The crystal was synthesized by electrocrystallization of a THF solution containing 1.51 m*M* BEDT-TTF and 22.7 m*M* (*n*-butyl)$_4$NHgBr$_3$ at 0.4 μA. The structure was solved by heavy-atom methods and subsequent Fourier methods using the Enraf-Nonius *Structure Determination Package* (Enraf-Nonius, 1985). No H atoms were included in the refinement. The weighting scheme was $w = 1/\sigma^2(F)$; $\sigma(F) = \sigma(F^2)/2F$; $\sigma(F^2) = [\sigma_{cs}^2 + (0.02|F|^2)^2]^{1/2}$. A solvent molecule (THF) is incorporated in the structure. It is disordered about the inversion site at the origin. As the C atoms of the inversion-center-related disodered THF molecules are approximately superimposed, only two THF C atoms were included with full occupancy.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71457 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1027]

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4-Methoxy-1-[(1*R*,4*S*,5*R*)-8-phenylmenthoxycarbonyl]pyridinium Hexachloroantimonate, $C_{23}H_{30}NO_3^+.SbCl_6^-$

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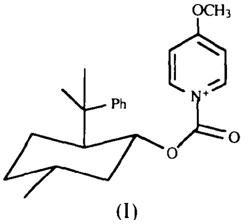
Abstract

The 4-methoxypyridinium and oxycarbonyl moieties are coplanar and approximately parallel to the phenyl ring. The latter is involved in a number of short intramolecular interactions with the pyridinium and the oxycarbonyl atoms. Crystal packing is characterized by the presence of hydrophobic and hydrophilic channels, the former consisting of phenylmenthyl groups and the latter of pyridinium and $SbCl_6^-$ ions.

Comment

The structure determination of the title compound was undertaken to establish the conformation of the cation (I). This is the first non-racemic *N*-acylpyridinium salt prepared in crystalline form. Chiral salts of this type have been prepared *in situ* and reacted with Grignard reagents to give synthetically useful 1-acyl-2-alkyl-2,3-dihydro-4(1*H*)-pyridinones (Comins, Goehring, Joseph & O'Connor, 1990; Comins & Hong, 1991; Comins & Dehghani, 1991; Comins, Hong & Salvador, 1991; Comins & LaMunyon, 1992; Comins & Killpack, 1993).



(I)

The X-ray work described here shows that the 4-methoxypyridinium moiety and the oxycarbonyl group, O(3)—C(7)—O(2) (Fig. 1), are coplanar, the deviations from the mean plane being C(1) −0.016, O(1) −0.010, C(2) −0.014, C(3) 0.026, C(4) 0.016, N(1) −0.013, C(5) 0.016, C(6) 0.019, C(7) −0.005, O(2) −0.014 and O(3) −0.006 Å. Atom C(8) of the cyclohexane ring lies close to this plane, deviating by only −0.073 Å. A similar coplanar arrangement of the oxycarbonyl group and the pyridinium moiety was observed in *N*-phenoxycarbonyl-4-dimethylaminopyridinium chloride (Bryant & King, 1992), which suggests possible conjugation between the oxycarbonyl and pyridine moieties in these compounds. The dihedral angle between the oxycarbonylpyridinium plane and the phenyl ring is 13.7°. They are, therefore, approximately parallel and in a favorable orientation for π–π stacking interactions. The phenyl ring interacts primarily with atoms C(4), N(1), C(7) and O(3) of the oxycarbonylpyridinium moiety (Fig. 1 and Table 3). The intramolecular interactions observed here are similar to, but more numerous than, those observed in a related neutral molecule reported previously from this laboratory (Singh, Comins & Killpack, 1990). The oxycarbonylpyridinium and the phenyl moieties, being bulky, occupy equatorial sites on the cyclohexane ring.

The crystal structure viewed down the *a* axis, Fig. 2, shows that the pyridinium moiety of the cations and the $SbCl_6^-$ anions pack alternately along the *c* axis at approximately $b = 0$ and $\frac{1}{2}$, forming hydrophilic channels which are separated by hydrophobic channels consisting of the phenyl and menthyl moieties. There are no close contacts between $SbCl_6^-$ ions and non-H atoms. There are, however, three H···Cl distances that are less than the sum of the van der Waals radii [2.95 Å (Bondi, 1964)]: H(3)···C(16^{i}) 2.86, H(20)···C(12^{ii}) 2.90 and H(14*A*)···C(14^{iii}) 2.84 Å [symmetry code: (i) *x*, *y*, *z*; (ii) $1 + x$, *y*, *z*; (iii) $-x$, $-\frac{1}{2} + y$, $-z$].

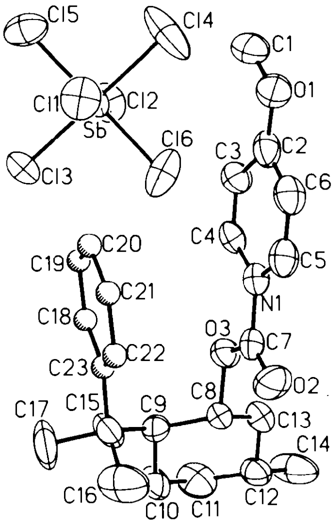


Fig. 1. View of the cation and the $SbCl_6$ anion. Thermal ellipsoids are drawn at the 50% probability level, except for the atoms of the phenyl ring, which are drawn as spheres of arbitary size. H atoms are omitted for clarity.

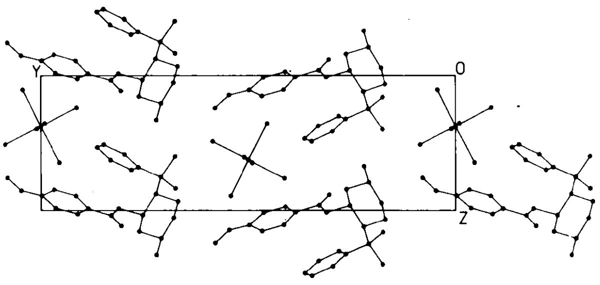


Fig. 2. Packing diagram viewed down the *a* axis.

Experimental

Crystal data

$(C_{23}H_{30}NO_3)[SbCl_6]$
$M_r = 702.97$
Monoclinic
$P2_1$
$a = 7.905$ (2) Å
$b = 24.110$ (11) Å
$c = 7.929$ (2) Å
$\beta = 96.52$ (2)°
$V = 1501.4$ (8) Å^3
$Z = 2$
$D_x = 1.55$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 13$-20°
$\mu = 1.5$ mm^{-1}
$T = 298$ K
Plates
0.27 × 0.15 × 0.10 mm
Colorless
Crystal source: slow evaporation of an acetonitrile-ether-hexane solution

Data collection

Siemens *R3m/μ* diffractometer
ω scans
Absorption correction: none
3924 measured reflections
3511 independent reflections
2466 observed reflections [$F_o \geq 5\sigma(F_o)$]
$R_{\rm int} = 0.010$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 31$
$l = 0 \rightarrow 10$
2 standard reflections monitored every 48 reflections intensity variation: 1.7%

Refinement

Refinement on *F*
$R = 0.047$
$wR = 0.056$
$S = 1.21$
2466 reflections
277 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0009F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.74$
$\Delta\rho_{\rm max} = 0.65$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.72$ e Å^{-3}
Extinction correction: Zachariasen
Extinction coefficient: 6.0 (3) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	*y*	*z*	$U_{\rm eq}$
Sb	0.0777 (1)	0.5000	0.6220 (1)	0.056 (1)
Cl(1)	0.3756 (3)	0.4906 (2)	0.6442 (4)	0.090 (1)
Cl(2)	−0.2194 (3)	0.5099 (2)	0.6029 (4)	0.093 (1)
Cl(3)	0.0563 (4)	0.4136 (1)	0.7608 (4)	0.080 (1)
Cl(4)	0.0974 (6)	0.5860 (2)	0.4880 (8)	0.165 (3)
Cl(5)	0.1020 (4)	0.5431 (2)	0.8921 (5)	0.104 (1)
Cl(6)	0.0504 (4)	0.4547 (2)	0.3567 (4)	0.116 (2)
C(1)	0.5116 (21)	0.5802 (5)	0.2424 (18)	0.105 (6)
O(1)	0.6228 (11)	0.5470 (4)	0.1461 (9)	0.086 (3)
C(2)	0.5794 (12)	0.4978 (9)	0.1089 (11)	0.069 (3)
C(3)	0.4330 (12)	0.4675 (4)	0.1545 (13)	0.064 (4)
C(4)	0.4000 (12)	0.4153 (4)	0.1075 (11)	0.056 (3)
N(1)	0.5076 (9)	0.3864 (3)	0.0128 (9)	0.052 (2)
C(5)	0.6524 (13)	0.4114 (5)	−0.0275 (13)	0.068 (4)
C(6)	0.6898 (13)	0.4636 (5)	0.0163 (13)	0.069 (4)
C(7)	0.4782 (13)	0.3301 (4)	−0.0382 (11)	0.059 (3)
O(2)	0.5723 (11)	0.3060 (4)	−0.1171 (10)	0.091 (4)
O(3)	0.3363 (8)	0.3124 (3)	0.0137 (8)	0.060 (2)
C(8)	0.2769 (13)	0.2551 (4)	−0.0350 (11)	0.058 (3)
C(9)	0.2476 (14)	0.2225 (4)	0.1227 (12)	0.060 (3)
C(10)	0.1501 (18)	0.1700 (5)	0.0668 (15)	0.088 (5)
C(11)	−0.0108 (16)	0.1801 (6)	−0.0551 (17)	0.099 (5)
C(12)	0.0252 (15)	0.2098 (4)	−0.2089 (13)	0.073 (4)
C(13)	0.1168 (16)	0.2638 (5)	−0.1579 (14)	0.075 (4)
C(14)	−0.1369 (22)	0.2212 (6)	−0.3304 (22)	0.137 (7)

C(15)	0.4086 (16)	0.2106 (5)	0.2494 (15)	0.081 (4)
C(16)	0.5393 (18)	0.1758 (7)	0.1632 (21)	0.126 (7)
C(17)	0.3664 (24)	0.1766 (7)	0.4021 (16)	0.148 (8)
C(18)	0.3894 (9)	0.2981 (4)	0.4162 (12)	0.111 (5)
C(19)	0.4530	0.3477	0.4882	0.127 (5)
C(20)	0.6182	0.3645	0.4676	0.123 (5)
C(21)	0.7199	0.3317	0.3749	0.116 (5)
C(22)	0.6563	0.2821	0.3028	0.110 (4)
C(23)	0.4911	0.2653	0.3234	0.075 (3)

Table 2. *Geometric parameters* (Å, °)

Sb—Cl(1)	2.352 (5)	Sb—Cl(2)	2.348 (5)
Sb—Cl(3)	2.372 (6)	Sb—Cl(4)	2.343 (7)
Sb—Cl(5)	2.369 (6)	Sb—Cl(6)	2.357 (6)
O(1)—C(1)	1.466 (18)	O(1)—C(2)	1.260 (22)
C(2)—C(3)	1.449 (17)	C(2)—C(6)	1.457 (18)
C(3)—C(4)	1.330 (14)	C(4)—N(1)	1.386 (13)
N(1)—C(5)	1.364 (14)	N(1)—C(7)	1.427 (13)
C(5)—C(6)	1.330 (17)	C(7)—O(2)	1.178 (14)
C(7)—O(3)	1.309 (13)	O(3)—C(8)	1.497 (12)
C(8)—C(9)	1.516 (14)	C(8)—C(13)	1.521 (15)
C(9)—C(10)	1.523 (16)	C(9)—C(15)	1.556 (16)
C(10)—C(11)	1.527 (18)	C(11)—C(12)	1.469 (18)
C(12)—C(13)	1.521 (16)	C(12)—C(14)	1.538 (20)
C(15)—C(16)	1.550 (21)	C(15)—C(17)	1.530 (20)
C(15)—C(23)	1.555 (15)		
Cl(1)—Sb—Cl(2)	179.3 (2)	Cl(1)—Sb—Cl(3)	90.3 (2)
Cl(2)—Sb—Cl(3)	89.8 (2)	Cl(1)—Sb—Cl(4)	90.1 (2)
Cl(2)—Sb—Cl(4)	89.9 (2)	Cl(3)—Sb—Cl(4)	179.2 (2)
Cl(1)—Sb—Cl(5)	89.8 (2)	Cl(2)—Sb—Cl(5)	89.5 (2)
Cl(3)—Sb—Cl(5)	88.2 (2)	Cl(4)—Sb—Cl(5)	91.1 (2)
Cl(1)—Sb—Cl(6)	90.7 (2)	Cl(2)—Sb—Cl(6)	90.0 (2)
Cl(3)—Sb—Cl(6)	90.2 (2)	Cl(4)—Sb—Cl(6)	90.5 (2)
Cl(5)—Sb—Cl(6)	178.4 (2)	C(1)—O(1)—C(2)	118.2 (10)
O(1)—C(2)—C(3)	128.3 (12)	O(1)—C(2)—C(6)	119.2 (11)
C(3)—C(2)—C(6)	112.5 (15)	C(2)—C(3)—C(4)	122.9 (11)
C(3)—C(4)—N(1)	121.1 (9)	C(4)—N(1)—C(5)	119.1 (8)
C(4)—N(1)—C(7)	122.9 (8)	C(5)—N(1)—C(7)	117.9 (8)
N(1)—C(5)—C(6)	121.7 (10)	C(2)—C(6)—C(5)	122.6 (11)
N(1)—C(7)—O(2)	121.8 (10)	N(1)—C(7)—O(3)	109.8 (8)
O(2)—C(7)—O(3)	128.4 (10)	C(7)—O(3)—C(8)	118.4 (8)
O(3)—C(8)—C(9)	109.8 (7)	O(3)—C(8)—C(13)	104.6 (8)
C(9)—C(8)—C(13)	113.9 (9)	C(8)—C(9)—C(10)	108.1 (8)
C(8)—C(9)—C(15)	116.0 (9)	C(10)—C(9)—C(15)	112.6 (9)
C(9)—C(10)—C(11)	114.1 (10)	C(10)—C(11)—C(12)	112.2 (11)
C(11)—C(12)—C(13)	109.1 (9)	C(11)—C(12)—C(14)	112.4 (11)
C(13)—C(12)—C(14)	110.6 (10)	C(8)—C(13)—C(12)	112.9 (9)
C(9)—C(15)—C(16)	110.6 (10)	C(9)—C(15)—C(17)	112.0 (11)
C(16)—C(15)—C(17)	105.9 (11)	C(9)—C(15)—C(23)	111.4 (9)
C(16)—C(15)—C(23)	110.7 (10)	C(17)—C(15)—C(23)	106.0 (10)
C(15)—C(23)—C(18)	115.9 (6)	C(15)—C(23)—C(22)	124.1 (6)

Table 3. *Selected non-bonded intramolecular distances* (Å) *including those showing interaction between the benzene ring and the N-acylpyridinium moiety*

C(4)···C(19)	3.415	O(3)···C(23)	2.853*
C(4)···C(20)	3.393*	O(3)···C(15)	3.098*
N(1)···C(21)	3.421	O(3)···C(18)	3.190*
C(7)···C(22)	3.126*	C(8)···C(23)	3.148*
C(7)···C(23)	3.258*		

* Distance is less than the sum of the respective van der Waals radii [r(C) = 1.70, r(N) = 1.55, r(O) = 1.52 Å (Bondi, 1964)].

The title compound was prepared from 4-methoxypyridine, (−)-8-phenylmenthyl chloroformate and antimony pentachloride using a procedure similar to that reported for the synthesis of other crystalline *N*-acylpyridinium salts (King & Bryant, 1992). Data were collected at scan rates ranging from 4 to 29.3° min^{-1}. Stationary backgrounds were counted on both sides of a peak, each for one half of the scan time. The structure was solved by direct methods and difference Fourier techniques. All non-H atoms, except for those belonging to the phenyl ring, were refined with anisotropic displacement parameters. The phenyl ring, C(18)-C(23), was refined as a rigid group assuming a regular hexagon of sides 1.39 Å. H atoms were placed in calculated positions and refined in the riding mode. All calculations were performed on a Data General microeclipse desktop computer. Software used: *SHELXTL* (Sheldrick, 1985) for structure solution, refinement and illustration; *CREDUC* (Le Page, 1982) for checking crystal symmetry.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71401 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1060]

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