The structure was solved in the $P1$ space group and *MISSYM* (Le Page, 1988) was used in order to detect a higher symmetry. The unit cell was ultimately found to be monoclinic.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: locally modified *NRC*-2 (Ahmed, 1968). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: BK1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Cyano-2-methylsparteine Perchlorate

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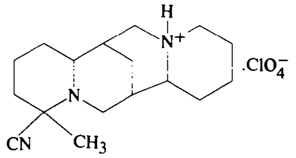
Abstract

The cation of the title salt, $C_{17}H_{28}N_3^+.ClO_4^-$, is built up of two quinolizidine moieties and has a *trans-A*/*B* and *cis-C*/*D* configuration. All four rings adopt chair conformations. The protonation that takes place at the N16 atom and subsequent creation of an intramolecular N$^+$—H···N hydrogen bond causes inversion of the N16 configuration compared with that of the free sparteine base. The perchlorate anion is disordered.

Comment

Sparteine is the most common among bis(quinolizidine) alkaloids isolated from lupine plants. Since the quinolizidine skeleton occurs in a number of natural compounds, sparteine is widely used as the model for studying the factors influencing the conformational/configurational changes. In this paper, we present the results of an X-ray structural analysis of 2-cyano-2-methylsparteine perchlorate, (I).



(I)

It has been shown that protonation of the free base is likely to cause inversion of configuration at the N16 atom. Generally, free bases of sparteine derivatives have a *trans* configuration (boat-chair conformation) of the *C*/*D* fragment, while the cations show a *cis*/chair-chair combination, *e.g.* sparteine (Skolik, Krueger & Wiewiórowski, 1970) and the sparteine cation (Borowiak, Bokii & Strutchkov, 1973), and 2-phenylsparteine (Boczoń, 1981; Katrusiak, Figas, Kałuski & Lesiewicz, 1989) and its cation (Kubicki, Borowiak & Boczoń, 1991). The *A*/*B* fragment was found to be *trans*/chair-chair in the free base as well as in the cation. Due to its thermodynamic stability, it is not susceptible to configurational/conformational changes.

The title compound is another example of this tendency. All four rings adopt chair conformations, with the asymmetry parameters (Duax & Norton, 1975) showing greater distortions from ideal values for the central *B* and *C* rings than for the terminal *A* and *D* ones. The *A*/*B* junction is *trans* [C2—N1—C6—C5 −57.3 (5) and C7—C6—N1—C10 of 51.9 (4)°], while the *C*/*D* junction is *cis* [C9—C11—N16—C17 49.8 (4) and C12—C11—N16—C15 51.8 (5)°]. The intramolecular N16$^+$—H16···N1 hydrogen bond [H16···N1 2.23 (4), N16···N1 2.841 (5) Å and N16—H16···N1 124 (3)°] stabilizes this system. This bond is signifcantly weaker that the one found in the 2-methylsparteine cation [N···N 2.710 (7) Å; Katrusiak, Hoser, Kałuski & Boczoń, 1980] and in the 2-phenylsparteine cation [2.742 (4) Å; Kubicki, Borowiak & Boczoń, 1991]. The protonation causes significant changes in the N—C bond lengths; the weighted mean values for atoms N1 and N16 are 1.490 (3) and 1.513 (5) Å, respectively. All other bond lengths and angles are typical, with a weighted mean value for the C_{sp^3}—C_{sp^3} bond length of 1.520 (2) Å.

The results of the IR spectral analysis of monocations of 2-methyl-, 2-phenyl-, 2-cyano-2-phenyl- and 2-cyano-2-methylsparteine show that an increase in the $\nu(N^+—H)$ band frequency is accompanied by an increase in the N···N distance, but there is no clear correlation. For further discussion, see Borowiak & Wolska (1995).

The methyl substituent occupies an equatorial position [C6—N1—C2—C22 177.0 (4) and C4—C3—C2—C22 −179.0 (5)°], as in the 2-methylsparteine cation, while the cyano group is in an axial position [C4—C3—C2—C21 62.1 (6) and C6—N1—C2—C21 −62.0 (4)°].

The perchlorate anion is disordered over two positions and takes part only in weak quasi-hydrogen-bond interactions with the cation. There are no other short intermolecular distances in the crystal structure.

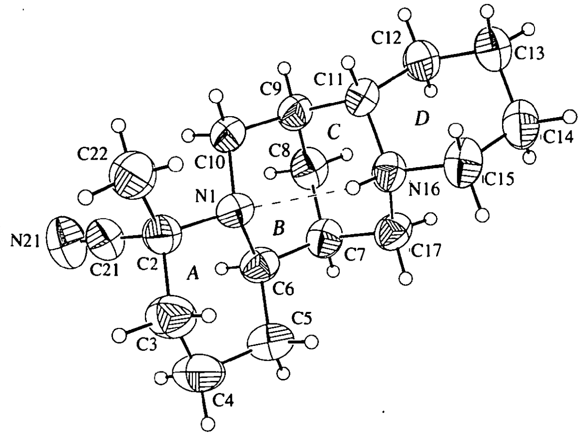


Fig. 1. Displacement ellipsoid representation of the title cation with the labelling scheme. The ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

Experimental

The synthesis of the title product has been described previously by Boczoń (1988). Crystals used for analysis were grown from methanol solution by slow evaporation.

Crystal data

$C_{17}H_{28}N_3^+.ClO_4^-$
$M_r = 373.87$
Orthorhombic
$P2_12_12_1$
$a = 9.8502 (11)$ Å
$b = 20.462 (2)$ Å
$c = 9.2056 (12)$ Å
$V = 1855.5 (3)$ Å^3
$Z = 4$
$D_x = 1.338$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 15 reflections
$\theta = 14.25–33.45°$
$\mu = 2.053$ mm^{-1}
$T = 293 (2)$ K
Prism
0.40 × 0.20 × 0.20 mm
Colorless

Data collection

Syntex $P2_1$ diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.93$, $T_{max} = 1.00$
2004 measured reflections
2004 independent reflections

1649 observed reflections $[I > 2\sigma(I)]$
$\theta_{max} = 70.13°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 11$
2 standard reflections monitored every 100 reflections
intensity decay: 3.3%

Refinement

Refinement on F^2
$R(F) = 0.056$
$wR(F^2) = 0.148$
$S = 1.055$
2004 reflections
245 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0844P)^2 + 1.0216P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0148 (15)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.04 (4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N1	1.0215 (4)	0.4193 (2)	0.6253 (4)	0.0453 (8)
C2	1.1078 (4)	0.4418 (2)	0.5017 (5)	0.0517 (10)
C21	1.1613 (5)	0.5084 (3)	0.5371 (6)	0.0611 (12)
N21	1.2002 (6)	0.5592 (2)	0.5699 (6)	0.0825 (14)
C22	1.0299 (6)	0.4445 (3)	0.3592 (5)	0.0671 (14)
C3	1.2292 (5)	0.3956 (3)	0.4845 (6)	0.0676 (13)
C4	1.3121 (6)	0.3882 (3)	0.6194 (7)	0.0744 (15)
C5	1.2192 (5)	0.3671 (2)	0.7437 (6)	0.0622 (12)
C6	1.1004 (4)	0.4134 (2)	0.7631 (5)	0.0493 (10)
C7	1.0079 (5)	0.3935 (2)	0.8887 (5)	0.0511 (10)
C8	0.8944 (5)	0.4434 (2)	0.9075 (5)	0.0583 (12)
C9	0.8116 (5)	0.4413 (2)	0.7684 (5)	0.0500 (10)
C10	0.9005 (5)	0.4619 (2)	0.6419 (5)	0.0520 (11)
C11	0.7435 (4)	0.3747 (2)	0.7455 (5)	0.0495 (10)
C12	0.6313 (5)	0.3598 (2)	0.8541 (6)	0.0603 (12)
C13	0.5719 (6)	0.2923 (3)	0.8340 (7)	0.0706 (14)
C14	0.6834 (6)	0.2411 (2)	0.8409 (6)	0.0653 (13)
C15	0.7912 (6)	0.2540 (2)	0.7287 (5)	0.0584 (11)
N16	0.8512 (4)	0.3213 (2)	0.7464 (4)	0.0457 (8)
C17	0.9453 (5)	0.3260 (2)	0.8752 (5)	0.0515 (10)
Cl1†	0.8002 (5)	0.6699 (2)	0.8234 (5)	0.0811 (11)
O1†	0.6800 (7)	0.6887 (3)	0.9046 (7)	0.106 (2)
O2†	0.8998 (8)	0.7094 (4)	0.9034 (9)	0.118 (3)
O3†	0.7945 (15)	0.6952 (4)	0.6901 (6)	0.163 (4)
O4†	0.8206 (11)	0.6054 (3)	0.8573 (12)	0.144 (4)
Cl1′‡	0.8365 (19)	0.6603 (9)	0.802 (2)	0.090 (6)
O1′‡	0.765 (2)	0.6028 (9)	0.746 (3)	0.088 (8)
O2′‡	0.717 (3)	0.6988 (12)	0.789 (5)	0.21 (3)
O3′‡	0.907 (3)	0.652 (2)	0.920 (2)	0.149 (15)
O4′‡	0.929 (3)	0.6662 (14)	0.691 (3)	0.124 (11)

† Occupancy of 0.81 (2). ‡ Occupancy of 0.19 (2).

Table 2. *Selected geometric parameters (Å, °)*

N1—C10	1.485 (5)	C7—C8	1.524 (6)
N1—C6	1.492 (5)	C8—C9	1.519 (7)
N1—C2	1.494 (6)	C9—C10	1.516 (6)
C2—C21	1.498 (7)	C9—C11	1.534 (6)
C2—C22	1.521 (7)	C11—C12	1.521 (6)
C2—C3	1.533 (6)	C11—N16	1.522 (5)

C21—N21	1.147 (6)	C12—C13	1.510 (7)
C3—C4	1.493 (8)	C13—C14	1.520 (7)
C4—C5	1.528 (8)	C14—C15	1.504 (7)
C5—C6	1.517 (6)	C15—N16	1.509 (5)
C6—C7	1.527 (7)	N16—C17	1.508 (5)
C7—C17	1.518 (6)		
C10—N1—C6	112.2 (3)	C8—C7—C6	110.2 (4)
C10—N1—C2	110.8 (3)	C9—C8—C7	106.2 (4)
C6—N1—C2	112.1 (3)	C10—C9—C8	109.2 (4)
N1—C2—C21	108.4 (4)	C10—C9—C11	113.2 (4)
N1—C2—C22	112.4 (4)	C8—C9—C11	112.1 (3)
C21—C2—C22	109.4 (4)	N1—C10—C9	112.3 (3)
N1—C2—C3	109.4 (4)	C12—C11—N16	111.0 (3)
C21—C2—C3	108.1 (4)	C12—C11—C9	113.9 (4)
C22—C2—C3	109.1 (4)	N16—C11—C9	109.3 (3)
N21—C21—C2	177.2 (5)	C13—C12—C11	112.6 (4)
C4—C3—C2	113.7 (4)	C12—C13—C14	110.2 (4)
C3—C4—C5	108.9 (4)	C15—C14—C13	111.1 (4)
C6—C5—C4	111.9 (4)	C14—C15—N16	111.3 (4)
N1—C6—C5	110.6 (4)	C17—N16—C15	112.5 (3)
N1—C6—C7	110.8 (3)	C17—N16—C11	112.8 (3)
C5—C6—C7	112.5 (4)	C15—N16—C11	112.4 (3)
C17—C7—C8	108.8 (4)	N16—C17—C7	111.8 (3)
C17—C7—C6	115.0 (4)		

H atoms were positioned riding on their parent C atoms, with fixed C—H distances and idealized angles, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The minor disorder component of the anion was initially restrained to have a similar geometry to the major component and was subsequently held fixed as a rigid group.

Data collection: *P*2₁ software. Cell refinement: *P*2₁ software. Data reduction: *PRADIR* (Jaskólski, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation* (Siemens, 1989). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Co-Crystallization of Stereoisomers of *N*,*N*′-Bis(2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide

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Abstract

X-ray analysis has revealed that two stereoisomers of the title compound, $C_{24}H_{28}N_2O_8$, co-crystallize in form (I). The unit cell of (I) contains equal numbers of the *N*,*N*′-bis(*trans*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide, (I*a*), and the *N*,*N*′-bis(*cis*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide, (I*b*), stereoisomers, each lying about crystallographic inversion centres. Fractional crystallization of the first mother liquor afforded crystals (II) containing only molecules of stereoisomer (I*a*), also with crystallographic inversion symmetry. The stereoisomer (I*a*) is Z-shaped in (I) and (II), whereas (I*b*) is maximally extended. In both (I) and (II), the molecules are linked about inversion centres by O—H···O hydrogen bonds.

Comment

The co-crystallization of enantiomers, in a 1:1 ratio, is relatively commonplace as evidenced by the popularity of such space groups as $P2_1/c$. In contrast, from the lack of reports in the literature, co-crystallization of other types of stereoisomers is much rarer. We were able to prepare serendipitously (see *Experimental* section) crystals of (I) which we subsequently showed to contain equal numbers of two different stereoisomers, *N*,*N*′-bis(*trans*-2-phenyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide, (I*a*) and *N*,*N*′-bis(*cis*-2-phenyl-5-hydroxymethyl-1,3-dioxan-