

# 11-*exo*-Ammonio-8-chlorobenzo[*b*]bicyclo[3.3.1]nona-2,6a(10a)-diene Chloride\*

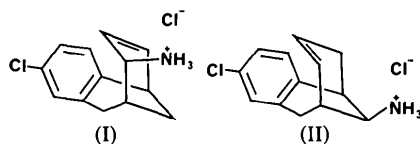
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**Abstract.**  $C_{13}H_{15}ClN^+ \cdot Cl^-$ ,  $M_r = 256.18$ , orthorhombic,  $Pbca$ ,  $a = 9.376$  (4),  $b = 16.353$  (8),  $c = 35.111$  (15) Å,  $U = 5383$  Å<sup>3</sup>,  $Z = 16$ ,  $D_x = 1.264$  Mg m<sup>-3</sup>,  $\mu$ (Cu  $K\alpha$ ) = 2.3 mm<sup>-1</sup>. Final  $R = 0.071$  for 1982 unique observed reflections. The two cations in the asymmetric unit display markedly different conformations.

**Introduction.** The title compound (I), also known by the trivial name Org.6997, is an inhibitor of neuronal uptake of 5-hydroxytryptamine (serotonin). It is isomeric with Org.6582 (II), the structure of which we have already reported (Jones, Kennard & Horn, 1979).



\* Systematic name: (5*R*\*,8*R*\*,9*S*\*)-(2-chloro-5,8,9,10-tetrahydro-5,9-methanobenzo[*b*]cycloocten-8-yl)ammonium chloride.

Rectangular thin plates were obtained from formic acid/diisopropyl ether. Data collection: Nonius CAD-4 diffractometer, monochromated Cu  $K\alpha$  radiation, crystal dimensions 0.6 × 0.4 × 0.05 mm,  $2\theta_{max} = 120^\circ$ , 4000 unique reflections, 1983 observed [ $F > 4\sigma(F)$ ]. No absorption correction was applied.

Initial attempts to solve the structure using the program *SHELXTL* were unsuccessful because of the very small number of phase relations involving reflections with odd  $k$ . Even when seven odd- $k$  reflections were forced into the starting set, no sensible  $E$  map was obtained. During the solution process the program selects a set of *ca* 200 reflections linked by strong phase relations (and then refines their phases); in the automatic mode, this led to the suppression of odd- $k$  reflections. To obviate this problem two tricks were used. First, a high  $E$  cutoff (1.8) was used while selecting the reflections for phase refinement, thus necessitating the rejection of fewer reflections. Secondly, the program was forced to pick at least 60% odd- $k$  reflections. The best resulting  $E$  map showed 31 of the 32 non-H atoms. Refinement proceeded to  $R = 0.16$

Table 1. Atom coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	Molecule 1				Molecule 2			
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ *	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ *
Cl(1)	2710 (2)	8256 (1)	2899 (1)	64 (1)				
Cl(2)	4185 (2)	9228 (1)	7162 (1)	69 (1)				
C(1)	2391 (8)	7468 (4)	1173 (2)	72 (3)	4323 (8)	10083 (3)	8866 (2)	73 (3)
C(2)	3989 (8)	7565 (4)	1192 (2)	65 (3)	5177 (8)	9835 (5)	8529 (2)	78 (3)
C(3)	4610 (7)	7850 (4)	1490 (2)	56 (2)	4675 (7)	9477 (4)	8225 (2)	66 (3)
C(4)	3849 (6)	8120 (4)	1843 (2)	49 (2)	3156 (7)	9247 (4)	8194 (2)	62 (2)
C(5)	2225 (7)	8013 (4)	1826 (2)	62 (3)	2368 (7)	9320 (4)	8572 (2)	66 (3)
C(6)	1444 (7)	8782 (4)	1687 (2)	66 (3)	2707 (8)	8590 (5)	8839 (2)	81 (3)
C(6a)	1442 (6)	8892 (4)	1263 (2)	56 (2)	3698 (8)	8753 (4)	9162 (2)	68 (3)
C(7)	1035 (7)	9650 (4)	1108 (2)	65 (3)	3846 (9)	8184 (5)	9458 (2)	89 (3)
C(8)	946 (8)	9751 (4)	729 (2)	70 (3)	4736 (11)	8319 (6)	9749 (2)	99 (4)
C(9)	1254 (8)	9142 (5)	478 (2)	79 (3)	5581 (11)	9012 (7)	9765 (2)	109 (5)
C(10)	1699 (8)	8399 (4)	623 (2)	73 (3)	5425 (9)	9578 (6)	9480 (2)	94 (3)
C(10a)	1789 (7)	8276 (4)	1011 (2)	59 (2)	4518 (8)	9465 (4)	9181 (2)	71 (3)
C(11)	1833 (8)	7303 (4)	1564 (2)	82 (3)	2752 (7)	10136 (4)	8756 (2)	71 (3)
N	4468 (5)	7688 (3)	2178 (1)	54 (2)	2439 (6)	9759 (3)	7886 (1)	66 (2)
Cl	445 (3)	10707 (1)	545 (1)	115 (1)	4872 (4)	7613 (2)	10119 (1)	162 (2)

\* Equivalent isotropic  $U$  calculated from anisotropic  $U$ .

Table 2. Bond lengths (Å)

	Molecule 1	Molecule 2
C(1)—C(2)	1.508 (12)	1.485 (12)
C(1)—C(10a)	1.544 (10)	1.510 (11)
C(1)—C(11)	1.495 (11)	1.525 (11)
C(2)—C(3)	1.284 (10)	1.307 (12)
C(3)—C(4)	1.497 (9)	1.477 (10)
C(4)—C(5)	1.534 (10)	1.526 (10)
C(4)—N	1.492 (8)	1.523 (9)
C(5)—C(6)	1.533 (11)	1.551 (11)
C(6)—C(6a)	1.498 (10)	1.490 (11)
C(6a)—C(7)	1.408 (11)	1.402 (11)
C(7)—C(8)	1.344 (11)	1.337 (13)
C(8)—C(9)	1.359 (12)	1.383 (16)
C(6)—Cl	1.755 (9)	1.743 (11)
C(10)—C(9)	1.382 (12)	1.373 (14)
C(10)—C(10a)	1.380 (11)	1.362 (12)
C(10a)—C(6a)	1.380 (10)	1.397 (11)
C(11)—C(5)	1.527 (11)	1.526 (11)

Table 3. Bond angles (°)

	Molecule 1	Molecule 2
C(2)—C(1)—C(10a)	106.8 (6)	109.6 (7)
C(2)—C(1)—C(11)	109.1 (7)	109.7 (7)
C(10a)—C(1)—C(11)	111.4 (7)	109.9 (7)
C(1)—C(2)—C(3)	121.6 (7)	125.4 (8)
C(2)—C(3)—C(4)	124.4 (7)	121.5 (8)
C(3)—C(4)—C(5)	114.1 (6)	112.5 (7)
C(3)—C(4)—N	109.2 (6)	109.8 (6)
C(5)—C(4)—N	111.3 (6)	111.2 (6)
C(4)—C(5)—C(6)	113.1 (6)	111.6 (7)
C(4)—C(5)—C(11)	110.4 (6)	108.8 (6)
C(6)—C(5)—C(11)	108.5 (6)	111.6 (7)
C(5)—C(6)—C(6a)	114.5 (7)	116.8 (7)
C(6)—C(6a)—C(7)	119.4 (7)	120.5 (8)
C(6)—C(6a)—C(10a)	123.3 (7)	121.9 (7)
C(7)—C(6a)—C(10a)	117.3 (7)	117.6 (8)
C(6a)—C(7)—C(8)	120.6 (7)	121.2 (9)
C(7)—C(8)—C(9)	122.6 (8)	121.7 (9)
C(7)—C(8)—Cl	119.2 (7)	120.4 (9)
C(9)—C(8)—Cl	118.2 (7)	118.0 (8)
C(8)—C(9)—C(10)	118.0 (8)	117.4 (9)
C(9)—C(10)—C(10a)	120.7 (8)	122.5 (10)
C(1)—C(10a)—C(6a)	118.4 (7)	117.1 (7)
C(1)—C(10a)—C(10)	120.7 (7)	123.3 (8)
C(6a)—C(10a)—C(10)	120.8 (7)	119.6 (8)
C(1)—C(11)—C(5)	109.3 (7)	106.6 (7)

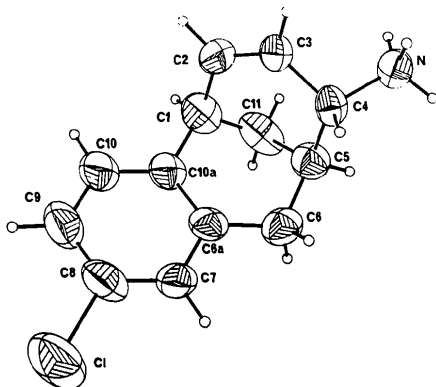


Fig. 1. Thermal ellipsoid (50%) plot of molecule 1, showing the atom-labelling scheme.

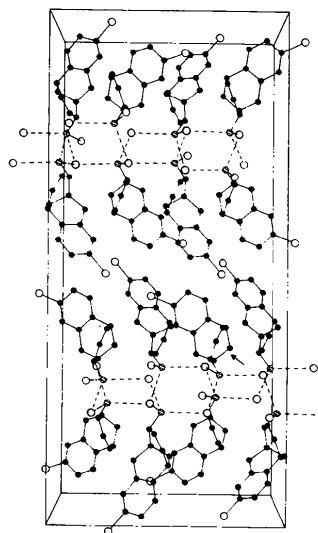
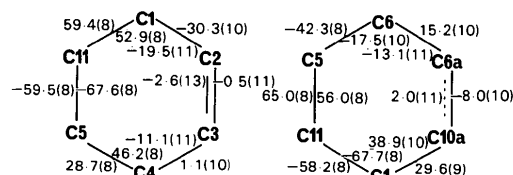
Fig. 2. Packing diagram viewed down *a* (H atoms omitted). N...Cl hydrogen bonds are indicated by broken lines. Open circles, Cl; filled circles, C; dashed circles, N. Molecules 1 and 2 may be clearly distinguished by the sofa form of the cyclohexene ring in 1 (arrowed).

Fig. 3. Torsion angles (°) of the cyclohexene and 'pseudo-cyclohexene' (containing one aromatic bond) rings; values for molecule 1 shown outside the rings, molecule 2 inside; sign convention as defined by Klyne &amp; Prelog (1960).

(isotropic), 0.09 (anisotropic) at which point all but four H atoms were located by a difference synthesis. In the final stages of refinement C—H bond lengths and H—C—H angles were fixed at 0.96 Å and 109.5°; an overall isotropic temperature factor [refining to 0.078 (4) Å<sup>2</sup>] was employed for H atoms; and one reflection clearly in error was omitted. The final  $R_w$  was 0.072, with a corresponding  $R$  of 0.071. The weighting scheme was  $w^{-1} = \sigma^2(F) + 0.0015F^2$ . Final atomic coordinates are given in Table 1, with derived bond lengths and angles and selected torsion angles in Tables 2 and 3 and Fig. 3, respectively.\* Diagrams of the structure are given in Figs. 1 and 2.

\* Lists of structure factors, anisotropic temperature factors, H-atom coordinates, least-squares planes, N...Cl hydrogen bonds and a complete list of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38015 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** Fig. 1 shows the high thermal motion (especially of the aromatic ring) of molecule 2. Because of this thermal motion, and also because of the rather small number of reflections collected from a weakly diffracting crystal, the precision of molecular dimensions is rather low. Despite this, a highly significant difference in conformation between the two molecules is observed (Figs. 2 and 3). The C(1)–C(2)–C(3)–C(4)–C(5)–C(11) rings show sofa and half-chair conformations for molecule 1 and 2 respectively [mean absolute deviations from the ideal values of Bucourt & Hainaut (1965) are 2 and 4°]. The C(6)–C(6a)–C(10a)–C(1)–C(11)–C(5) rings are not close to ideal conformations, for molecule 1 being between half-chair (7°) and sofa (9°), for molecule 2 between sofa (9°) and 1,3-diplanar (9°) (mean absolute deviations in parentheses). The pharmacological implications of this will be discussed elsewhere.

The packing diagram (Fig. 2) shows a striking similarity to Org.6582 (Jones *et al.*, 1979), with a belt of anions running parallel to **b**. Six short N···Cl contacts (3.15–3.25 Å), interpreted as N–H···Cl hydrogen bonds, are observed.

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### 3,3,6,6-Tetramethoxy-1,2,4,5-tetramethyl-1,4-cyclohexadiene

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**Abstract.** C<sub>14</sub>H<sub>24</sub>O<sub>4</sub>, monoclinic, *C*2/*c*, *a* = 14.043 (3), *b* = 11.506 (2), *c* = 8.851 (3) Å, β = 104.94 (2)°, *V* = 1381.8 (6) Å<sup>3</sup>, *D<sub>x</sub>* = 1.232 Mg m<sup>-3</sup>, *Z* = 4. For the 3055 data measured at *ca* 90 K the final *R* is 0.072, being 0.046 for the 2231 reflections with *I* > 2σ(*I*). The conformation of the dimethyl acetal groups is *anti,anti* rather than that favoured by the anomeric effect. The O–C–O angle is 99°.

**Introduction.** The geometries of acetals, in particular the coupling between torsion angles, bond lengths and bond angles, are of especial interest in connection with the anomeric effect (Szarek & Horton, 1979; Tvaroška & Bleha, 1979). Of the possible spatial arrangements of the acetal group, the *anti,anti* arrangement is the rarest, having been hitherto encountered only in molecules in which the acetal group is adjacent to C atoms bearing a high density of negative charge (Jackson–Meisenheimer complexes: Destro, Gramaccioli & Simonetta, 1968; Ueda, Sakabe, Tanaka & Furusaki, 1968; Messmer &

Palenik, 1971) or is conformationally fixed by being part of a bicyclic system (Norrestam, Bock & Thøgersen, 1981; Zheng, Qin, Gu & Zheng, 1981). The discovery that the *anti,anti* conformation can be realized in quinone bisacetals by appropriate substitution of the 1,4-cyclohexadiene ring (Jaroszewski, 1979) provided us with an opportunity of investigating the geometry of the *anti,anti* dimethyl acetal group in a relatively nonpolar environment (Ettlinger, Jaroszewski, Nørskov-Lauritsen & Watson, 1982). This paper describes the crystal structure of one such compound, 3,3,6,6-tetramethoxy-1,2,4,5-tetramethyl-1,4-cyclohexadiene.

