)–C(9)–C(11)–N(16)	–4.3 (6)
Ring D	N(16)–C(11)–C(12)–C(13)	–60.8 (8)
	C(11)–C(12)–C(13)–C(14)	60.5 (10)
	C(12)–C(13)–C(14)–C(15)	–60.3 (10)
	C(13)–C(14)–C(15)–N(16)	60.1 (9)
	C(14)–C(15)–N(16)–C(11)	–59.1 (7)
	C(15)–N(16)–C(11)–C(12)	59.6 (7)

Table 5. *Asymmetry parameters*

Ring A	$\Delta C_5^3 = 1.2$	Ring C	$\Delta C_8^9 = 1.1$
	$\Delta C_2^{2,3} = 2.5$		$\Delta C_3^{1,7} = 5.4$
	$\Delta C_2^{1,2} = 5.7$		
Ring B	$\Delta C_5^1 = 2.4$	Ring D	$\Delta C_8^{12,13} = 0.5$
	$\Delta C_2^{1,10} = 4.7$		$\Delta C_5^3 = 0.6$
	$\Delta C_2^{6,7} = 14.3$		$\Delta C_3^1 = 1.1$

The mean values of the C–C and C–N bond lengths are 1.527 and 1.522 Å, respectively. The former value agrees with 1.537 Å given by Sutton (1965). The deviation of the latter from the value of 1.500 Å reported by Birnbaum (1967) should not be given too much credit since the accuracy of the results is low.

Tables 2 and 3 also contain geometrical data for the perchlorate anions. A curious feature of this structure is that the temperature factors of the two perchlorate anions (which are similarly bonded in the structure) differ so significantly. The thermal parameters of the ClO<sub>4</sub><sup>–</sup>(2) O atoms are more than four times higher than those of ClO<sub>4</sub><sup>–</sup>(1) O atoms. We can give no simple reasonable explanation for this phenomenon. The Cl–O distances are considerably shorter than the accepted value of 1.46 Å (Truter, Cruickshank & Jeffrey, 1960), particularly in the case of ClO<sub>4</sub><sup>–</sup>(2), but little physical significance should be given to these values since no librational corrections were taken into consideration.

The conformation of the molecule may be described in terms of torsion angles listed in Table 4 and of asymmetry parameters (Duax & Norton, 1975) given in Table 5. The  $\Delta C_5$  and  $\Delta C_2$  values for rings A and D are low and thus both these rings show a good approximation to the ideal chair conformation. Similarly ring B

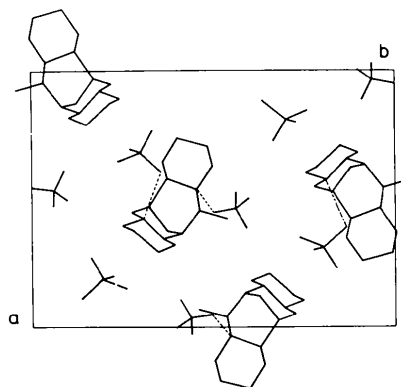


Fig. 2. Projection of the crystal structure onto the (001) plane. Hydrogen bonds are shown with broken lines.

has a symmetrical chair conformation, but mirror symmetry through N(1) and C(8) prevails in this case indicating a slight distortion towards a sofa conformation. The asymmetry parameters for ring C show a highly symmetrical boat conformation.

The methyl group is in the equatorial position with the C(17)–C(18) bond forming an angle of 27.5° with the least-squares plane defined by atoms C(9), C(11), C(7), C(17).

The boat conformation of ring C is stabilized by the methyl group in the equatorial position and such a conformation of the di-cation skeleton results in anion–di-cation hydrogen-bonding interactions different from those found in the case of  $\alpha$ -isosparteine diperchlorate (Przybylska, 1974). Each of the two ClO<sub>4</sub><sup>–</sup> groups is hydrogen bonded only to one of the N<sup>+</sup>–H centres of the di-cation (Fig. 2). Respective distances are: N(1)⋯O(1) 2.937 Å and N(16)⋯O(8) 2.969 Å.

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