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Varacinium chloride

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Key indicators

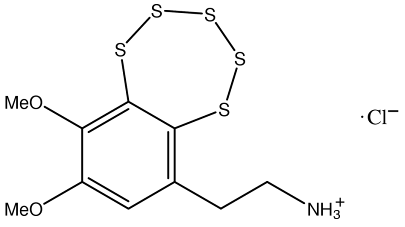
Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.007 Å
R factor = 0.054
wR factor = 0.133
Data-to-parameter ratio = 21.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title compound, $C_{10}H_{14}NO_2S_5^+\cdot Cl^-$, the seven-membered ring adopts a chair conformation. The crystal structure is stabilized by N—H···Cl hydrogen bonds.

Comment

In the course of our work toward the synthesis of antibiotic varacin A, the title compound, (I), was obtained as an unexpected product in 90% yield. After careful examination of the X-ray crystallographic data and other resources, we believe that we have obtained the antibiotic varacin fortuitously with a new methodology. We propose that the varacin A formed in the reaction reacted with S_8, generated from the quenching agent $Na_2S_2O_7$, and subsequently afforded compound (I). In fact, a similar equilibrium between varacin and varacin A + S_8 was first reported by Makarieva *et al.* (1995). The first synthetic approach of varacin was reported by Danishefsky & Behar (1993).



(I)

A view of the molecule, with atomic labeling, is shown in Fig. 1. The S—S distances (Table 1) are similar to those observed in S_8 (Sato *et al.*, 1995) and the S—Csp^2 distances are comparable to those found in benzopentathiepine (Feher & Engelen, 1979). The seven-membered ring adopts a chair conformation. In the crystal, the molecules are linked by Cl^- ions through N—H···Cl hydrogen bonds (Table 2) to form a network structure.

Experimental

To a solution of *N*-Boc-4-ethylamino-6,7-dimethoxy-1,2,3-benzotrithiole 2-oxide (42.0 mg, 0.108 mmol) in THF (5 ml) was added NaI (oven dried, 81.5 mg, 0.540 mmol) in water (3 ml) and 20% *v*/*v* $HClO_4$ (2.0 ml) at 273 K. The reaction mixture was kept at 323 K overnight and cooled to room temperature when the reaction was complete. After quenching with saturated aqueous $Na_2S_2O_7$, the aqueous mixture was extracted with CH_2Cl_2 (3 × 25 ml). The combined organic extracts were washed with water (20 ml) and brine (20 ml) and dried over Na_2SO_4 to give the title compound (24.1 mg, 90%) as a yellow film after rotary evaporation. ^{1}H NMR δ (CD_3OD):

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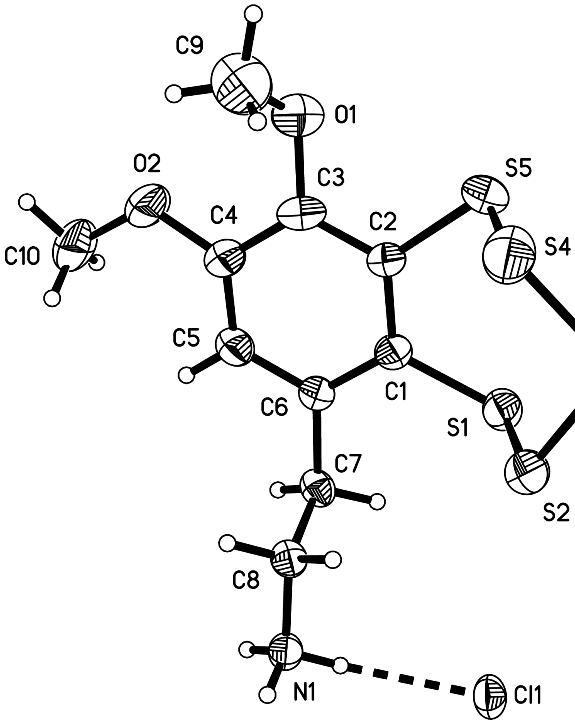

Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids.

7.14 (*s*, 1H), 3.97 (*s*, 3H), 3.82 (*s*, 3H), 3.35 (*m*, 1H), 3.25 (*m*, 1H), 3.16 (*m*, 2H); 13 C NMR δ (CD_3OD) 156.67, 151.24, 141.94, 140.29, 136.31, 62.18, 57.03, 41.67, 35.07; EIMS *m*/*z* (%) 381 (5), 343 (3), 342 (23), 340 $[(M-Cl)^+$, 100], 323 (54), 276 (20), 259 (34), 226 (17). The title compound was then recrystallized from a CH_2Cl_2–hexane (8:1) solvent system.

Crystal data

$C_{10}H_{14}NO_2S_5^+\cdot Cl^-$
$M_r = 375.97$
Monoclinic, $P2_1/c$
$a = 16.891$ (3) Å
$b = 10.6971$ (16) Å
$c = 9.1959$ (13) Å
$\beta = 101.673$ (4)°
$V = 1627.2$ (4) Å^3
$Z = 4$

$D_x = 1.535$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1998 reflections
$\theta = 1$–27.5°
$\mu = 0.87$ mm^{-1}
$T = 294$ (2) K
Needle, yellow
0.28 × 0.10 × 0.08 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.778$, $T_{\max} = 0.928$
10836 measured reflections

3720 independent reflections
1234 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.083$
$\theta_{\max} = 27.6°$
$h = -16 \rightarrow 21$
$k = -13 \rightarrow 13$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.133$
$S = 0.81$
3726 reflections
174 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.777 (4)	S3—S4	2.054 (2)
S1—S2	2.036 (2)	S4—S5	2.043 (3)
S2—S3	2.051 (2)	S5—C2	1.773 (5)
C1—S1—S2—S3	−93.78 (17)	S2—S1—C1—C2	83.4 (4)
S1—S2—S3—S4	73.00 (11)	S1—C1—C2—S5	−4.9 (6)
S2—S3—S4—S5	−75.16 (11)	S4—S5—C2—C1	−74.6 (4)
S3—S4—S5—C2	93.11 (19)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*B*···Cl1	0.89	2.26	3.107 (3)	160
N1—H1*A*···Cl1$^{\rm i}$	0.89	2.33	3.129 (4)	149
N1—H1*C*···Cl1$^{\rm ii}$	0.89	2.27	3.098 (3)	154

Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

All the H atoms were placed in geometrically calculated positions and included in the final refinement in the riding model approximation. As a result of the small size and poor diffraction quality of the crystal, the ratio of observed to unique reflections is low (33%).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SHELXTL-NT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

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