

O(6) in the H_5O_2^+ unit is associated with shorter O—O interactions than is O(7) (Fig. 4, Table 6). As pointed out by Andersen (1971) this feature could be taken as evidence that the H_5O_2^+ ion is preferably described by the formula $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$. The present investigation confirms this conclusion (Table 6). A neutron diffraction investigation (Lundgren & Tellgren, 1974) has shown the existence of the hydrated H_3O^+ ion in picrylsulphonic acid tetrahydrate.

A perspective drawing of the 1,3-indandione-2-nitronate ion is shown in Fig. 5.

References

- ANDERSEN, E. K. (1971). *Experimentelle Studier over Strukturen af Hydroxyquinoner og deres Salte*, pp. 48–49. Dissertation, Odense Universitetsforlag.
- ANDERSEN, E. K. & ANDERSEN, I. G. (1975). *Acta Cryst.* **B31**, 379–383.
- BRAVIC, G., BECHTEL, F., GAULTIER, J. & HAUW, C. (1976). *Cryst. Struct. Commun.* **5**, 1–8.
- BRAVIC, G., GAULTIER, J. & HAUW, C. (1974a). *Cryst. Struct. Commun.* **3**, 215–217.
- BRAVIC, G., GAULTIER, J. & HAUW, C. (1974b). *Cryst. Struct. Commun.* **3**, 219–222.
- CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLET, p. 114. Oxford: Pergamon Press.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
- KLEWE, B. (1972). *Acta Chem. Scand.* **26**, 1049–1057.
- LUNDGREN, J. O. & TELLGREN, R. (1974). *Acta Cryst.* **B30**, 1937–1947.
- NEILANDS, O., STRADINS, J. & VANAGS, G. (1960). *Dokl. Akad. Nauk SSSR*, **131**, 1084–1087.
- NELSON, G. L., LEVY, G. C. & CARGIOLI, J. D. (1972). *J. Amer. Chem. Soc.* **94**, 3089–3096.
- SILVERMAN, J., KRUKONIS, A. P. & YANNONI, N. F. (1974). *Cryst. Struct. Commun.* **3**, 261–264.
- SIMONSEN, O. (1973). *Acta Cryst.* **B29**, 2600–2602.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STOTHERS, J. B. (1972). *Carbon-13 NMR Spectroscopy*, pp. 196–205. New York: Academic Press.
- STRADINS, J., NEILANDS, O., FREIMANIS, J. & VANAGS, G. (1959). *Dokl. Akad. Nauk SSSR*, **129**, 3–6.
- SUTOR, D. J., LLEWELLYN, F. J. & MASLEN, H. S. (1954). *Acta Cryst.* **7**, 145–152.
- WANAG, G. (1936). *Chem. Ber.* **69**, 1066–1074.

Acta Cryst. (1977). **B33**, 3049–3054

The Crystal and Molecular Structure of Episparteine N(16)-Oxide Sesquiperchlorate

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$[(\text{C}_{15}\text{H}_{27}\text{N}_2\text{O})_2\text{H}]^{3+}(\text{ClO}_4^-)_3$; $M_r = 802.1$; monoclinic, $C2$; $a = 25.943(3)$, $b = 8.137(1)$, $c = 9.132(1)$ Å; $\beta = 105.13(1)^\circ$; $Z = 2$; $D_m = 1.431$, $D_x = 1.440$ g cm $^{-3}$; $R = 0.035$ and $R_w = 0.030$ for 1138 reflections. The boat conformation for ring C deduced from NMR data is observed. The perchlorate group is disordered around the twofold axis. The O atom in the N-oxide group forms a strong hydrogen bond with the equivalent O atom of another molecule [O...O distance equals 2.435(4) Å].

Introduction

The structure of sparteine N(16)-oxide sesquiperchlorate was determined by Srivastava & Przybylska (1969) using X-ray analysis. The sparteine skeleton of this compound (Fig. 1a) consists of a two-chair *trans*-quinolizidine A/B system, and a two-chair *cis*-quinolizidine C/D system.

Episparteine N(16)-oxide, the compound for the present study, was obtained by Bratek-Wiewiórowska, Skolik, Łangowska & Wiewiórowski (1974) as a product of a mild reduction of the lactam group of

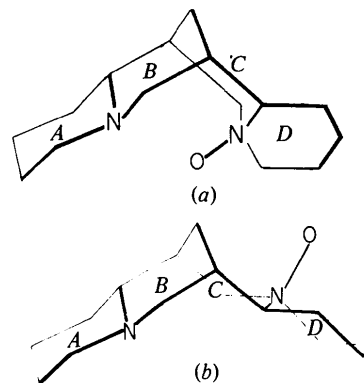


Fig. 1. (a) Sparteine N(16)-oxide. (b) Episparteine N(16)-oxide.

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lupamine *N*(16)-oxide with lithium aluminum hydride or sodium borohydride. According to chemical and physico-chemical evidence, the new sparteine *N*(16)-oxide (Fig. 1*b*) consists of a chair-chair *trans*-quinolizidine *A/B* system and a boat-chair *trans*-quinolizidine *C/D* system.

The X-ray analysis of the sesquiperchlorate of this compound was carried out in order to confirm these results. It is also of interest to study the influence of the perchlorate groups on the conformation of the sparteine skeleton and the formation of hydrogen bonds in this new compound.

Experimental

The new sparteine *N*(16)-oxide sesquiperchlorate crystallized from ethanol solution as colorless crystals. The dimensions of the crystal used for data collection were 0.08 × 0.1 × 0.13 mm. A preliminary study was carried out on a precession camera, and from the systematic absences the space group was determined as *C*2.

Diffraction data were collected at room temperature on a Syntex *P*2₁ diffractometer using Cu *K*α radiation and a graphite monochromator. The $\theta/2\theta$ scan method was used with a 2θ speed of 2° min⁻¹. A standard reflection was measured after every 16 reflections. 1323 reflections were collected for $2\theta < 114^\circ$ (excluding systematic absences) and 1128 reflections had $I >$

$2\sigma(I)$. The intensities were corrected for the Lorentz and polarization factors but absorption corrections were not applied, because the linear absorption coefficient and the size of the crystal were both small.

Crystal data

Formula [(C₁₅H₂₇N₂O)₂H]³⁺(ClO₄⁻)₃, $M_r = 802.1$, monoclinic, space group *C*2, $Z = 2$, $a = 25.943$ (3), $b = 8.137$ (1), $c = 9.132$ (1) Å, $\beta = 105.131$ (9)°, $V = 1860.86$ Å³, $\lambda_{\text{Cu } K\alpha} = 1.5418$ Å, $D_m = 1.431$, $D_x = 1.440$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 28.5$ cm⁻¹, $F(000) = 852$.

Solution of the structure and its refinement

The unit cell contains two molecules of 2(C₁₅H₂₆N₂O)·3HClO₄. Because there are four equivalent positions in the space group *C*2, four Cl atoms may occupy general positions with the remaining two on twofold axes. A sharpened Patterson synthesis gave the coordinates of the Cl atoms at (0.0, 0.0, 0.0) and (0.2988, 0.4277, 0.7734). The initial *R* value with the two Cl atoms included was 44.6%. The least-squares refinement and the subsequent electron density calculations showed the positions of non-hydrogen atoms, except for some of the O atoms of the perchlorate group around the twofold axis. These O atoms were considerably displaced from their positions assumed on the basis of the symmetry imposed by the twofold axis,

Table 1. Fractional atomic coordinates ($\times 10^4$) and, for the hydrogen atoms only, isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Cl(1)	1986 (0)	-878 (2)	2129 (1)	H(1)	1544 (11)	5780 (40)	2240 (30)	1.6 (6)
Cl(2)	0 (0)	0 (0)	0 (0)	H(2)	2274 (11)	4800 (40)	1830 (30)	2.3 (7)
O(1)	1493 (1)	-1773 (5)	1708 (4)	H(2')	1969 (11)	3120 (40)	1530 (30)	2.0 (7)
O(2)	1959 (2)	291 (5)	3268 (4)	H(3)	1955 (18)	4470 (70)	-690 (50)	8.5 (14)
O(3)	2074 (1)	-67 (5)	847 (4)	H(3')	1686 (14)	5740 (60)	-370 (40)	4.9 (10)
O(4)	2403 (1)	-2035 (5)	2745 (5)	H(4)	964 (15)	4150 (70)	-1830 (40)	5.8 (10)
O(5)	156 (5)	850 (10)	1237 (7)	H(4')	1137 (16)	2720 (60)	-860 (40)	5.5 (10)
O(6)	398 (5)	-44 (50)	-766 (17)	H(5)	753 (11)	5580 (40)	100 (30)	2.1 (7)
O(7)	-184 (4)	-1538 (9)	241 (12)	H(5')	484 (11)	3710 (40)	-50 (30)	2.1 (7)
O(8)	-394 (4)	700 (12)	-1127 (11)	H(6)	1110 (11)	2800 (40)	1790 (30)	2.2 (7)
O(9)	482 (1)	6298 (4)	5530 (3)	H(7)	417 (11)	3940 (50)	2560 (30)	3.1 (8)
N(1)	1589 (1)	4750 (4)	2377 (3)	H(8)	1122 (15)	2490 (50)	4360 (40)	5.2 (10)
N(16)	754 (1)	6944 (4)	4494 (3)	H(8')	715 (13)	3710 (40)	5120 (4)	3.4 (8)
C(2)	1950 (1)	4193 (7)	1410 (4)	H(9)	1645 (13)	4440 (50)	5980 (40)	3.9 (8)
C(3)	1706 (2)	4575 (6)	-223 (5)	H(10)	2161 (11)	5190 (40)	4290 (30)	2.3 (7)
C(4)	1161 (2)	3901 (7)	-809 (5)	H(10')	1965 (14)	3390 (50)	4110 (40)	5.4 (10)
C(5)	806 (2)	4446 (6)	185 (4)	H(11)	1488 (11)	7080 (40)	4450 (30)	1.8 (7)
C(6)	1037 (1)	3971 (6)	1823 (4)	H(12)	1971 (15)	7330 (50)	7020 (40)	4.7 (10)
C(7)	700 (1)	4357 (6)	2907 (4)	H(12')	1409 (13)	6890 (50)	7340 (40)	3.6 (8)
C(8)	990 (2)	3716 (5)	4468 (5)	H(13)	1628 (20)	9660 (70)	7720 (60)	9.1 (14)
C(9)	1472 (2)	4782 (6)	5017 (4)	H(13')	1715 (15)	9680 (60)	6010 (50)	6.1 (11)
C(10)	1852 (2)	4466 (6)	4025 (4)	H(14)	820 (14)	590 (50)	5980 (40)	4.6 (9)
C(11)	1342 (1)	6618 (6)	5094 (4)	H(14')	637 (14)	9010 (60)	6720 (40)	5.5 (10)
C(12)	1554 (2)	7408 (6)	6626 (5)	H(15)	278 (12)	8900 (50)	4050 (30)	3.0 (7)
C(13)	1447 (2)	9227 (8)	6619 (5)	H(15')	841 (12)	9170 (60)	3710 (30)	3.7 (7)
C(14)	854 (2)	9550 (6)	5956 (5)	H(16)	0 (0)	6570 (100)	5000 (0)	7.2 (17)
C(15)	660 (2)	8789 (6)	4421 (5)	H(17)	676 (9)	6880 (40)	2310 (30)	0.9 (6)
C(17)	544 (1)	6180 (6)	2957 (4)	H(17')	215 (10)	6410 (40)	2750 (30)	1.0 (6)

thus suggesting disordered arrangements. In order to find those O atoms of the disordered perchlorate group the difference Fourier map was calculated when R was 0.286. After six cycles of a full-matrix least-squares refinement for all non-hydrogen atoms, except two O, R decreased to 0.128. A difference Fourier map showed the two remaining O atoms and after the next six cycles of least-squares refinement R decreased to 0.105. At this stage, the anisotropic refinement for non-hydrogen atoms was carried out bringing the R and R_w values to 0.075 and 0.067 respectively for 1128 reflections. Subsequent difference Fourier maps showed the positions of all H atoms. Anisotropic least-squares refinement for non-hydrogen atoms with isotropic parameters for H was carried out for several cycles. The final R and R_w values were 0.035 and 0.030 respectively. The refinement was made by the full-matrix least-squares method. The weights used in minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ were $w = F_o/A$ if $F_o < A$ and $w = A/F_o$ if $F_o \geq A$, where A was equal to 100. Reflections were eliminated from matrix formation if their weights were less than 0.1, or in the last stage, less than 0.05.

The final positional and isotropic thermal parameters are listed in Table 1.*

All crystallographic calculations were carried out on a PDP-11/45 computer with the *Enraf-Nonius Structure Determination Package* (1975).

Discussion

(a) The molecular structure

A projection of the episparteine $N(16)$ -oxide sesquiperchlorate structure with atomic notation is presented in Fig. 2, the thermal ellipsoids at 50% probability in Fig. 3. As was predicted by Bratek-Wiewiórowska *et al.* (1974) the cation consists of a chair-chair *trans*-quinolizidine A/B system and a boat-chair *trans*-quinolizidine C/D system. Bond distances and angles are shown in Tables 2 and 3. The C—C bonds vary from 1.479 to 1.541 Å with a mean value of 1.511 Å. The shortest C—C bond, 1.479 Å, is between C(3) and C(4); the corresponding bond was also found to be the shortest C—C in sparteine $N(16)$ -oxide sesquiperchlorate (Srivastava & Przybylska, 1969). The deviations from Sutton's (1965) value of 1.537 Å probably relate to the accuracy of this refinement and the presence of disorder and may have little chemical significance. There are six N—C bonds with lengths varying from 1.419 to 1.528 Å with a mean value of 1.511 Å, which is in good agreement with the C—N bond length of 1.500 Å (Birnbaum, 1967). The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32627 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

C—C—C angles vary from 106.3 to 115.1° with a mean value of 111.9°. The smallest value, 106.3° at C(8), is due to the shorter C—N bonds which make the angle C(7)—C(8)—C(9) smaller. The same effect was observed in sparteine $N(16)$ -oxide sesquiperchlorate in all chair conformations reported by Srivastava & Przybylska (1969) and in α -isosparteine diperchlorate (Przybylska, 1974).

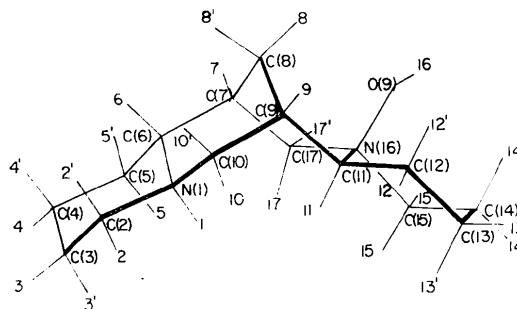


Fig. 2. A projection of episparteine $N(16)$ -oxide and the atomic notation.

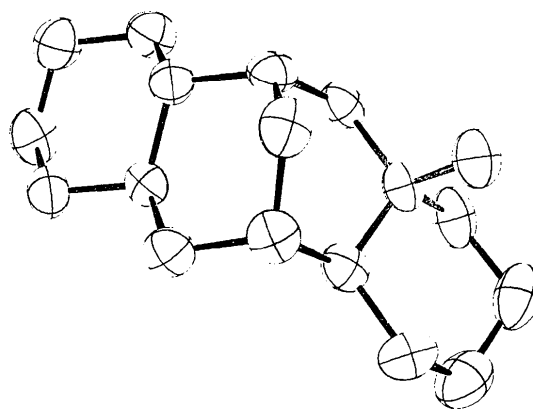


Fig. 3. The thermal ellipsoids at 50% probability of episparteine $N(16)$ -oxide (Johnson, 1976).

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

C(2)—C(3)	1.493 (5)	N(1)—C(6)	1.528 (4)
C(3)—C(4)	1.479 (6)	N(1)—C(10)	1.499 (4)
C(4)—C(5)	1.519 (5)	N(16)—C(11)	1.503 (4)
C(5)—C(6)	1.510 (4)	N(16)—C(15)	1.520 (5)
C(6)—C(7)	1.515 (5)	N(16)—C(17)	1.501 (4)
C(7)—C(8)	1.520 (5)	N(16)—O(9)	1.419 (3)
C(7)—C(17)	1.541 (6)		
C(8)—C(9)	1.498 (5)	Cl(2)—O(5)	1.296 (11)
C(9)—C(10)	1.524 (5)	Cl(2)—O(6)	1.391 (16)
C(9)—C(11)	1.538 (5)	Cl(2)—O(7)	1.377 (8)
C(11)—C(12)	1.507 (5)	Cl(2)—O(8)	1.371 (16)
C(12)—C(13)	1.506 (7)	Cl(1)—O(1)	1.434 (3)
C(13)—C(14)	1.522 (7)	Cl(1)—O(2)	1.425 (3)
C(14)—C(15)	1.494 (6)	Cl(1)—O(3)	1.414 (3)
N(1)—C(2)	1.515 (4)	Cl(1)—O(4)	1.434 (3)

The distances and angles in two perchlorate groups are listed in Tables 2 and 3. The perchlorate group with its Cl atom, Cl(2), lying on the twofold axes is disordered. The temperature factors for the four O atoms attached to this Cl are significantly higher than those for the O atoms of the second normal perchlorate group. O(6) which lies very close to the twofold axis shows rather large temperature factors. This can be explained by the fact that O(6) is the most loosely bound O of this ClO₄⁻. However, the distances and angles do not deviate from a tetrahedral arrangement. Since no occupancy factor was taken into consideration, not much physical significance should be given to those values. To describe better the disorder of this ClO₄⁻ further refinement on a larger set of data would be needed.

The C—H bonds vary from 0.83 to 1.09 Å with a mean value of 0.96 Å, and the H—C—H and C—C—H angles are in the range of 93 to 124° with a mean of 111°.

The torsion angles and the least-squares planes for the four rings are listed in Table 4. The torsion angles for all rings in the chair conformation are in good agreement with those reported by Przybylska (1974). Ring *B* is flattened by the N(1) atom, the torsion angles for the N(1)—C bonds are 46.4 and 47.4° and the distance for atom N(1) from the plane C(6), C(7), C(9), C(10) is 0.56 Å. Ring *C*, with the boat conformation, is also flattened, by N(16), and the torsion angles for the bonds C(17)—C(7) and C(9)—C(11) are 5.1 and 3.8°.

A short intramolecular contact of 2.785 (5) Å (Table 5) between O(9) and C(8) is caused by the boat conformation, which brings these atoms closer together.

(b) The crystal structure

The molecule is hydrogen bonded through O(1) (Fig. 4) with the N(1)—H(1)···O(1) distance 2.891 Å (Table 5). This hydrogen bonding probably has an influence on the reduction of the thermal vibration of the O(1) atom and also on the lengthening of the Cl(1)—O(1) bond (1.434 Å).

The molecules form dimers by strong hydrogen bonds, utilizing O(9), around the twofold axes. The distance between the two O atoms from the two molecules is extremely short (2.435 Å, Table 5) and is in very good agreement with the value of 2.479 Å found by Srivastava & Przybylska (1969) in sparteine *N*(16)-oxide sesquiperchlorate, which has an all-chair conformation. This value is also very close to Speakman's (1967) weighted mean of 2.446 (3) Å for symmetric hydrogen bonds. The H atom involved in the present structure was found in the difference map to be on the twofold axis, as required by the twofold symmetry. On the basis of the rather high temperature factor of this H and the O—H—O angle of 159°, it would be difficult to judge if this hydrogen bond is symmetric or not. The same phenomenon was reported by Srivastava & Przybylska (1969). It is interesting to notice from these two structures that the O atom in the *N*-oxide group shows a strong tendency to form a strong hydrogen bond with the equivalent atom of another molecule. This hydrogen-bond formation may be related to the appearance of twofold axes in the series of compounds with the sparteine ring systems.

It is also interesting that the perchlorate anions in structures of α -isosparteine diperchlorate (Przybylska, 1974), sparteine *N*(16)-oxide sesquiperchlorate

Table 3. Bond angles with their corresponding e.s.d.'s (°)

C(2)—N(1)—C(6)	110.6 (3)	C(13)—C(14)—C(15)	111.1 (3)
C(2)—N(1)—C(10)	110.6 (2)	C(14)—C(15)—N(16)	110.9 (3)
C(10)—N(1)—C(6)	114.2 (3)	C(11)—N(16)—C(15)	109.0 (3)
N(1)—C(2)—C(3)	110.7 (3)	C(15)—N(16)—C(17)	110.8 (3)
C(2)—C(3)—C(4)	113.6 (3)	C(11)—N(16)—C(17)	110.7 (3)
C(3)—C(4)—C(5)	110.3 (3)	C(11)—N(16)—O(9)	108.9 (2)
C(4)—C(5)—C(6)	111.8 (3)	C(15)—N(16)—O(9)	107.1 (3)
N(1)—C(6)—C(5)	108.5 (3)	C(17)—N(16)—O(9)	110.4 (2)
C(5)—C(6)—C(7)	116.5 (3)	C(7)—C(17)—N(16)	113.1 (3)
N(1)—C(6)—C(7)	110.4 (3)		
C(6)—C(7)—C(8)	108.2 (3)	O(5)—Cl(2)—O(6)	110.4 (1.6)
C(6)—C(7)—C(17)	114.8 (3)	O(5)—Cl(2)—O(7)	112.8 (1.1)
C(8)—C(7)—C(17)	111.8 (3)	O(5)—Cl(2)—O(8)	115.8 (1.0)
C(7)—C(8)—C(9)	106.3 (3)	O(6)—Cl(2)—O(7)	113.0 (2.2)
C(8)—C(9)—C(10)	108.5 (3)	O(6)—Cl(2)—O(8)	98.0 (1.6)
C(8)—C(9)—C(11)	113.8 (3)	O(7)—Cl(2)—O(8)	106.1 (1.2)
C(10)—C(9)—C(11)	112.0 (3)		
N(1)—C(10)—C(9)	112.1 (3)	O(1)—Cl(1)—O(2)	108.9 (2)
C(9)—C(11)—C(12)	115.2 (3)	O(1)—Cl(1)—O(3)	109.9 (2)
C(9)—C(11)—N(16)	111.6 (3)	O(1)—Cl(1)—O(4)	107.5 (2)
C(12)—C(11)—N(16)	110.7 (3)	O(2)—Cl(1)—O(3)	110.0 (2)
C(11)—C(12)—C(13)	113.1 (4)	O(2)—Cl(1)—O(4)	109.1 (2)
C(12)—C(13)—C(14)	109.7 (4)	O(3)—Cl(1)—O(4)	111.3 (2)

Table 4. *Torsion angles (°) and the least-squares planes*

Ring A		Ring C	
N(1)—C(2)—C(3)—C(4)	-54.5	C(9)—C(11)—N(16)—C(17)	-51.2
C(2)—C(3)—C(4)—C(5)	53.6	C(11)—N(16)—C(17)—C(7)	50.5
C(3)—C(4)—C(5)—C(6)	-56.0	N(16)—C(17)—C(7)—C(8)	5.1
C(4)—C(5)—C(6)—N(1)	58.4	C(17)—C(7)—C(8)—C(9)	-58.2
C(5)—C(6)—N(1)—C(2)	-58.3	C(7)—C(8)—C(9)—C(11)	58.0
C(6)—N(1)—C(2)—C(3)	56.3	C(8)—C(9)—C(11)—N(16)	-3.8
Ring B		Ring D	
N(1)—C(6)—C(7)—C(8)	-58.2	N(16)—C(11)—C(12)—C(13)	-55.9
C(6)—C(7)—C(8)—C(9)	69.2	C(11)—C(12)—C(13)—C(14)	53.5
C(7)—C(8)—C(9)—C(10)	-67.4	C(12)—C(13)—C(14)—C(15)	-54.7
C(8)—C(9)—C(10)—N(1)	56.4	C(13)—C(14)—C(15)—N(16)	58.9
C(9)—C(10)—N(1)—C(6)	-46.4	C(14)—C(15)—N(16)—C(11)	-59.6
C(10)—N(1)—C(6)—C(7)	47.4	C(15)—N(16)—C(11)—C(12)	57.1

Equations of the least-squares planes

$$\text{Ring A: } 0.1764x + 0.9505y - 0.2558z = 3.7613$$

$$\text{Ring B: } 0.0531x + 0.9707y - 0.2346z = 2.8891$$

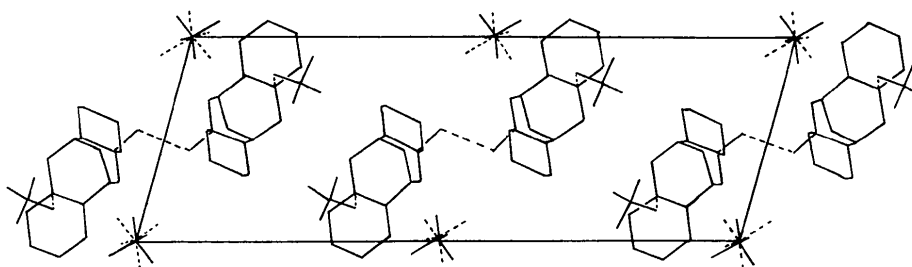
$$\text{Ring C: } 0.7359x + 0.2150y - 0.6421z = -0.0646$$

$$\text{Ring D: } 0.4046x + 0.4946y - 0.7692z = 0.1158$$

Deviations of atoms from the planes

Ring A	$\Delta(\text{Å})$	Ring B	$\Delta(\text{Å})$	Ring C	$\Delta(\text{Å})$	Ring D	$\Delta(\text{Å})$
N(1)	0.004	C(6)	-0.010	C(9)	-0.008	N(16)	-0.011
C(2)	-0.003	C(7)	0.011	C(11)	0.008	C(11)	0.011
C(4)	0.003	C(9)	-0.011	C(7)	0.008	C(14)	0.011
C(5)	-0.004	C(10)	0.010	C(17)	-0.008	C(13)	0.011
C(3)*	0.617	N(1)*	0.560	C(8)*	-0.708	C(12)*	-0.636
C(6)*	-0.703	C(8)*	-0.798	N(16)*	-0.613	C(15)*	0.690

* Atom excluded from the calculation of the plane.

Fig. 4. Unit-cell contents and molecular packing of episparteine *N*(16)-oxide sesquiperchlorate. Dashed lines represent hydrogen bonds.Table 5. *The intra- and intermolecular distances (Å) and angles (°)*

<i>x</i>	<i>y</i>	<i>z</i>	<i>x-z</i>	<i>x-y</i>	<i>y-z</i>	<i>x-y-z</i>	
O(9)...	H(8)—	C(8)	2.785	2.25	1.04	111	intra
O(1)...	H(1)—	N(1)	2.891	2.04	0.85	173	
O(9)...	H(16)...	O(9)	2.435	1.24	1.24	159	
O(8)...	H(6)—	C(6)	3.117	2.48	0.97	123	

whole structure of episparteine *N*(16)-oxide sesquiperchlorate. The thermal parameters are rather high and the molecule, including one perchlorate group, is more disordered than those in an all-chair conformation (Srivastava & Przybylska, 1969).

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References

(Srivastava & Przybylska, 1969) and in the present compound are disordered around the twofold axes.

The change of the ring C from a chair to a boat conformation seems to influence the stability of the

- BIRNBAUM, G. (1967). *Acta Cryst.* **23**, 526–535.
 BRATEK-WIEWIÓROWSKA, M. D., SKOLIK, Y., ŁANGOWSKA, K. & WIEWIÓROWSKI, M. (1974). *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **22**, 1025–1036.

- Enraf-Nonius Structure Determination Package* (1975). Manual edited by B. FRENZ & Y. OKAYA. Molecular Structure Corporation, College Station, Texas, USA.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- PRZYBYLSKA, M. (1974). *Acta Cryst.* B30, 2455–2459.
- SPEAKMAN, J. C. (1967). *Chem. Commun.* pp. 32–33.
- SRIVASTAVA, S. N. & PRZYBYLSKA, M. (1969). *Acta Cryst.* B25, 1651–1658.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. London: The Chemical Society.

Acta Cryst. (1977). B33, 3054–3059

The Crystal Structure of *tert*-Butyloxycarbonyl-L-prolyl-L-leucylglycine Hydrate

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Crystals of the title compound are monoclinic, $P2_1$, with $a = 10.036$ (1), $b = 18.142$ (2), $c = 6.191$ (1) Å, $\beta = 101.77$ (2)°, $Z = 2$. The final R is 0.037 for 1498 non-zero reflexions. The peptide molecule is folded into a β -turn of type I, in which Pro and Leu are at the corner and an intramolecular hydrogen bond is formed between NH of Gly and CO of the oxycarbonyl group. The folding is essentially the same as that found in some peptides having an X -Pro-Leu-Gly- sequence (X : any acyl group). Two common rules in the foldings of peptides are found: (i) the $NC^\alpha C'$ angle of the second residue, Pro in this peptide, in the four residues involved in the β -turn of type I is extraordinarily larger than the $NC^\alpha C'$ angles of the residues having other conformations; (ii) the most probable conformation of the Leu residues in peptides has a *trans* zigzag chain of $C^{\delta 1}-C^\gamma-C^\beta-C^\alpha-C'$.

Introduction

The X-ray studies have shown that, although only a few linear oligopeptides with three or more amino acid residues have so far been obtained as single crystals suitable for X-ray experiments, most of these peptides are folded into one of three structures, β -sheet, polyproline II type helix and β -turn. In particular, all those having the X -Pro-Leu-Gly- sequence (X : any acyl group) are folded into the β -turn conformation.

The crystal structures of a series of oligopeptides, benzyloxycarbonyl(*Z*)-Gly-Pro (Tanaka, Kozima, Ashida, Tanaka & Kakudo, 1977), *Z*-Gly-Pro-Leu (Yamane, Ashida, Shimonishi, Kakudo & Sasada, 1976), *Z*(*p*-Br)-Gly-Pro-Leu-Gly (Ueki, Ashida, Kakudo, Sasada & Katsube, 1969), *Z*(*o*-Br)-Gly-Pro-Leu-Gly-Pro (Ueki, Bando, Ashida & Kakudo, 1971) and *Z*-Gly-Pro-Leu-Gly-Pro (Bando, Tanaka, Ashida & Kakudo, 1973), have been determined, the last two pentapeptides having a substrate specificity for the enzyme collagenase. In this series each member has its own characteristic structural feature; the dipeptide has a β -sheet-type hydrogen bond, the tripeptide has a *cis* peptide bond at the Gly-Pro linkage, and the tetra- and

pentapeptides are folded at the Pro-Leu parts into the typical β -turn of type I [hereafter abbreviated as β -I turn (Venkatachalam, 1968)]. The structures of a few more peptides with a similar sequence have also been reported; *S*-benzyl-Cys-Pro-Leu-Gly-NH₂ (Rudko & Low, 1975) has a β -I turn at the Pro-Leu part, and Pro-Leu-Gly-NH₂ (Reed & Johnson, 1973) has a β -II turn with Leu-Gly at the corner.

The present peptide, *tert*-butyloxycarbonyl(Boc)-Pro-Leu-Gly, is therefore expected to fold into a β -I turn conformation. In this conformation, however, the C=O bond of Boc and the N-C $^\alpha$ bond of Pro should be *cis*, contrary to the *trans* arrangement found in all the Boc (or *tert*-amyloxycarbonyl)-Pro structures reported so far (Matsuzaki, 1974; Benedetti, Ciajolo & Maisto, 1974; Kartha, Ashida & Kakudo, 1974; Robert 1976).

Experimental

Crystal data

tert-Butyloxycarbonyl-L-prolyl-L-leucylglycine hydrate (needle crystal from an ethyl acetate-hexane solution), C₁₈H₃₁N₃O₇, $M_r = 401.46$. Monoclinic, $P2_1$,