C(1)—C(6)—C(5)	120.5 (3)	C(13)—N(12)—C(17)	109.9 (2)
C(6′)—C(1′)—C(2′)	119.9 (2)	C(13)—N(12)—S(11)	114.2 (2)
C(6′)—C(1′)—N(10)	120.4 (2)	C(17)—N(12)—S(11)	113.4 (2)
C(2′)—C(1′)—N(10)	119.3 (2)	N(12)—C(13)—C(14)	109.2 (3)
C(3′)—C(2′)—C(1′)	117.8 (3)	O(15)—C(14)—C(13)	112.0 (3)
C(3′)—C(2′)—C(7′)	120.8 (3)	C(14)—O(15)—C(16)	109.4 (2)
C(1′)—C(2′)—C(7′)	121.4 (3)	O(15)—C(16)—C(17)	111.5 (3)
C(4′)—C(3′)—C(2′)	122.3 (3)	N(12)—C(17)—C(16)	108.4 (2)

C(2)—C(1)—N(8)—C(9)	171.1 (2)
C(6)—C(1)—N(8)—C(9)	−10.6 (4)
C(1)—N(8)—C(9)—N(10)	−7.5 (4)
C(1)—N(8)—C(9)—S(11)	173.4 (2)
N(8)—C(9)—N(10)—C(1′)	179.4 (2)
N(8)—C(9)—S(11)—N(12)	−1.0 (2)
C(9)—N(10)—C(1′)—C(2′)	−97.4 (3)
C(9)—N(10)—C(1′)—C(6′)	89.6 (3)
C(9)—S(11)—N(12)—C(13)	−114.4 (2)
C(9)—S(11)—N(12)—C(17)	118.6 (2)

Table 3. *Parameters of the intramolecular hydrogen bonding (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	$H_{norm}\cdots A$†	$D—H_{norm}\cdots A$
N(8)—H···N(12)	0.83 (3)	2.18 (3)	2.724 (3)	2.07	119
C(6)—H···N(10)	0.88 (3)	2.35 (3)	2.932 (4)	2.24	120

† Data for normalized H-atom positions are based on bond lengths of N—H = 1.04 and C—H = 1.09 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. 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.

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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: KA1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2,6,6-Tetramethylpiperidinium Chloride

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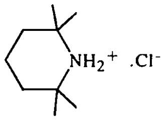
Abstract

Crystals of 2,2,6,6-tetramethylpiperidinium chloride, $C_9H_{20}N^+.Cl^-$, crystallized from dichloromethane solution. Hydrogen bonding between the piperidinium and chloride ions [$d(N—H\cdots Cl) = 3.16$ and 3.30 Å] links the units into alternating chains running parallel to the crystallographic *b* axis.

Comment

We have proposed that the reaction of molybdenum hexacarbonyl with certain bis-dialkylaminophosphine oxides to form cage-like complexes proceeds *via* the elimination of a molecule of the dialkylamine (Wong *et al.*, 1988). We have recently isolated the by-product of one such reaction and characterized it as its hydrochloride salt, (I).



(I)

2,2,6,6-Tetramethylpiperidinium chloride crystallized from dichloromethane solution as small prisms. The molecular structure is shown in Fig. 1. The coordinates of the N—H protons were refined using a fixed isotropic displacement parameter, while all other protons were refined using a fixed riding model.

The structure shows the expected deviations from idealized cyclohexane geometry seen in other structures containing this cation (Johnson, Polborn & Noth, 1991;

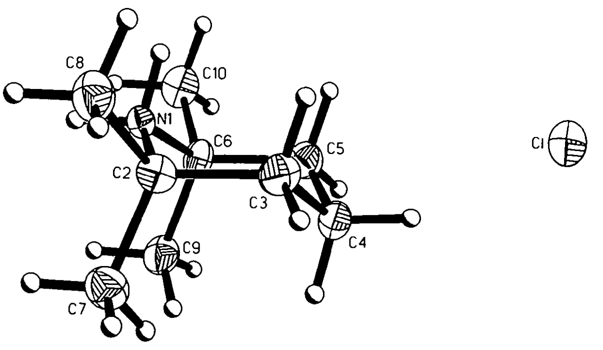


Fig. 1. Molecular structure of 2,2,6,6-tetramethylpiperidinium chloride showing 50% probability ellipsoids.

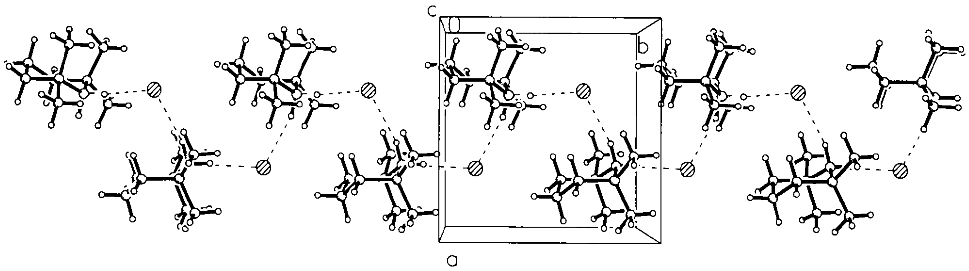


Fig. 2. Packing diagram showing the zigzag chain running parallel to the *b* axis.

Harrison, Stucky & Gier, 1994) with the C2—N1—C6 bond angle opening to 120.6 (2)° and the N1—C2—C3 and N1—C6—C5 bond angles being reduced [107.3 (2) and 106.3 (2)°, respectively]. The chloride and piperidinium ions are linked into zigzag chains that run parallel to the *b* axis *via* hydrogen bonding; N1—H1*A*···Cl(x, $y - 1$, z) = 3.159 (3) Å and N1—H1*B*···Cl($-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$) = 3.299 (3) Å (see Fig. 2). The hydrogen-bond angles are N1—H1*A*···Cl = 173 (3)° and N1—H1*B*···Cl = 165 (3)°. The piperidine rings stack in the *a* direction, but without significant intermolecular contacts.

The overall structure is isomorphous with the hydrobromide analogue (Walkinshaw, Cowley & Mehrotra, 1984), where the hydrogen-bond distances of 3.34 and 3.48 Å reflect the increased size of the Br^- ion, relative to the Cl^- ion, as does the increase in the *b* axis (the chain axis) length from 8.91 to 9.30 Å.

Experimental

The title compound was isolated during workup of the reaction of $Mo(CO)_6$ with (2,2,6,6-tetramethylpiperidino)(diethylamino)phosphine oxide as the hydrochloride salt.

Crystal data

$C_9H_{20}N^+.Cl^-$
$M_r = 177.71$
Orthorhombic
$P2_12_12_1$
$a = 8.7537 (15)$ Å
$b = 8.9098 (13)$ Å
$c = 12.992 (2)$ Å
$V = 1013.3 (3)$ Å^3
$Z = 4$
$D_x = 1.165$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 4.84$–$12.48°$
$\mu = 0.321$ mm^{-1}
$T = 158 (2)$ K
Small prism
0.4 × 0.3 × 0.15 mm
Colorless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scans (*SHELXTL*; Sheldrick, 1985)
$T_{\min} = 0.3592$, $T_{\max} = 0.3799$
3804 measured reflections
1790 independent reflections
1394 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0599$
$\theta_{\max} = 24.98°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity decay: 3.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0405$
$wR(F^2) = 0.0845$
$S = 0.819$
1790 reflections
106 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.005$

$\Delta\rho_{\max} = 0.257$ e Å^{-3}
$\Delta\rho_{\min} = -0.206$ e Å^{-3}
Extinction correction: none
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)
Flack parameter = 0.08 (10)

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

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

	x	y	z	$U_{\rm eq}$
Cl	0.17837 (8)	0.33654 (8)	0.29046 (6)	0.0282 (2)
N1	0.1617 (3)	−0.3194 (3)	0.2327 (2)	0.0190 (5)
C2	0.2266 (3)	−0.2289 (3)	0.3212 (2)	0.0217 (7)
C3	0.2281 (3)	−0.0645 (3)	0.2877 (3)	0.0263 (8)
C4	0.3057 (4)	−0.0411 (3)	0.1839 (2)	0.0297 (8)
C5	0.2272 (3)	−0.1338 (3)	0.1015 (2)	0.0259 (7)
C6	0.2258 (3)	−0.3021 (3)	0.1242 (2)	0.0230 (7)
C7	0.3834 (4)	−0.2848 (4)	0.3519 (2)	0.0309 (8)
C8	0.1162 (4)	−0.2539 (4)	0.4101 (2)	0.0321 (8)
C9	0.3831 (3)	−0.3753 (3)	0.1154 (2)	0.0297 (8)
C10	0.1157 (4)	−0.3827 (4)	0.0543 (2)	0.0313 (8)

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

N1—C2	1.515 (4)	C3—C4	1.525 (4)
N1—C6	1.525 (4)	C4—C5	1.516 (4)
C2—C7	1.513 (4)	C5—C6	1.528 (4)
C2—C8	1.523 (4)	C6—C10	1.506 (4)
C2—C3	1.528 (4)	C6—C9	1.528 (4)
C2—N1—C6	120.6 (2)	C5—C4—C3	110.4 (2)
C7—C2—N1	111.4 (2)	C4—C5—C6	113.7 (3)
C7—C2—C8	109.1 (2)	C10—C6—N1	105.9 (2)
N1—C2—C8	105.1 (2)	C10—C6—C9	109.2 (2)
C7—C2—C3	112.5 (3)	N1—C6—C9	110.9 (2)
N1—C2—C3	107.3 (2)	C10—C6—C5	110.9 (3)
C8—C2—C3	111.2 (3)	N1—C6—C5	106.3 (2)
C4—C3—C2	112.7 (2)	C9—C6—C5	113.4 (2)

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A *cis,trans,cis,cis*-[4.5.5.5]Fenestrane Derivative

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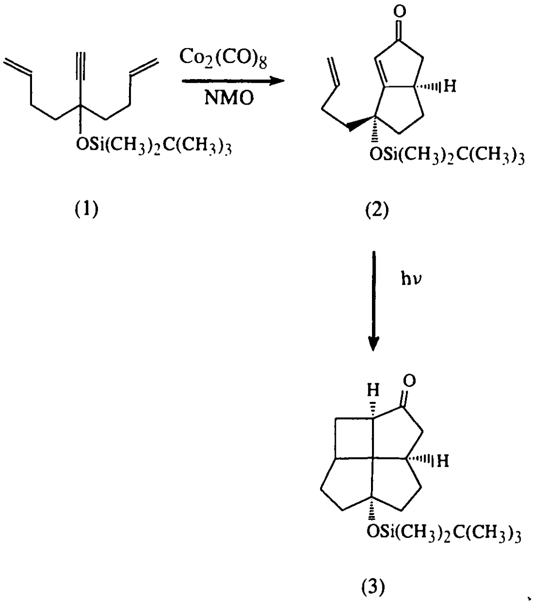
Abstract

The title compound, *rel*-(1*R*,4*R*,7*S*,10*R*)-7-(*tert*-butyldimethylsilyloxy)tetracyclo[5.4.1.$0^{4,12}$.$0^{10,12}$]dodecan-2-one, $C_{18}H_{30}O_2Si$, has been prepared and its structure determined. The geometry of the central $C(C)_4$ substructure of the fenestrane skeleton shows a considerable distortion from an ideal tetrahedral arrangement towards planarity. Values of 127.0 (2) and 131.1 (2)° are observed for the bond angles at the bridgehead atoms of the *trans*-bicyclo[3.3.0]octane subunit.

Comment

Fenestranes are of considerable interest because of the planarizing distortions observed in several cases. The planarizing distortions in the central $C(C)_4$ subunit of this class of compound can be enhanced *inter alia* by construction of *trans*-fused bicyclo[3.3.0]octane subunits (Luef & Keese, 1993). In a systematic search for fenestranes having large distortions, the title compound, (3), was prepared by a $Co_2(CO)_8$-induced cyclocarbonylation reaction of (1) (Thommen, 1995), followed by a photo-induced olefin–enone cycloaddition.



The structure of (3) shows remarkable features both around the central C atom and in the *trans*-fused bicyclo[3.3.0]octane substructure (Table 2). The architecture of fenestrane (3) induces a deformation of the tetrahedral angles in the central $C(C)_4$ substructure towards planarity. The angles C4—C12—C10 and C1—C12—C7 have values of 120.2 (2) and 131.1 (2)°, respectively, which are similar to those observed in the two previously studied [4.5.5.5]fenestranes containing a *trans*-fused [3.3.0]octane substructure (Hirschi, Luef, Gerber & Keese, 1992; Wang, Thommen & Keese, 1996). The largest deviations observed so far are 129.2 (5) and 128.3 (6)° in the all-*cis* [4.4.4.5]fenestrane series (Rao, George, Wolff & Agosta, 1985). The C3—C4—C5 bond angle at the bridgehead of the *trans*-bicyclo[3.3.0]octane substructure is 127.0 (2)°. Compared with the average bond angles of 126 (4) and 127 (6)° found for corresponding bridgehead angles in 19 *trans*-bicyclo[3.3.0]octane subunits retrieved (Hirschi, Luef, Gerber & Keese, 1992) from the Cambridge Structural Database (Allen *et al.*, 1987), C3—C4—C5 is typical but C1—C12—C7, with a value of 131.1 (2)°, is rather large.

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