

2-Phenylsparteine N(16)-Oxide Monoperchlorate

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Abstract. $[(C_{21}H_{30}N_2O)H]^+ \cdot ClO_4^-$, $M_r = 426.9$, orthorhombic, $P2_12_12_1$, $a = 11.706$ (1), $b = 12.587$ (2) and $c = 14.837$ (1) Å, $V = 2186.3$ Å³, $Z = 4$, $D_m = 1.258$ g cm⁻³. $R = 0.066$ and $R_w = 0.076$ for 1835 reflections. The four rings in sparteine are in the chair conformation. There is a very strong *intra*-molecular hydrogen bond between O(16) and N(1), with a distance of 2.471 Å.

Introduction. This work is part of a series of X-ray studies on the conformations and structural properties of sparteine derivatives. The title compound is the first sparteine *N*-oxide with a phenyl group attached to C(2) to be studied by X-rays.

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Table 1. Fractional atomic coordinates ($\times 10^4$) for nonhydrogen atoms

	x	y	z
Cl	2952 (1)	3676 (1)	3363 (1)
N(1)	6692 (4)	3279 (3)	2518 (3)
N(16)	8742 (3)	2111 (4)	3273 (3)
C(2)	6110 (5)	3979 (5)	1849 (4)
C(3)	6625 (6)	5087 (5)	1863 (5)
C(4)	6575 (8)	5594 (5)	2797 (6)
C(5)	7221 (7)	4856 (5)	3447 (5)
C(6)	6611 (5)	3771 (5)	3451 (4)
C(7)	7179 (6)	3025 (5)	4139 (4)
C(8)	6470 (5)	1984 (5)	4157 (4)
C(9)	6694 (5)	1482 (5)	3249 (4)
C(10)	6195 (5)	2184 (4)	2497 (4)
C(11)	7951 (5)	1140 (4)	3142 (3)
C(12)	8254 (7)	250 (5)	3820 (5)
C(13)	9488 (8)	-62 (6)	3831 (6)
C(14)	200 (5)	921 (6)	4013 (5)
C(15)	1 (5)	1784 (6)	3320 (5)
C(17)	8436 (5)	2775 (5)	4082 (4)
C(18)	6167 (5)	3525 (5)	900 (4)
C(19)	7135 (6)	3133 (6)	527 (4)
C(20)	7178 (7)	2756 (6)	-354 (4)
C(21)	6237 (8)	2792 (6)	-861 (5)
C(22)	5243 (9)	3194 (8)	-533 (5)
C(23)	5197 (5)	3563 (7)	368 (4)
O(1)	3264 (6)	3522 (6)	2460 (3)
O(2)	1838 (4)	4010 (7)	3485 (5)
O(3)	3578 (8)	4487 (8)	3711 (7)
O(4)	3157 (11)	2782 (7)	3843 (5)
O(16)	8719 (3)	2737 (3)	2484 (2)

The crystals were provided by Professor M. Wiewiórowski of the Chemistry Department, A. Mickiewicz University, Poznań, Poland (Boczoń, Pieczonka & Wiewiórowski, 1976). A crystal of dimensions $0.18 \times 0.21 \times 0.26$ mm was used for the data collection on a CAD-4 diffractometer. The cell dimensions were obtained by a least-squares refinement of the setting angles of 22 reflections with θ within 28 – 41° . The θ – 2θ scan method was used to measure 4083 reflections in the hkl and $\bar{h}kl$ octants up to $2\theta = 122^\circ$ (Cu $K\alpha$). The symmetry-related reflections were averaged to give 1835 independent observable reflections.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined by a full-matrix

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters (Å²) for hydrogen atoms

	x	y	z	B_{iso}
H(1)	761 (4)	315 (4)	240 (3)	7.2 (1.2)
H(2)	522	406	204	8.0
H(3)	754	498	169	8.0
H(3')	617	557	138	8.0
H(4)	697	634	274	8.0
H(4')	568	554	297	8.0
H(5)	721	521	408	8.0
H(5')	807	471	312	8.0
H(6)	572	393	362	8.0
H(7)	706	343	480	8.0
H(8)	684	150	469	8.0
H(8')	558	223	424	8.0
H(9)	617	78	322	8.0
H(10)	642	181	186	8.0
H(10')	528	224	260	8.0
H(11)	809	83	244	8.0
H(12)	782	-45	369	8.0
H(12')	812	57	449	8.0
H(13)	976	-30	314	8.0
H(13')	971	-59	435	8.0
H(14)	1114	76	397	8.0
H(14')	998	128	465	8.0
H(15)	1051	251	349	8.0
H(15')	1026	149	266	8.0
H(17)	868	230	468	8.0
H(17')	893	351	405	8.0
H(19)	793	307	95	12.0
H(20)	796	247	-63	12.0
H(21)	617	241	-149	12.0
H(22)	439	339	-96	12.0
H(23)	443	376	70	12.0

least-squares program, *FLINUS*, a Brookhaven National Laboratory version of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\Sigma w(F_o - kF_c)^2$ with $w^{-1} = [\sigma_c^2 |F_o|^2 + (0.05 |F_o|^2)^2] / 2 |F_o|$, where σ_c is the deviation depending on counting statistics. Only H(1) on atom N(1) was located in a difference Fourier map; the other H positions were calculated assuming the usual C–H distance of 1.07 Å. The positional and thermal parameters for the H atoms were included in the structure-factor calculations but, except for H(1), were not refined. The positional and thermal (isotropic) parameters of this H atom were refined in the last two cycles. The final *R* and *R_w* for the 1835 reflections were 0.066 and 0.076 respectively.* The atomic scattering factors used for Cl, O, N and C were those of Doyle & Turner (1968) and for H those of Stewart, Davidson & Simpson (1965).

The atomic coordinates for the non-hydrogen atoms are given in Table 1 and the parameters for the H atoms in Table 2.

Discussion. A projection of the cationic part of the molecule with the atomic notation is shown in Fig. 1 and an *ORTEP* stereodrawing (Johnson, 1976) at 50% probability in Fig. 2. Bond distances and angles have been calculated using the values in Tables 1 and 2. The torsion angles around various single bonds have been calculated for the four groups in the sparteine moiety. The equations of various planes were obtained in the usual manner and atomic deviations calculated.*

The C–C bond distances vary from 1.498 to 1.550 Å, with a mean value of 1.527 Å, which agrees well with Sutton's (1965) values of 1.537 Å. The mean C–C–C angle excluding C(6)–C(7)–C(17) and C(10)–C(9)–C(11) is equal to 109.8°; the latter

angles are 120.8 and 116.6° respectively. Regular tetrahedral values for these angles would bring N(1) and O(16) too close together (Przybylska, 1974). The mean value of 1.502 Å for the C–N(1) bonds, involving a protonated N atom and three C(*sp*³) atoms agrees well with that of 1.500 Å reported by Birnbaum (1967). The three C–N(16) bonds are significantly longer, with a mean of 1.527 Å. Such C–N bond lengthening was also reported for lupanine *N*-oxide monopерchlorate (Kałuski, Gusiev, Struchkov, Skolik, Baranowski & Wiewiórowski, 1972).

The four rings in the sparteine skeleton are in chair conformations. The observed torsion angles show that rings *B*, *C* and *D* are flattened by the N atoms. As expected, the torsion angles around C–N(16) are small; for example a minimum value of 46.1° is found around C(11)–N(16). The phenyl ring is planar within one standard deviation and the dihedral angle between the phenyl and the C(2)–C(3)–C(5)–C(6) planes is 61.1°.

There is a very strong intramolecular hydrogen bond, N(1)–H(1)···O(16). The N···O distance is 2.471 (6) Å, and the angle around the H is 160.6 (3)°. This extremely short *intramolecular* hydrogen bond has an influence on the stability of the molecule and the puckering of the sparteine rings.

The bond lengths in ClO₄[−] range from 1.353 to 1.401 Å, with a mean of 1.373 Å. The angles in the

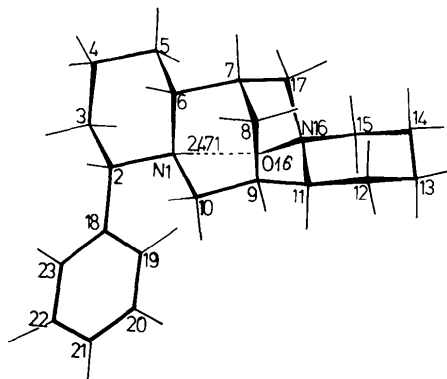


Fig. 1. A projection of 2-phenylsparteine *N*(16)-oxide monopерchlorate with the atomic notation.

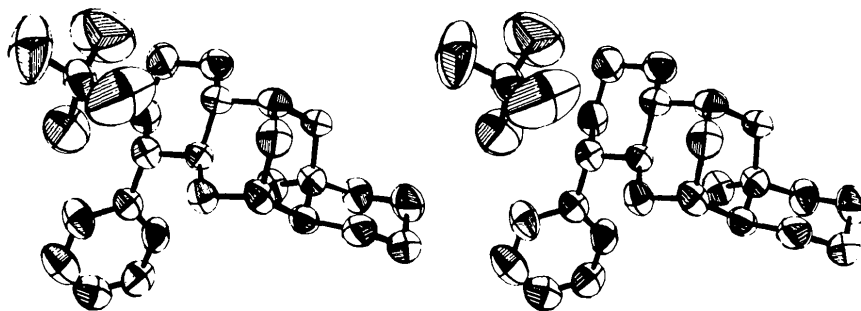


Fig. 2. *ORTEP* stereodrawing at 50% probability.

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, torsion angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32861 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

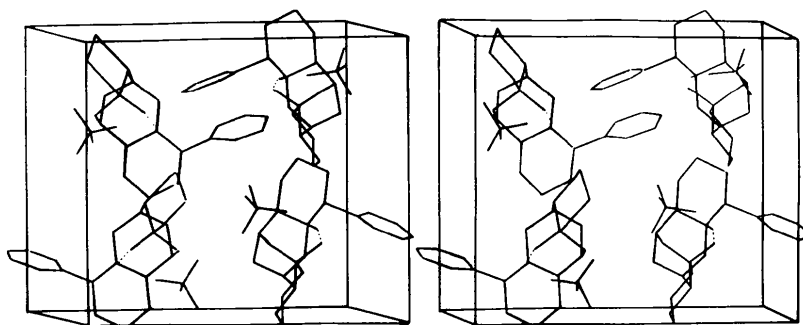


Fig. 3. The unit-cell contents and molecular packing. Dashed lines represent hydrogen bonds.

group are between 103.3 and 114.4° , with a mean of 109.4° . The perchlorate group shows relatively high thermal motion but no definite indication of disorder was found.

The molecular packing and the unit-cell contents are shown in Fig. 3 as a stereoview.

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Dihydroxy-5,6 Cannénone

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Abstract. $C_{22}H_{30}O_3$, orthorhombic, space group $P2_12_12_1$, $a = 24.136$ (7), $b = 20.541$ (5), $c = 7.548$ (2) Å, $Z = 8$. The structure was solved by direct methods. The parameters were refined by full-matrix least-squares calculations using 3544 observed reflexions. The H atoms were included in the calculation. The refinement converged at $R = 0.053$ and $R_w = 0.062$. The molecules show a planar conformation. The bonds and angles are in good agreement with expected values.

Introduction. L'étude du stéroïde SC-5233, décrite dans cet article, s'inscrit dans le cadre général d'un travail consacré à des stéroïdes antagonistes de l'aldostérone.

Les mesures d'intensités ont été effectuées sur un diffractomètre Philips PW 1100 en utilisant la radiation Mo $K\alpha$. Seules les intensités des réflexions ont été mesurées, le fond continu résultant d'une série unique de mesures effectuées en fonction de l'angle θ .

La structure de ce composé a été déterminée à l'aide