Geometry and Conformation of Thietanium Ions from Diffraction Data and *Ab Initio* Calculations

by **Riccardo Destro*** and **Emanuele Ortoleva**

Dipartimento di Chimica Fisica ed Elettrochimica and Centro CNR CSRSRC, Università di Milano,
via Golgi 19, I-20133 Milano

and **Giorgio Modena** and **Lucia Pasquato***

Centro CNR Meccanismi di Reazioni Organiche and Dipartimento di Chimica Organica, Università di Padova,
via Marzolo 1, I-35131 Padova

and **Vittorio Lucchini**

Dipartimento di Scienze Ambientali, Università di Venezia, Dorsoduro 2137, I-30123 Venezia

Dedicated to Prof. *Richard Neidlein* on the occasion of his 70th birthday

Four-membered ring thiosulfonium ions may be obtained quantitatively and under mild conditions by anionotropic rearrangement of *C*-(*tert*-butyl)-substituted thiiranium ion precursors. Thus, *t*-4-(*tert*-butyl)-*r*-1,2,2,*c*-3-tetramethylthietanium tetrafluoroborate or hexachloroantimonate (**2a** or **2b**, resp.) were formed from thiiranium ion **1**. The thietanium salts **2a** and **2b** were characterized by X-ray crystal-structure analysis. Their cation geometry was also optimized by *ab initio* calculations at the RHF/6-31G*//RHF/6-31G* level, as were those of its stereoisomer **3** and of the unsubstituted *S*-methylthietanium ion **5**. Comparison of **2**, **3**, and **5** with **4** – the only other thietanium ion studied by XRD, where the C-atoms of the thioniacyclobutane ring are part of a trinorbornane skeleton – indicates that, in these systems, relief from substituent overcrowding is easily achieved by a folding of the four-membered ring along the line connecting the two opposite C-atoms. The corresponding ring-deformation normal mode has a calculated frequency as low as 109 cm^{-1} in ion **5**, to be compared with a frequency of 138 cm^{-1} in methylcyclobutane. For thietanium ion **2**, the frequencies of the two normal modes involving such ring deformation have calculated values of 61 and 85 cm^{-1}.

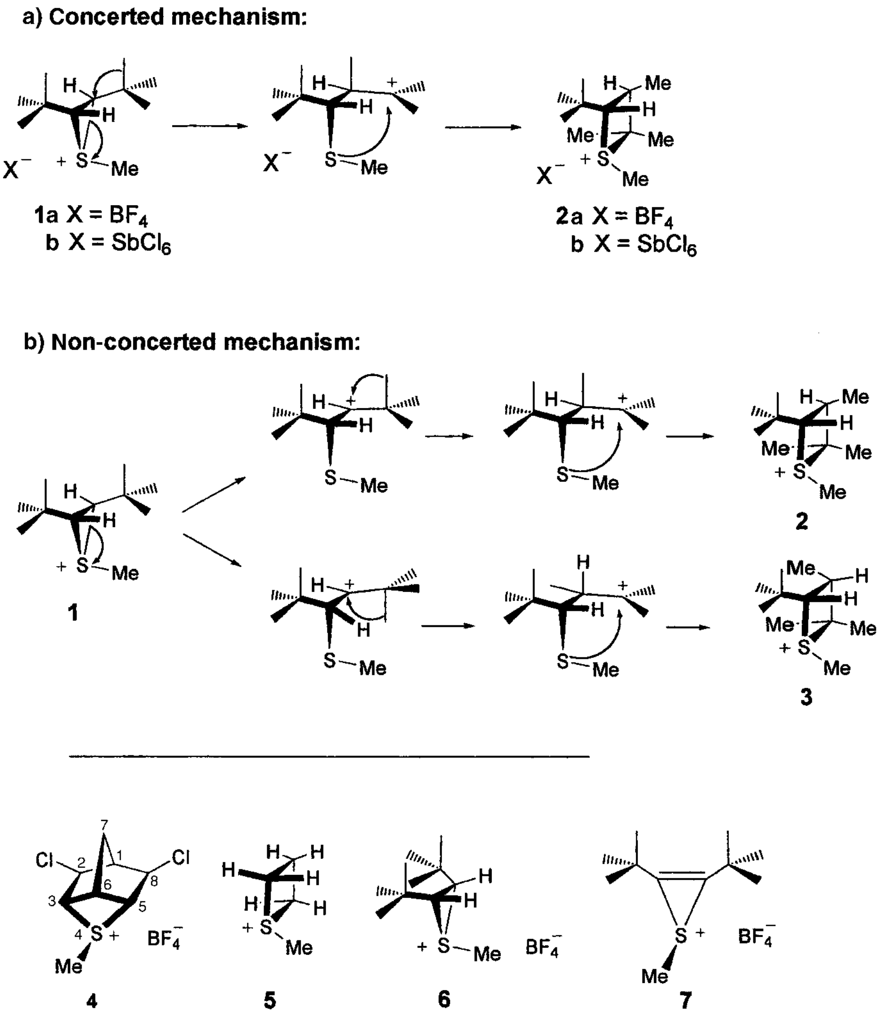
Introduction. – Although thietanium ions are exotic species, there are several examples of four-membered cyclic sulfonium salts reported in the literature [1–6].

In our studies of the thiiranium-ion chemistry, we found that (*tert*-butyl)-substituted thiiranium ions undergo, in the absence of nucleophiles, a concerted and stereoselective anionotropic methyl rearrangement to the corresponding thietanium ions (see *Scheme*, *a*) [7–9]. It has been shown [8] that a non-concerted mechanism would lead to the contemporaneous formation of **2** and **3** (*Scheme*, *b*), but the latter species has not been observed.

To the best of our knowledge, only one X-ray structure of a thietanium salt has been so far reported [10], that of (2*S**,8*R**)-2,8-dichloro-4-'*anti*'-methyl-4-thioniatricyclo[3.2.1.0^{3,6}]octane tetrafluoroborate (**4**), where all three C-atoms of the thietanium ring belong to a trinorbornane skeleton.

We report here the structure of the less-rigid thietanium ion **2**, as derived from a single-crystal X-ray analysis and computational studies at the RHF/6-31G*//RHF/6-

Scheme



31G* level. Calculations were carried out also for its stereoisomer **3** and the unsubstituted *S*-methyl ion **5**. Geometry and conformation of the latter were compared with those of **2**–**4**.

Results and Discussion. – Experimental and calculated bond lengths and angles of thietanium ion **2a** are listed in *Table 1*. The ORTEP plot with the atomic numbering scheme adopted for the X-ray analysis of **2a** is shown in the *Figure*. For the experimental bond distances, values corrected for thermal motion, according to the rigid-body TLS treatment of the ADPs [12], are reported. The correction implies a lengthening of 0.006–0.014 Å for all bonds not involving H-atoms.

Table 1. *Experimental and Calculated Selected Bond Lengths* [Å] *and Angles* [°] *for the Cation of* **2a**, *Compared with Those Found* [10] *in Thietanium Ion* **4** *and Calculated for Thietanium Ions* **3** *and* **5**. For convenience, **2**–**5** are all arbitrarily numbered according to the *Figure*.

	2a		**3**	**4**	**5**
	exp.[a]	calc.[a]	calc.[a]	exp.	calc.[a]
Bond lengths [Å]					
S–C(1)	1.797(2)	1.808	1.807	1.797(8)	1.811
S–C(2)	1.896(2)	1.890	1.885	1.832(5)	1.845
S–C(3)	1.864(2)	1.862	1.856	1.844(5)	1.845
C(2)–C(8)	1.556(3)	1.561	1.568	1.526(8)	1.543
C(3)–C(8)	1.560(3)	1.552	1.564	1.569(7)	1.543
Bond angles [°]					
C(1)–S–C(2)	110.6(1)	111.7	111.6	102.8(3)	104.2
C(1)–S–C(3)	109.3(1)	109.5	110.9	102.8(4)	104.2
C(2)–S–C(3)	76.44(9)	77.2	77.0	74.1(2)	77.3
C(8)–C(2)–S	87.6(1)	88.2	88.6	93.4(3)	92.0
C(8)–C(3)–S	88.7(1)	89.5	89.8	91.5(3)	92.0
C(2)–C(8)–C(3)	96.5(2)	97.5	96.1	91.4(4)	96.6
Puckering angle [°][b]	145.1(1)	150.6	149.0	– 148.3(3)	– 164.3

[a] This work. [b] Defined as the torsion angle S–C(2)–C(3)–C(8) (see *Fig.*).

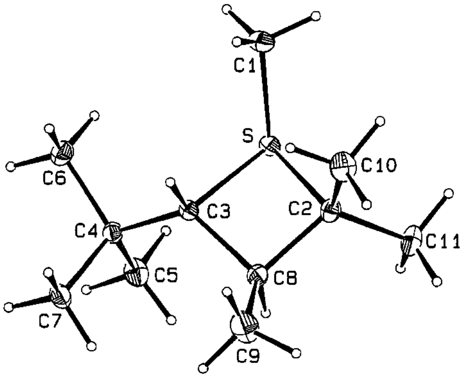


Figure. *ORTEP* [11] *Plot with atomic-numbering scheme for the thietanium cation of the tetrafluoroborate salt* **2a**

The *ab initio* optimized geometry of thietanium ion **2** is very similar to that found experimentally in the solid state: differences do not exceed 0.015 Å and 1.5° in bond lengths and bond angles, respectively. The overall molecular conformations are also nearly alike, with differences in torsion angles within 4–5°. The largest (yet not severe) discrepancy is in the conformation of the four-membered ring, which is flatter in the calculated than in the experimental ion structure (see the value of the puckering angle in *Table 1*). Anion-cation interactions in the crystal may be responsible for the observed conformational differences: inspection of intermolecular contacts reveals some short separations, <2.5 Å, between F-atoms of the anion and H-atoms of the Me group C(1), to be compared with the sum of *van der Waals* radii, 2.7 Å.

As previously observed in the thiiranium ions **1** and **6** and the thiirenium ion **7** [13], the endocyclic S–C bonds are significantly longer than the exocyclic S–C bond. The difference of *ca.* 0.03 Å in the length of the two S–C ring bonds of **2a** is clearly related to the hindrance between the Me groups C(1) and C(10) (see *Fig.*): thanks to the lengthening of the S–C(2) bond and a C(1)–S–C(2)–C(10) torsion angle of 12.2(1)°, the two methyl C-atoms become separated by 3.100(3) Å, a distance still significantly shorter than the sum of the *van der Waals* radii of the C-atoms (3.4 Å), yet longer than the separation between Me atoms C(10) and C(9) (2.996(4) Å).

On passing from the thiiranium-ion structures [13] to that of the thietanium ion, the expected pyramidal arrangement at the S-atom is maintained, the endocyclic angle at the S-atom increases by *ca.* 30°, while the values of the two exocyclic C–S–C angles depend on the nature of the substituents at the endocyclic C-atoms and their arrangement with respect to the *S*-Me group, with experimental values in the range 105–112° in ions **1**, **2**, and **6**.

In view of the subsequent comparison of **2** with other thietanium ions, it is interesting to note (see *Fig.*) the pseudoequatorial position of the substituent atoms C(4) and C(11), at a separation of 4.838(3) Å in the experimental structure and 4.818 Å in the optimized geometry. The corresponding *ab initio* calculated distance is only slightly longer in **3** (4.965 Å), where the Me group C(9) lies on the same side of the ring as the ^{t}Bu and the C(11) Me groups. As seen in *Table 1*, the ring-puckering angle of **3** is about the same as that of **2**, and close similarity between the two stereoisomers is shown also by all bond lengths and angles reported in *Table 1*. This indicates that the position of the Me group C(9) is not crucial in determining the overall conformation of these cations. Isomer **2** is more stable than **3** by 5.2 kcal mol^{-1}; the two normal modes involving most of the ring deformation have frequencies as low as 42 and 59 cm^{-1} in **2**, to be compared with 61 and 85 cm^{-1} in **3**. In both ions, these are the lowest frequencies.

To better understand the effects of steric interactions between substituent groups on the ring conformation of thietanium ions, we optimized *ab initio* the geometry of the C-unsubstituted *S*-methylthietanium ion **5**; the most relevant bond lengths and angles are reported in *Table 1*. All four ring bonds are shorter than those calculated for ions **2** and **3**, and the two exocyclic C–S–C angles are narrower by 5–6°. The most interesting feature of **5** appears to be the puckering angle of the thietanium ring, opposite in sign (see *Table 1*) with respect to those of the ring of **2** and **3**. This implies that, in thietanium ion **2**, atoms C(1) and C(8) (see *Fig.*) lie on opposite sides of the plane defined by atoms S, C(2) and C(3), while in **5**, both C(1) and C(8) lie on the same side. Investigations on the possible existence of another stable conformer of **5** having the ring conformation of **2** and **3** were unsuccessful. The folding of the four-membered ring along the line C(2)···C(3) (*Fig.*) appears as the most convenient way for these systems to reduce, when necessary, steric hindrance between the substituents at the C-atoms in α position to the S-atom. The lowest calculated frequency of the normal modes of **5**, 109 cm^{-1}, corresponds to such a ring deformation, with the second lowest value, 193 cm^{-1}, related to the vibration of the *S*-Me group. For the two similar normal modes in methylcyclobutane, we calculated, at the same level of theory, frequency values of 138 and 272 cm^{-1}, respectively.

As stated in the *Introduction*, the only other reported thietanium-ion X-ray structure [10] is that of salt **4**, with refcode DAMGAZ in the *Cambridge Database* [14].

The experimental bond distances and angles relevant for the comparison with **2**, **3**, and **5** are reported in *Table 1*. The close similarity of bond lengths in **4** and **5** is evident (but those of **4** were not corrected for thermal motion), while the difference in bond-angle values is particularly marked for the endocyclic angles at atoms S and C(8). The conformation of the four-membered ring in the two ions is also similar, the puckering angle having the same sign, but the difference in value is as large as 16°, the ring being much flatter in **5** than in **4**. Clearly, the ring geometry and conformation in the case of **4** are strictly dictated by the presence of the trinorbornane skeleton, incompatible with a sign reversal of the puckering angle, that is with a ring conformation as in **2**: only if atoms corresponding to C(4) and C(11) are in axial position, can their separation amount to 2.414 Å, as found in **4**.

Conclusions. – Thietanium ions may be easily and quantitatively obtained from (*tert*-butyl)-substituted thiiranium ions by ring enlargement, as reported for thietanium ions **2**. Relief from overcrowding in stereoisomers **2** and **3** requires a pseudoequatorial arrangement of the ^{t}Bu group. This is achieved by folding the ring in a way opposite to that occurring in the calculated unsubstituted *S*-methylthietanium ion **5**, and observed in **4**. The presence in the latter ion of a rigid trinorbornane skeleton requires the axial position for the substituents at the ring C-atoms adjacent to S-atom, and ring angular deformations up to 5–6° with respect to **2**, **3**, and **5**.

Experimental Part

Single-Crystal X-Ray analysis of **2a** *and* **2b**. As in the case of the thiiranium salt **1a** [13], crystals of *t*-4-*tert*-butyl-*r*-1,2,2,*c*-3-tetramethylthietanium tetrafluoroborate (**2a**) and hexachloroantimonate (**2b**) suitable for X-ray analysis were grown from sat. solns. of the salt in dry CH_2Cl_2, by addition of pentane until turbidity, and then kept at −20°. The X-ray measurements were performed on a *Siemens/Bruker-P4* diffractometer using graphite-monochromatized Mo*Kα* radiation (λ 0.71073 Å). *Table 2* shows details of the data collection and refinement. Data of **2b** were corrected for absorption. The structures were solved by direct methods with the SHELXS-86 program [15].

The BF_4^- anion of **2a** was found to be extensively disordered and was approximately modeled as three interpenetrating tetrahedra with different fractional occupancy, but having in common the B-atom. Restraints of similarity in B–F and F–F distances were imposed in the full-matrix least-squares refinement, based on F^2 and carried out with the SHELXL-93 program system [16]. No disorder affected the cation, where the S- and C-atoms were refined anisotropically, as were the atoms of the anion. The atomic numbering scheme adopted for the X-ray analysis is shown in the *Figure*.

Although the structure of the hexafluoroantimonate salt **2b** refined to an R_1 index of 0.0396 for the 2508 observed reflections, the poor quality of the crystal (several anomalous intensity profiles, 52 inconsistent equivalents, large R_{int}) resulted in values of the C–C bond lengths that vary in the range 1.46–1.61 Å (with uncertainties of *ca.* 0.01 Å), and in 9 residues in the final difference map as large as 0.5–0.8 eÅ^{-3} in the anion region. Thus, a detailed discussion of the experimental conformation of the thietanium ion in **2b** (only marginally different from that of the cation of **2a**) seems inappropriate, and the data have not been deposited. Full crystallographic data for the structure of **2a** have instead been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-120559. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (fax: +44-(1223)-336033; e-mail: deposit@ccdc.cam.ac.uk).

ab initio *Calculations.* The geometry and the energy of thietanium ions **2**, **3**, and **5** were computed *ab initio* at the RHF/6-31-G*//RHF/6-31G* level with the Spartan 4.0 program package [17] (the 6-31G* basis set includes d functions for second- and higher-row elements; for sulfur, see [18]).

Table 2. *Crystal Data and Structure Refinement for* **2a** *and* **2b**

	2a	**2b**
Empirical formula	$C_{11}H_{23}BF_4S$	$C_{11}H_{23}Cl_6SSb$
M_r	274.16	521.80
T [K]	293(2)	293(2)
Crystal size [mm]	0.50 × 0.40 × 0.13	0.25 × 0.20 × 0.12
Crystal system	orthorhombic	orthorhombic
Space group, no.	*Pbca*, 61	*Pbca*, 61
Unit-cell dimensions [Å]		
a	13.557(1)	10.574(2)
b	11.377(1)	16.023(3)
c	19.280(2)	24.214(4)
Volume [Å^3]	2973.7(5)	4102.5(12)
Z	8	8
Density (calc.) [g cm^{-3}]	1.225	1.690
Absorption coeff. [mm^{-1}]	0.238	2.22
$F(000)$	1168	2064
θ Range for data collection [°]	2.1 – 25.0	2.1 – 25.0
Index ranges	$-16 < h < 16$	$-12 < h < 12$
	$0 < k < 13$	$-19 < k < 19$
	$-22 < l < 22$	$0 < l < 28$
Reflections collected	10040	13737
Independent reflections (R_{int})	2610 (0.032)	3616 (0.052)
Decay of standards [%]	1.16	3.45
Refinement:		
Data/restraints/parameters	2610/121/233	3616/0/180
Weighting parameter (a)[a])	0.0661	0.0668
Final R indices ($I > 2\sigma(I)$)		
R_1	0.0380	0.0396
wR_2	0.0942	0.0972
R indices (all data):		
R_1	0.0622	0.0591
wR_2	0.1014	0.1038
Goodness of fit (obs.)	1.004	1.031
Largest $\Delta\rho$ peak, hole [e Å^{-3}]	0.17, −0.15	0.77, −0.81

[a]) $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

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