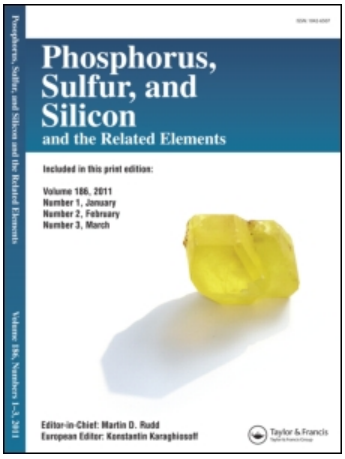

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X-RAY CRYSTAL STRUCTURE OF 1-METHYL-*EXO, EXO*-3,5-DICHLORO-8-THIATRICYCLO[2.2.1.1^{2,6}]-OCTANE TETRAFLUOROBORATE

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X-RAY CRYSTAL STRUCTURE OF 1-METHYL-*EXO,EXO*-3,5-DICHLORO-8-THIATRICYCLO[2.2.1.1^{2,6}]-OCTANE TETRAFLUOROBORATE

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The synthesis and characterization by X-ray crystallography of the 1-methyl-*exo,exo*-3,5-dichloro-8-thiatricyclo[2.2.1.1.^{2,6}]octane cation (**II**) is described. Compound **II** is prepared from the reaction of *exo,exo*-3,5-dichloro-8-thiatricyclo[2.2.1.1.^{2,6}]octane (**I**) with trimethyloxonium tetrafluoroborate in nitromethane. Crystals of (**II**) belong to the space group, *Pbca*, with cell dimensions (298°K) of a = 9.269(2) Å, b = 12.112(3) Å, c = 2.418(4) Å, V = 2404.7(8) Å^3, (Z = 8. Solution and refinement of the intensity data gave final residuals of R_F = 5.60% and R_w = 6.26% using 1289 unique reflections with $(F_0) > 3\sigma(F_0)$.

INTRODUCTION

Norbornadiene reacts with sulfur dichloride to produce *exo,exo*-3,5-dichloro-8-thiatricyclo[2.2.1.1.^{2,6}]octane (**I**).[1] The proposed mechanism[1] for this reaction involves initial *endo* attack of SCl_2 on norbornadiene to form a bridged sulfonium ion intermediate. Trans attack by the chlorine anions liberated from reacted SCl_2 produces **I**.

Interest in the structural elucidation and the synthesis of sulfonium salts[2] prompted us to investigate the conversion of **I** to its sulfonium salt **II** (see Scheme 1). Methylation of **I** was accomplished with trimethyloxonium tetrafluoroborate.[3,6] Previous attempts to synthesize **II** from **I** using methyl iodide were unsuccessful.[1]

We report here a structural study of **II** using ^{1}H and ^{13}C NMR and single-crystal X-ray diffraction. Results presented for **II**, support the mechanism for the formation of **I** (*vida supra*).

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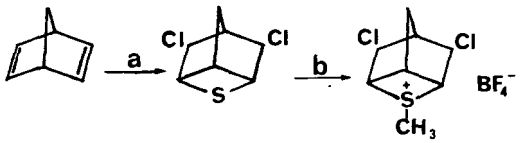

I II

a = SCl_2; b = $(CH_3)_3O^+BF_4^-$

SCHEME 1

RESULTS AND DISCUSSION

^1H and ^{13}C NMR results for **II** are given in Table I. Figure 1 shows the cation structure and numbering scheme used in the assignment of these resonances and the subsequent discussion of X-ray results. Selected bond distances and angles are given in Table II. The average C—S^+ bond length in **II** is 1.824(5) Å. This value falls within the range of known C—S^+ bond distances given by Perozzi *et al.*[4a] (1.753(2) to 1.882(3) Å range) and the average C—S^+ length for known compounds given by Britton and Dunitz (1.813(35)Å).[4b] Additionally, these C—S^+ bond distances all fall in or near the range reported for neutral thiols (1.77(2) Å–1.81(3)),[4a] consistent with their single bond character. The exocyclic C—S bond in **II** is approximately 0.03 Å shorter than the C—S bonds forming the ring. The apparent shortening is probably affected by the librational motion of the external methyl group making comparisons between external and internal bond distances questionable.

TABLE I

^1H and ^{13}C NMR resonance data

Assignment*	H (δ)
H1a, H1b, H1c	3.28 (3 H, s)
H2, H6	4.98 (2 H, bs)
H3, H5	3.98 (2 H, d)
H7	3.16 (1 H, s)
H4	4.57 (1 H, m)
H8a, H8b	2.1 (2 H, bs)
Assignment*	**C (δ)**
C1	24.1 (1 C, q)
C2, C6	57.7 (2 C, d)
C3, C5	59.3 (2 C, d)
C7	53.9 (1 C, d)
C4	38.9 (1 C, d)
C8	34.6 (1 C, t)

*s = singlet, d = doublet, t = triplet, q = quarter, bs = broad singlet, m = multiplet.

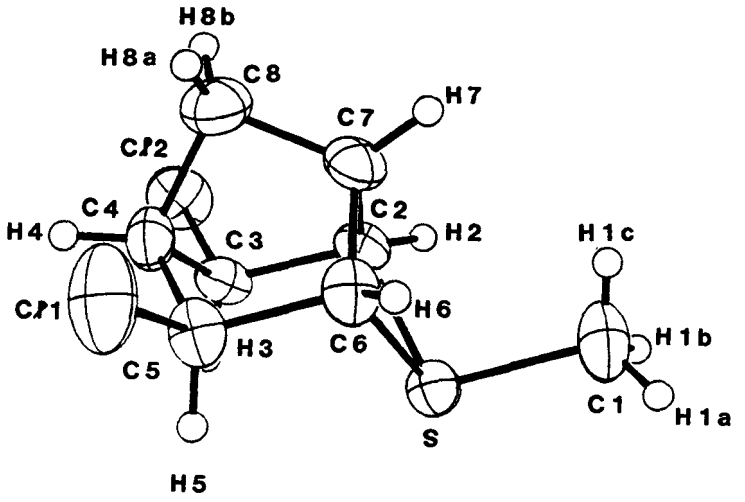

FIGURE 1 ORTEP of 1-methyl-*exo*,*exo*-3,5-dichloro-8-thiatricyclo[2.2.1.1.^{2,6}]octane cation (II).

TABLE II

Selected bond distances and angles for **II**

	(a) Bond distances (Å)		
C(1)—S	1.797(8)	C(5)—C(6)	1.535(8)
C(2)—S	1.844(5)	C(6)—C(7)	1.526(8)
C(6)—S	1.832(5)	C(7)—C(8)	1.510(8)
C(2)—C(3)	1.553(7)	Cl(1)—C(5)	1.799(5)
C(2)—C(7)	1.569(7)	Cl(2)—C(3)	1.793(5)
C(3)—C(4)	1.513(7)	S · · · F(1)	2.940(3)[a]
C(4)—C(5)	1.508(8)	S · · · F(2)	2.861(3)[b]
C(4)—C(8)	1.525(7)	S · · · F(5)	2.985(3)[b]
	(a) Bond angles (deg)		
C(1)—S—C(2)	102.8(4)	C(8)—C(4)—C(5)	103.1(4)
C(1)—S—C(6)	102.8(3)	C(4)—C(5)—C(6)	102.7(4)
C(2)—S—C(6)	74.1(2)	C(4)—C(5)—Cl(1)	111.8(4)
S—C(2)—C(7)	91.5(3)	Cl(1)—C(5)—C(6)	108.6(4)
S—D(2)—C(3)	105.9(3)	C(5)—C(6)—C(7)	102.9(4)
C(7)—C(2)—C(3)	101.5(4)	C(5)—C(6)—S	107.0(4)
C(2)—C(3)—C(4)	103.2(4)	S—C(6)—C(7)	93.4(3)
C(2)—C(3)—Cl(2)	108.2(3)	C(6)—C(7)—C(2)	91.4(4)
Cl(2)—C(3)—C(4)	112.5(3)	C(6)—C(7)—C(8)	106.7(4)
C(3)—C(4)—C(5)	105.9(4)	C(8)—C(7)—C(2)	105.1(4)
C(3)—C(4)—C(8)	102.4(4)	C(7)—C(8)—C(4)	94.4(4)

[a]sulfur transformation: $1.0 + \bar{x}$, $\bar{y}$, $1.0 + \bar{z}$.
[b]sulfur transformation: x, $0.5 + \bar{y}$, $-0.5 + \bar{z}$.

Examination of Figure 1 and Table II shows the sulfur atom to have pyramidal geometry. The molecular arrangement serves to confirm initial *endo* attack of SCl_2 on norbornadiene followed by trans attack of the chlorines liberated from reacted SCl_2. The structural results suggest that a non-bonding pair of electrons occupy a pseudo-axial position on the sulfur atom. Pseudo-equatorial positioning of the methyl group in **II** is consistent with that found for substituents in previous

structures in which the sulfur atom is a member of a five-or six-atom ring.[4a] The external C—S^+—C angles (⟨av⟩ = 102.8°(5)°) in **II** agree with the known average for sulfonium salts (102.5[4a]–102.4(2.2)°[4b]). The internal C—S^+—C angle of 74.1(2)° is considerably smaller. The trend toward smaller internal C—S^+—C angles in rings, has been reported previously,[4a,5,6] but the difference between internal and external angles in **II** exceeds the range previously reported. The greater decrease in **II** is due to bridging between C(2) and C(6) through C(7). The bridging arrangement serves to pull C(2) and C(6) closer together collapsing the internal C—S^+—C angle. The remaining bond parameters are within expected ranges.

The tetrafluoroborate anion was found to be disordered in its arrangement within the lattice. Several modeling schemes were tried. The model used for final refinement of the anion involved a fractional occupancy of several fluorine sites. F(2), F(4), F(5) and F(6) were each assigned half occupancies while F(1) and F(3) were assigned full occupancies. The B—F bond lengths and F—B—F angles involving F(1), F(2), F(3), and F(4) were fixed at 1.366 Å and 109.5° respectively while F(5) and F(6) were allowed to refine unrestricted. The result approximated two interpenetrating tetrahedra with two coinciding F atoms, F(1) and F(3). The BF_4-disorder is not unusual and is a result of the poor fit of the anion in a lattice whose dimensions is largely determined by cation packing. Sulfur · · · fluorine interionic contact distances are provided in Table IV.

EXPERIMENTAL

Commercial grade norbornadiene (Aldrich) was freshly distilled prior to use. Sulfur dichloride (MCB) and trimethyloxonium tetrafluoroborate (Alfa) were used as received. Mass spectroscopy was performed on a Du Pont 101 GC-MSDS System. ^1H and ^{13}C NMR analysis was carried out on a JOEL FX-270 Spectrometer. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 and referred to internal TMS. Single-crystal X-ray studies were performed on a Nicolet P3 diffractometer.

Preparation. 1-Methyl-*exo,exo*-3,5-dichloro-8-thiatricyclo[2.2.1.1.^{2,6}]octane tetrafluoroborate (**II**): The reaction and reagent manipulations were performed under N_2. *Exo,exo*-3,5-dichloro-8-thiatricyclo[2.2.1.1^{2,6}]octane (**I**) (4.36 g, 22.3 mmol) in a minimum of nitromethane was added to trimethyloxonium tetrafluoroborate (3.62 g, 24.5 mmol) in 20 mL of nitromethane and stirred for 1.5 hours at room temperature. The nitromethane was removed under vacuum and the crude sulfonium salt was dissolved in acetone and precipitated by the addition of anhydrous ether. The dissolution and precipitation procedure was repeated several times, followed by several washings with ether to yield 1 g(6.6 mmol, 30%) of **II**: mp 200–202° (d). *Anal.* calcd. for $C_8H_{11}BCl_2F_4S$: C, 32.4; H, 3.7. Found: C, 33.0; H, 4.0. Mass Spectrum (**II**) (70 eV): m/e 209 (M^+), 208 (M-1), and lesser ions at 246, 244, 230, 228, 196, 194, 174 and 172.

Collection and Processing of Diffraction Data. A colorless crystal of **II** (0.21 × 0.24 × 0.27 mm) grown from acetone/diethyl ether was affixed to a glass fiber. Unit-cell parameters are provided in Table III and were obtained from the angular settings of 25 reflections (22° ≤ 2θ ≤ 25°). Details of the intensity data collection and refinement procedures are also provided in Table III. The orthorhombic space group, *Pbca*, was uniquely determined by systematic absences in the intensity data. All crystallographic computations were performed on the University of Delaware Data General Nova 4 computer using data collection, solution and refinement programs contained in the Nicolet Corporation P3 and SHELXTL (version 3.0) packages. Corrections to the data for Lorentz and polarizations effects were applied. No absorption correction was applied due to the low absorption coefficient (μ = 7.26 cm^{-1}) and uniform crystal dimensions. Redundant and equivalent data were averaged (R(I) = 3.25%).

TABLE III

Crystal and refinement data

formula	$C_8H_{11}BCl_2F_4S$
space group	*Pbca*
a, Å	9.269(2)
b, Å	12.112(3)
c, Å	21.418(4)
V, Å^3	2404.7(8)
molecular weight	296.95
ρ(calcd), g cm^{-3}	1.64
temp, °C	25
radiation	graphite-monochromated MoK_α (λ = 0.71073 Å)
abs. coeff., cm^{-1}	7.26
scan speed, deg/min	variable 3.0–19.0
2θ scan range, deg	$3° \leq 2\theta \leq 45°$
scan technique	$\theta/2\theta$
data collected	+h, +k, +l
scan width, deg	$1.8 + \Delta(\alpha_1 - \alpha_2)$
ignorance factor[a]	0.0008
unique factor	1572
unique data with ($F_0 \geq 30(F_0)$)	1289
Standard reflections	3 stds/150 rflns
R_F	5.60%
Rw_F	6.26%

[a]Weight = $[\sigma^2(F) + g(F^2)]^{-1}$.

Solution and Refinement of the Structure. The locations of the sulfur and chlorine atoms were obtained from the solutions of highest combined figures of merit obtained from the direct-methods routine SOLV. Subsequent difference Fourier syntheses yielded the locations of the remaining non-hydrogen atoms. Disorder in the tetrafluoroborate anion forced constraint of the B—F bond lengths and angles (*vida infra*). Anisotropic treatment of all non-hydrogen atoms, followed by Fourier syntheses located all hydrogen atoms except H8a and H8b. The latter two were placed in appropriate positions. All nonhydrogen atoms were refined with anisotropic temperature factors; found hydrogen atoms were refined isotropically; idealized hydrogen atoms were treated as fixed contributions. Final residuals were R_F = 5.60%, R_{wF} = 6.26% and GOF = 1.75 for these 1289 unique reflections with $|F_0| > 3\sigma(|F_0|)$. The largest peak in the final difference Fourier synthesis was 0.51e Å^{-3} and was located 1.02 Å from F(2).

Final positional parameters are given in Table IV. A listing of observed versus calculated structure factors and anisotropic thermal parameters are available as supplementary material.

ACKNOWLEDGEMENT

Synthesis of **II** was performed by Mr. M. Zapf (Towson State University). The National Science Foundation partially funded the purchase of the X-ray diffractometer used in these studies.

SUPPLEMENTARY MATERIAL AVAILABLE

Anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Requests should be accompanied by the full literature citation for this paper.

TABLE IV

Final atomic positional parameters

Atom	X/A	Y/B	Z/C
S	0.4802(2)	0.0777(1)	0.3146(1)
CL1	0.5534(2)	0.4199(1)	0.3551(1)
CL2	0.7235(2)	0.0501(2)	0.4842(1)
F1	0.3979(4)	0.3230(3)	0.6945(2)
F2	0.4309(5)	0.1466(4)	0.6684(5)
F3	0.6144(1)	0.2452(1)	0.7062(1)
F4	0.5294(3)	0.2801(1)	0.6102(1)
F5	0.4273(8)	0.1555(6)	0.6646(8)
F6	0.5351(15)	0.3101(13)	0.6204(6)
B	0.4932(3)	0.2487(3)	0.6700(2)
Cl	0.3039(8)	0.0195(7)	0.3029(5)
H1a	0.268(15)	0.027(10)	0.266(6)
H1b	0.312(9)	−0.062(6)	0.306(4)
H1c	0.254(8)	0.038(6)	0.332(3)
C2	0.5062(5)	0.0645(4)	0.3997(2)
H2	0.488(5)	−0.032(5)	0.410(2)
C3	0.6589(5)	0.1114(4)	0.4133(2)
H3	0.723(4)	0.100(3)	0.385(2)
C4	0.6324(5)	0.2341(4)	0.4198(2)
H4	0.705(5)	0.271(4)	0.436(2)
C5	0.5850(6)	0.2734(4)	0.3562(3)
H5	0.655(5)	0.243(3)	0.325(2)
C6	0.4401(6)	0.2140(4)	0.3473(3)
H6	0.378(4)	0.241(3)	0.328(2)
C7	0.4088(6)	0.1681(4)	0.4123(3)
H7	0.309(6)	0.161(4)	0.417(2)
C8	0.4934(6)	0.2378(5)	0.4578(3)
H8a	0.503(6)	0.207(5)	0.499(3)
H8b	0.456(6)	0.311(5)	0.461(3)

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