Table 5. *Hydrogen-bonded interactions*

The columns labelled *x′*, *y′*, *z′* give the symmetry of the acceptor atom *Y′*. Reference molecule in *x*, *y*, *z*.

X	H	*Y′*	*x′*	*y′*	*z′*	*X*···*Y′*	H···*Y′*	*X*–H···*Y′*
N	H(N*B*)	O	−*x*	1 − *y*	−*z*	2·95 Å	2·25 Å	130°
N	H(N*A*)	Cl	−*x*	−*y*	−*z*	3·07	2·19	164
O	H(O)	Cl	−*x*	−*y*	−*z*	3·06	2·24	170

form a network of hydrogen bonds running in the *b* direction. A molecule is connected in one direction directly to a centrosymmetrically related molecule through pairs of N—H···O bonds. In the opposite direction the molecules are held together by the intercalated Cl ions through pairs of N—H···Cl and O—H···Cl hydrogen bonds. The side chain of the molecule is in this way tightly locked through the hydrogen-bonding system, while the hydrophobic parts of the molecule, *i.e.* the indene ring system and the cyclopentane ring, are not taking part in any intermolecular bonding. This gives rise to the proportionately high thermal vibration of this part of the molecule. In the *a* and *c* directions there are no connexions other than van der Waals contacts holding the structure together. This explains the rod shape of the crystals with the long direction corresponding to the *b* axis. No distances violating ordinary packing requirements are found in the structure apart from the hydrogen bonds.

I wish to thank Professor Peder Kierkegaard and Mr Bengt Karlsson for placing the Philips 1100 diffractometer at Stockholm University at my disposal. My sincere thanks are also due to Professor Diego Carlström for his help and guidance and to Ingrid Hacksell for typing the manuscript. The investigation was supported by the Swedish Medical Research Council (Project No. 114) and Karolinska Institutets Forskningsfonder.

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Acta Cryst. (1978). B**34**, 3131–3134

Sparteine *N*(16)-Oxide Monoperchlorate

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(*Received* 22 *March* 1978; *accepted* 24 *May* 1978)

Abstract. $C_{15}H_{27}N_2O^+.ClO_4^-$, $M_r = 350{\cdot}9$, orthorhombic, $P2_12_12_1$, $a = 16{\cdot}089$ (2), $b = 12{\cdot}656$ (2), $c = 8{\cdot}314$ (2) Å, $V = 1687{\cdot}7$ Å^3, $Z = 4$, $D_c = 1{\cdot}38$ g cm^{-3}, $R = 0{\cdot}047$, $R_w = 0{\cdot}052$ for 1279 reflections. The four rings in the sparteine cation are in the chair conformation. There is a very strong intramolecular hydrogen bond between N(1) and O(16), of length 2·492 (6) Å.

Introduction. From the IR and NMR investigations (Wiewiórowski & Baranowski, 1967; Baranowski, Skolik & Wiewiórowski, 1964; Skolik, Łangowska & Wiewiórowski, 1972, 1975) and from p*Ka* values it is known that the sparteine *N*(16)-oxide cation ($I.H^+$) of the title compound has an all-chair conformation in both the solid and liquid states. The all-chair conformation of the cation $I.H^+$ is stabilized by a strong intramolecular hydrogen bond shown in Fig. 1. The chemical and spectroscopic results were confirmed by the X-ray analysis of sparteine *N*(16)-oxide sesquiperchlorate [$2I.3HClO_4$, Fig. 2(*a*)] (Srivastava & Przybylska,

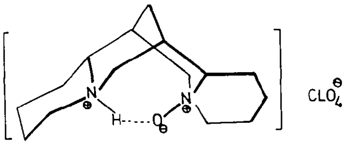
1969) and recently of 2-phenylsparteine *N*(16)-oxide monoperchlorate [II.$HClO_4$, Fig. 2(*b*)] (Małuszyńska & Okaya, 1977*b*).

The X-ray analysis of the title compound was undertaken to establish the geometry of the short intramolecular hydrogen bond and its influence on the structural details of the cation I.H^+. Furthermore, the comparison of the crystal and molecular structure of I.$HClO_4$ with the known structures of 2I.3$HClO_4$ and II.$HClO_4$ could explain the influence of the deprotonation of 2I.3$HClO_4$ on the shortening of the intramolecular hydrogen bond in I.$HClO_4$ (Skolik *et al.*, 1972, 1975). It was also interesting to find out whether the unexpected stronger basicity of II than I gives rise to significant changes in the geometry of this hydrogen bond existing in I.$HClO_4$ and II.$HClO_4$ (Boczoń, Pieczonka & Wiewiórowski, 1977).

The crystals were provided by Professor M. Wiewiórowski, who suggested this structure determination.

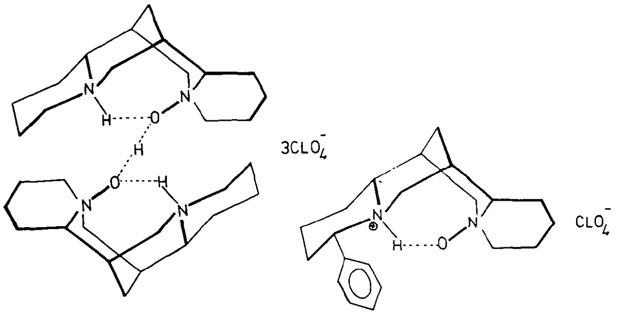
A crystal of dimensions 0·33 × 0·2 × 0·05 mm was used on the Syntex $P2_1$ diffractometer. The cell dimensions were obtained by a least-squares refinement of the setting angles of 15 reflections. The θ–2θ method was used to measure 1334 reflections up to 2θ = 114° (Cu $K\alpha$). 1279 reflections, for which $I > 1{\cdot}96\sigma(I)$, were considered as observed and included in the calculations.

The structure was solved by the heavy-atom method and refined by a full-matrix least-squares program *FMLS* from the XTL-System (Syntex, 1976). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_c^2(F)$, where σ_c is the standard deviation depending on counting statistics. Only 18 H atoms out of 27 were found on the difference Fourier map. The rest were calculated assuming the usual C—H distance of 1·07 Å and the tetrahedral angle of 109·5°. The positional and thermal parameters were included in the structure factor calculations but, apart from H(1), were not



I.$HClO_4$

Fig. 1. The conformation of the cation of sparteine *N*(16)-oxide monoperchlorate.



2I.3$HClO_4$ (*a*)

II.$HClO_4$ (*b*)

Fig. 2. The conformation of the cation of (*a*) sparteine *N*(16)-oxide sesquiperchlorate and (*b*) 2-phenylsparteine *N*(16)-oxide monoperchlorate.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *for nonhydrogen and* ($\times 10^3$) *for hydrogen atoms*

The isotropic thermal parameters are 5·8 (1·8) for H(1) and 6·0 Å^2 for all other H atoms.

	x	*y*	*z*
Cl	3364 (2)	7420 (1)	804 (2)
O(1)	4099 (4)	7258 (5)	−93 (9)
O(2)	2689 (4)	6909 (5)	71 (10)
O(3)	3248 (5)	8488 (5)	1002 (13)
O(4)	3527 (5)	6907 (6)	2306 (8)
O(16)	1075 (3)	7817 (4)	3573 (5)
N(1)	302 (3)	6117 (4)	3727 (6)
N(16)	1460 (3)	7776 (4)	5126 (6)
C(2)	−257 (4)	5737 (6)	2452 (9)
C(3)	230 (5)	5515 (6)	907 (8)
C(4)	904 (5)	4694 (6)	1213 (9)
C(5)	1495 (5)	5125 (5)	2572 (8)
C(6)	972 (4)	5353 (5)	4066 (8)
C(7)	1516 (4)	5747 (5)	5478 (7)
C(8)	965 (5)	5866 (5)	6962 (8)
C(9)	346 (4)	6729 (5)	6606 (8)
C(10)	−202 (4)	6393 (6)	5169 (8)
C(11)	771 (4)	7814 (5)	6398 (8)
C(12)	1116 (5)	8194 (6)	8032 (9)
C(13)	1612 (5)	9220 (6)	7945 (9)
C(14)	2347 (5)	9017 (6)	6768 (10)
C(15)	1985 (4)	8772 (6)	5118 (9)
C(17)	2005 (4)	6803 (5)	5230 (8)
H(1)	62 (4)	700 (6)	320 (8)
H(2)	−78	631	215
H(2′)	−51	508	289
H(3)	59	627	75
H(3′)	−24	525	13
H(4)	123	457	21
H(4′)	64	401	157
H(5)	182	579	216
H(5′)	193	459	287
H(6)	69	460	451
H(7)	196	520	559
H(8)	127	607	812
H(8′)	66	524	718
H(9)	−10	697	741
H(10)	−64	714	487
H(10′)	−53	575	545
H(11)	33	849	599
H(12)	156	765	867
H(12′)	58	822	865
H(13)	186	941	903
H(13′)	125	980	753
H(14)	268	959	652
H(14′)	268	846	733
H(15)	156	942	456
H(15′)	240	871	428
H(17)	239	685	420
H(17′)	240	692	619

refined. The positional and thermal (isotropic) parameters of this H atom were refined in the last few cycles of refinement. The final *R* and R_w for 1279 reflections were 0·047 and 0·052, respectively.* All calculations were carried out on a NOVA 1200 computer using programs included in the Syntex XTL/E-XTL *Structure Determination System* (Syntex, 1976).

The atomic coordinates and thermal parameters for all the atoms are given in Table 1.

Discussion. The X-ray analysis confirmed the all-chair conformation of the sparteine skeleton deduced from spectroscopic data and also the existence of a short intramolecular hydrogen bond between N(1) and O(16).

The bond distances and angles are given in Fig. 3(*a*) and (*b*). The C—C bond lengths vary from 1·511 to 1·541 Å with a mean value of 1·528 Å. The mean of the C—C—C angles is 109·9°, excluding angles C(6)—C(7)—C(17) and C(10)—C(9)—C(11). These two angles are 118·3 and 114·9° respectively, and show deviations from the tetrahedral arrangement similar to those in II.$HClO_4$ (Małuszyńska & Okaya, 1977*b*), α-isosparteine diperchlorate (Przybylska, 1974) and 2I.3$HClO_4$ (Srivastava & Przybylska, 1969), where all the rings in the sparteine cation are in the chair conformation. The mean value of 1·483 Å for the three C—N^+ bonds is 3σ shorter than the value of 1·500 Å cited by Birnbaum (1967) and the value of 1·502 Å found in sparteine *N*(16)-oxide with a phenyl ring attached to C(2). The C—N bonds, where the N forms the *N*-oxide, are longer (mean value of 1·525 Å). Such lengthening was reported in other sparteine *N*-oxide derivatives [in episparteine *N*(16)-oxide sesquiperchlorate (Małuszyńska & Okaya, 1977*a*); II.$HClO_4$ (Małuszyńska & Okaya, 1977*b*); 2I.3$HClO_4$ (Srivastava & Przybylska, 1969); lupanine *N*(16)-oxide monoperchlorate (Kałuski, Gusiev, Struchkov, Skolik, Baranowski & Wiewiórowski, 1972)].

The cation of the title compound consists of a chair–chair *trans*-quinolizidine *A*/*B* system and a chair–chair *cis*-quinolizidine *C*/*D* system. The torsion angles given in Fig. 3(*c*) show that ring *C* is the one most flattened by the N atom. As in II.$HClO_4$ the smallest torsion angle of 43·0° is observed around the C(11)—N(16) bond.

There is a strong intramolecular hydrogen bond, N(1)···O(16). The N···O distance is 2·492 (6) Å, [N(1)—H = 1·06 (7), H···O = 1·47 (7) Å] and the angle around the H atom is 160 (6)°. A similar hydrogen bond was found in II.$HClO_4$ [N(1)···O(16) = 2·471 (6) Å, ∠N(1)—H—O(16) = 160·6 (3)°] and in 2I.3$HClO_4$ [N(1)···O(16) = 2·626 (7) Å, ∠N(1)—H—O(16) = 142·1°]. The unexpected stronger basicity of II (Boczoń *et al.*, 1977) in comparison with that of I is reflected in the rather small changes in the length and geometry of the intramolecular hydrogen bonds existing in their perchlorate salts.

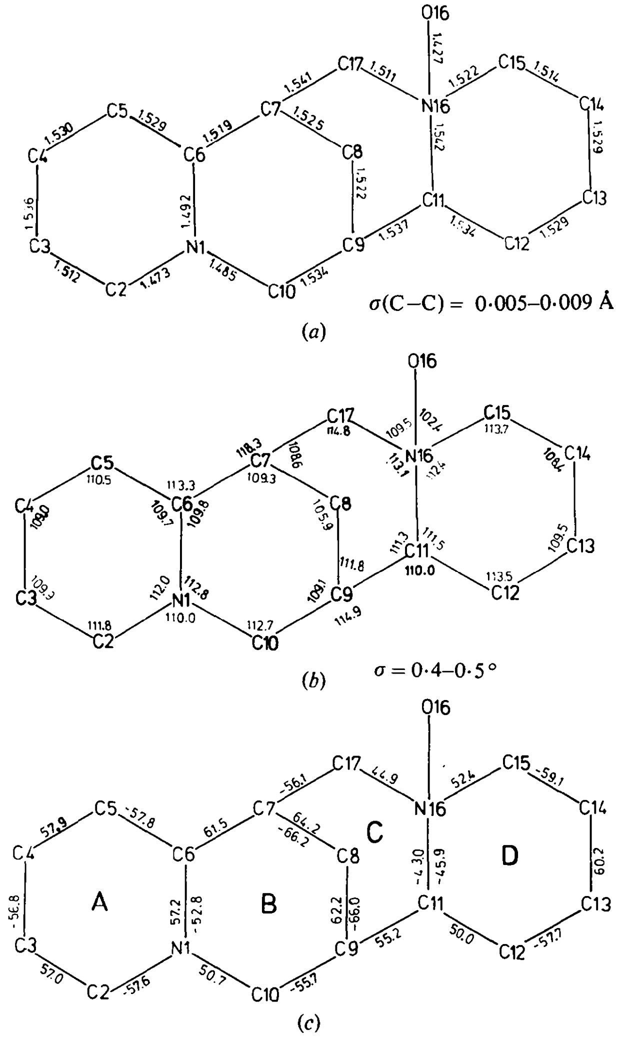


Fig. 3. A projection of the cation of sparteine *N*(16)-oxide monoperchlorate; (*a*) the bond lengths (Å), (*b*) the valence angles (°), (*c*) the endocyclic torsion angles (°).

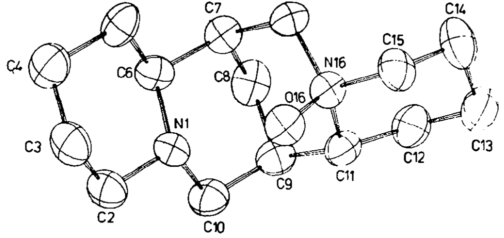


Fig. 4. *ORTEP* (Johnson, 1965) drawing of the cation at 50% probability.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33653 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The bond lengths in ClO_4^- range from 1·387 to 1·428 Å, with a mean of 1·409 Å and the angles in this group are between 104·4 and 113·7°, with a mean of 109·4°. The thermal parameters of the O atoms are high, but there are no indications of disorder.

A projection of the cation with the thermal ellipsoids at 50% probability is presented in Fig. 4.

Apart from van der Waals contacts, there are no other intermolecular interactions.

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Acta Cryst. (1978). B**34**, 3134–3137

The Structures of Anhydrous 1,5- and 2,6-Diazanaphthalene

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(*Received* 18 *November* 1977; *accepted* 5 *June* 1978)

Abstract. Both molecules have the formula $C_8H_6N_2$. 1,5-Diazanaphthalene: tetragonal, $P4_{1,3}2_12$ ($P4_12_12$ was chosen), $a = b = 7{\cdot}4079$ (3), $c = 24{\cdot}089$ (2) Å, $Z = 8$, $V = 1321{\cdot}9$ (1) Å^3, $D_x = 1{\cdot}308$ g cm^{-3}, weighted $R = 0{\cdot}041$, μ(Mo $K\alpha$) = 0·76 cm^{-1}. 2,6-Diazanaphthalene: monoclinic, $P2_1/c$, $a = 4{\cdot}8281$ (4), $b = 5{\cdot}5254$ (3), $c = 12{\cdot}0834$ (8) Å, $\beta = 94{\cdot}28$ (2)°, $Z = 2$, $V = 321{\cdot}46$ (4) Å^3, $D_x = 1{\cdot}345$ g cm^{-3}, weighted $R = 0{\cdot}042$, μ(Mo $K\alpha$) = 0·78 cm^{-1}. Data collection for both cases was carried out at 20°C. The X-ray proton geometries differ from those previously proposed [Lee & Gilson (1976). *Can. J. Chem.* **54**, 2783–2787] on the basis of NMR experiments.

Introduction. In our laboratory, the chemical and physical properties of diazanaphthalenes are studied [*e.g.* Huiszoon, van Hummel & van den Ham (1977)].

In this paper we report the X-ray analysis of those isomers that can be expected to be centrosymmetric: 1,5- and 2,6-diazanaphthalene. The dihydrates of these compounds have been investigated earlier by Brufani, Fedeli, Giacomello, Riccieri & Vaciago (1966). Our interest in the crystal structures of the anhydrous compounds originates from our objective to compare experimental heats of sublimation of all diazanaphthalenes with heats of sublimation calculated on the basis of intermolecular force fields.

Recently, Lee & Gilson (1976) reported an NMR study on the title compounds. From the NMR data and with the aid of the X-ray data of Brufani *et al.* (1966), these authors proposed proton geometries. These geometries differ from those derived by the present X-ray experiment.

1,5- and 2,6-diazanaphthalene were prepared following the instructions of Albert (1960) and Danieli & Ricci (1973) respectively. Both compounds were purified by passing them through a column packed with basic alumina. After thorough drying over molecular sieves, the solvent was evaporated and the residual compounds were sublimed *in vacuo*. The crystals were sealed in Lindemann-glass capillaries. Special dry

Table 1. *Details of data collection*

Compound	θ-range (°)	Scan width (°)	Scan time (s)	Number of reflexions measured
1,5-Diazanaphthalene	3·0–25·0	1·50	50	2792 ($k, l \le 0$)
2,6-Diazanaphthalene	2·5–35·0	1·60	40	3142 ($l \ge 0$)

Detector aperture in both cases: horizontal: 2°, vertical: 1°.