3,4-disubstituted sydnone derivatives (55–79°) are larger than those of the 3-substituted sydnone derivatives (2–39°). This dihedral angle can also be described as the torsional angle of C(1)—N(1) and C(7)—C(9). The larger torsional angle of 3,4-disubstituted sydnone derivatives can be understood as the steric effect from these two bulky groups on the neighboring atoms of the sydnone ring, namely N(1) and C(7).

The C(7)—C(9) bond lengths of compounds (1) and (2) [1·444 (2) and 1·453 (4) Å] are shorter than those of compounds (3) and (4) [1·465 (3) and 1·464 (4) Å]. The dihedral angles between the sydnone ring and the plane of the sp^2 orbitals of the double bond on the 4-substituent of the compounds (1) and (2) [sydnone ring and —C(7)—C(9)—O(3)—C(11)—, 2·5 (2)°; sydnone ring and —C(7)—C(9)—C(10)—N(3)—O(3)—, 12·7 (1)°] are also smaller than the corresponding angles of compounds (3) and (4) (49·8 and 28·0°).

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(±)-(5α,8α,9α)-2-Chloro-5,8,9,10-tetrahydro-5,9-methanobenzocycloocten-8-amine Hydrochloride Sesquihydrate

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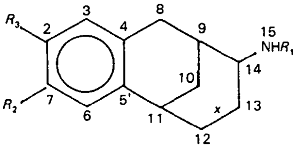
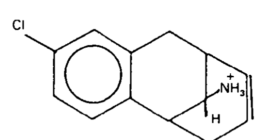
Abstract. $C_{13}H_{15}ClN^+.Cl^-.1\cdot5H_2O$, $M_r = 283\cdot20$, triclinic, $P\bar{1}$, $a = 19\cdot329\,(4)$, $b = 10\cdot316\,(2)$, $c = 7\cdot410\,(4)$ Å, $\alpha = 98\cdot803\,(4)$, $\beta = 100\cdot091\,(4)$, $\gamma = 87\cdot034\,(2)$°, $U = 1437\cdot1$ Å^3, $Z = 4$, $D_x = 1\cdot309$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot391$ mm^{-1}, $F(000) = 596$, $T = 293$ K, $R = 0\cdot051$ for 3325 reflexions. There are two independent cations in the asymmetric unit with very similar dimensions. The bicyclo[3.3.1]nonane system adopts a distorted sofa–sofa conformation. The structure contains hydrophobic and hydrophilic regions. In the latter there is extensive hydrogen bonding connecting the R—NH_3^+ groups, the anions and the water molecules.

Introduction. The title compound, known by the number Org 6997 (Savage, Sleigh & Clark, 1980), is of pharmacological interest in that it shows activity in animal models which are believed to be predictive for the treatment of disorders of the central nervous system. In particular it could be a useful agent for the treatment of depression.





(II)

(I) $R_1 = H_2^+\ (Cl^-)$, $R_2 = H$, $R_3 = Cl$, $x = C{=}C$.
(III) $R_1 = COMe$, $R_2 = OMe$, $R_3 = H$, $x = C{-}C$.

The sesquihydrate reported here has proved to be more suitable for drug formulation than the anhydrous material which was the subject of an earlier structure determination (Jones & Sheldrick, 1982). Structures have now been reported for the title cation (I), the isomer (II) (Jones, Kennard & Horn, 1979) and the related compound (III) (Murray-Rust, Murray-Rust & Middlemiss, 1982).

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Experimental. Crystals of the title compound were supplied by Organon Laboratories Ltd as rectangular prisms. Preliminary photographs suggested a triclinic system. Unit-cell dimensions were refined from 25 reflexions with $\theta \simeq 14°$ using an Enraf–Nonius CAD-4F diffractometer. Data were collected for one hemisphere of a crystal $0\cdot5 \times 0\cdot2 \times 0\cdot15$ mm, mounted in a Lindemann-glass capillary to a θ limit of 25°. 5194 reflexions scanned gave 5031 unique reflexions (internal consistency 0·015) of which 3325 with $F > 3\sigma(F)$ were used in the refinement. Ranges of indices $0 \leq h \leq 22$, $-12 \leq k \leq 12$, $-8 \leq l \leq 8$. The intensities of two standard reflexions were checked every hour, and the orientation of the crystal verified every 300 reflexions. Data were corrected for the Lorentz and polarization terms, and for a drift in intensity of 2% during data collection. A ψ-scan absorption correction was used. Correction factors ranged from 0·95 to 1·08.

All calculations performed on the Dundee University DEC 10 computer using *SHELX76* (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering parameters were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved with the direct-methods routine *EEES* and developed by conventional difference synthesis and least-squares refinement, first with isotropic and then anisotropic thermal parameters. Three ill-defined areas of electron density on the difference map were assigned as two water molecules with rather large thermal parameters, and a third water molecule divided between two adjacent sites. This model refined on F to convergence at R 0·051, with H atoms introduced at calculated positions except for the NH_3^+ groups and the water molecule O(41) for which the H atoms were located on a difference synthesis. The H atoms associated with O(42) and O(431)/O(432) were not included. All H atoms were given individual isotropic thermal parameters which were refined. Final refinement: 295 parameters in three blocks, $R = 0\cdot051$, $wR = 0\cdot067$, $w = 1\cdot4967/[\sigma(F)^2 + 0\cdot000768F^2]$, $(\Delta/\sigma)_{\text{mean}} = 0\cdot054$, $(\Delta/\sigma)_{\text{max}} = 1\cdot80$ for U_{iso} of H atom linked to N; all other $\Delta/\sigma < 0\cdot7$; max. difference peak = 0·49, min. = −0·025 e Å^{-3}.

Discussion. Atomic coordinates for the two independent cations of (I) with the anions Cl(16) and Cl(36) and the associated water molecules are given in Table 1,* with bond lengths in Table 2. The atom numbering is defined in formula (I). The cations are shown as a combined stereopair in Fig. 1. The two cations have very similar dimensions, the differences between corresponding bond lengths are all within 3σ and mostly within 1σ. The greatest variation in bond angles is found at C(9) and C(11) where differences of up to 5σ are observed. The conformations of the two cations are very similar (Fig. 2) whereas Jones & Sheldrick (1982) reported different conformations for the two unique cations in the anhydrous crystal, with their molecule 1 very close to the present structure. For the cyclohexene ring the mean absolute torsion-angle deviation from the idealized sofa conformation of Bucourt & Hainaut (1965) is 3° for each molecule in the present determination and the mean absolute deviation from molecule 1 of Jones & Sheldrick is 2° for each molecule. For the

Table 1. *Coordinates* ($\times 10^4$) *for non*-H *atoms and equivalent isotropic temperature factors* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
O(41)	8860 (2)	2512 (3)	1217 (5)	105 (1)
O(42)	9839 (2)	8393 (3)	3545 (7)	137 (1)
O(431)†	9542 (4)	9172 (6)	9452 (13)	98 (3)
O(432)†	298 (3)	1105 (6)	2378 (14)	103 (3)
Cl(1)	5981 (1)	4102 (1)	−592 (2)	80 (1)
C(2)	6332 (2)	4536 (3)	1752 (5)	57 (1)
C(3)	7030 (2)	4262 (3)	2347 (5)	50 (1)
C(4)	7323 (2)	4597 (3)	4196 (4)	45 (1)
C(5)	6909 (2)	5248 (3)	5421 (5)	50 (1)
C(6)	6203 (2)	5499 (4)	4798 (6)	65 (1)
C(7)	5910 (2)	5145 (4)	2972 (6)	68 (1)
C(8)	8084 (2)	4212 (3)	4837 (5)	55 (1)
C(9)	8408 (2)	4830 (3)	6796 (4)	47 (1)
C(10)	7865 (2)	4881 (4)	8075 (5)	57 (1)
C(11)	7253 (2)	5766 (4)	7384 (5)	58 (1)
C(12)	7516 (2)	7095 (3)	7347 (5)	59 (1)
C(13)	8162 (2)	7286 (3)	7091 (5)	52 (1)
C(14)	8686 (2)	6197 (3)	6823 (4)	47 (1)
N(15)	9321 (2)	6430 (3)	8341 (5)	55 (1)
Cl(16)	615 (1)	4496 (1)	7710 (1)	59 (1)
Cl(21)	4829 (1)	8234 (1)	5311 (2)	92 (1)
C(22)	5362 (2)	8561 (4)	7488 (6)	62 (1)
C(23)	5916 (2)	9398 (3)	7748 (5)	58 (1)
C(24)	6345 (2)	9632 (3)	9442 (5)	51 (1)
C(25)	6213 (2)	9025 (4)	10896 (5)	58 (1)
C(26)	5635 (2)	8216 (5)	10593 (7)	81 (1)
C(27)	5211 (2)	7981 (4)	8901 (7)	78 (1)
C(28)	6936 (2)	10582 (4)	9693 (6)	68 (1)
C(29)	7434 (2)	10696 (3)	11569 (5)	62 (1)
C(30)	7011 (2)	10577 (4)	13091 (6)	80 (1)
C(31)	6713 (2)	9211 (5)	12717 (5)	75 (1)
C(32)	7298 (3)	8195 (4)	12630 (5)	72 (1)
C(33)	7902 (2)	8419 (3)	12128 (5)	61 (1)
C(34)	8042 (2)	9704 (3)	11587 (5)	54 (1)
N(35)	8686 (2)	10283 (3)	12848 (5)	60 (1)
Cl(36)	8610 (1)	1119 (1)	7156 (1)	74 (1)

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

† Disordered water: occupancies 0·48 (1) and 0·52 (1) for O(431) and O(432), respectively.

Table 2. *Bond lengths* Å *of Org* 6997 *for non*-H *atoms*

	Molecule 1	Molecule 2*		Molecule 1	Molecule 2*
Cl(1)—C(2)	1·748 (4)	1·751 (4)	C(9)—C(10)	1·527 (5)	1·527 (7)
C(2)—C(3)	1·373 (5)	1·378 (5)	C(10)—C(11)	1·520 (5)	1·518 (7)
C(3)—C(4)	1·386 (4)	1·374 (5)	C(5)—C(11)	1·518 (4)	1·508 (5)
C(4)—C(5)	1·388 (5)	1·392 (6)	C(11)—C(12)	1·493 (5)	1·505 (6)
C(5)—C(6)	1·387 (5)	1·396 (6)	C(12)—C(13)	1·324 (6)	1·326 (7)
C(6)—C(7)	1·373 (6)	1·367 (6)	C(13)—C(14)	1·487 (5)	1·493 (5)
C(7)—C(2)	1·382 (6)	1·362 (7)	C(14)—C(9)	1·531 (5)	1·516 (5)
C(4)—C(8)	1·517 (5)	1·512 (5)	C(14)—N(15)	1·513 (4)	1·510 (5)
C(8)—C(9)	1·532 (4)	1·538 (5)			

* Molecule 2 has atom numbers C(20+n).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43674 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pseudo-cyclohexene ring C(4), C(5), C(11), C(10), C(9), C(8), the mean absolute deviations from the previous structure are 3 and 4°. This ring is mid-way between the ideal sofa and half-chair conformations. The conformation at C(14) can be described as *exo*. A model of the molecule has sufficient flexibility to allow the torsion angle C(8)—C(9)—C(14)—N(15) to adopt any value between *ca* 130° where the bonds to C(9) and C(14) and to C(11) and C(12) are almost eclipsed and *ca* 170° where these bonds are staggered. The observed values, 147·9 (3) and 147·3 (2)°, lie at the mid-point of this range making the 1,4-cyclooctadiene ring C(4)—C(5)—C(11)—C(12)—C(13)—C(14)—C(9)—C(8) symmetrical about the plane C(9)—C(10)—C(11) and (apart from bond lengths) symmetrical about the plane C(3)—C(4)—C(10)—C(13) in a simple dihedral conformation. This conformation appears to give the best compromise to avoid eclipsed geometry among the many bonds in the molecule.

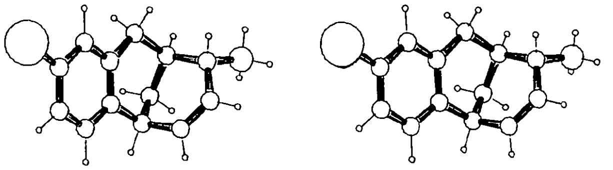

Fig. 1. Org 6997. Stereodiagram of cation 1 (left) and cation 2 (right), to show minor conformational differences.

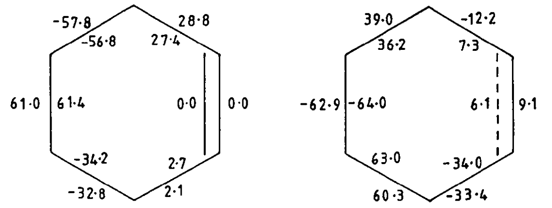

Fig. 2. Torsion angles (°) of the cyclohexene and 'pseudo-cyclohexene' (containing one aromatic bond) rings; values for molecule 1 shown outside the rings, molecule 2 inside. E.s.d.'s are 0·2–0·3°.

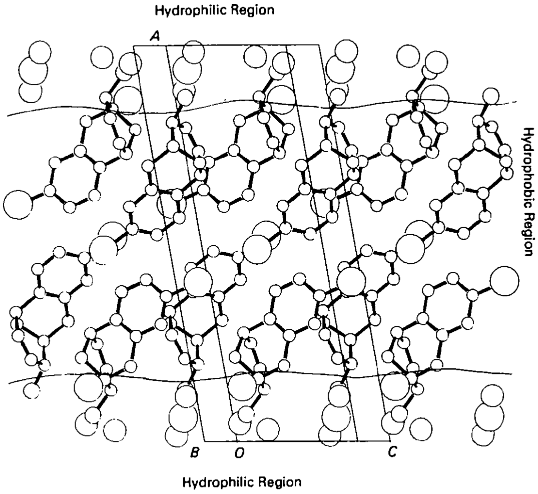

Fig. 3. The packing arrangement viewed along the *b* orthogonal axis. Hydrophilic regions contain the hydrogen bonding and hydrophobic regions contain the cations.

Comparison of (I), (II) and (III) shows several differences. The double bond makes the conformation of the central bicyclo[3.3.1]nonane system distorted-[C(4)]—sofa[C(13)] in (I) and distorted[C(4)]—half-chair[C(13)] in (II) whereas (III) adopts sofa[C(4)]—chair[C(13)]. The distorted ring in (II) is very similar to that in (I), mean absolute torsion-angle deviation 3°. The methylene group at C(13) in (III) increases the crowding of the ring system which is relieved by increasing the dihedral angle between the planes C(7), C(2), C(3), C(4), C(5), C(6) and C(9), C(11), C(12), C(14) from 101·6 (4) and 106·2 (6)° in (I) to 111·5° in (III). At C(14) the N atom is *exo* in (I) and *endo* in (III). Examination of a model indicates that (III) is much less flexible than (I).

The structure of (I) contains no ion pairing. There is very extensive hydrogen bonding, involving the chloride ions Cl(16) and Cl(36), water molecules O(41), O(42), O(431), O(432) and the R—NH_3^+ groups N(15) and N(35). Since the H atoms of several water molecules were not located, the existence of individual hydrogen bonds has not been proved. Fig. 3 shows that the crystal is made up of hydrophobic regions separated by sheets of hydrogen bonding parallel to the *bc* plane and occupying the region $-0{\cdot}1 < a < 0{\cdot}1$, to give a structure resembling infinite planar micelles. This hydrogen bonding may well be responsible for the smaller thermal parameters and standard deviations of coordinates in the present structure. The isotropic thermal parameters ($\AA^2 \times 10^3$) for Cl(1) in the present structure are 80 (1) and 92 (1) compared with 115 (1) and 162 (2) in the earlier report. The average C and N thermal parameters are 55 (1) and 66 (1) compared with 65 (3) and 78 (3).

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