

Supporting Information

Experimental

Crystal Data for 8b, 10b and 11b. Crystal data for the three salts are reported in Table S1, together with refinement details. The intensity data have been collected at room temperature. Unit cell constants were obtained by least-squares treatment of setting angles measured both before and after intensity data collection. In the case of **8b** cell dimensions were also determined twice during intensity measurements, because of significant variations of the unit cell edges a and c during X-ray exposure. The data reported in Table S1 for **8b** are therefore averaged values from four data sets.

Table S1

Setting angles and intensity data were measured on a Siemens P4 diffractometer, equipped with graphite-monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Diffracted intensities were collected with the ω - 2θ scan technique, at a fixed speed of 3 deg min^{-1} in 2θ . Stationary background counts were recorded on each side of the reflection and the ratio of peak counting time to background counting time was 2:1. Data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by direct methods with the SHELXS-86 program,¹ and their full matrix least-squares refinement, based on F^2 , was carried out using the SHELXL-93 program system.²

In **10b** the cation lies on a crystallographic mirror plane. The BF_4^- anions are found at two distinct special positions, namely along the screw axis 6_3 at $x=0, y=0$ and along the inversion axis 6 at $x=2/3, y=1/3$. In both cases the anions are disordered, and each of them was

described by two 50:50 partial occupancy tetrahedra, with the B-F distances constrained to be approximately equal. The non-H atoms, including those of the disordered BF_4^- groups, were refined with anisotropic thermal parameters. All the H atoms were placed in calculated positions, except those of the methyl group bonded to the S atom, which were located on a difference map and not refined further. The H atoms were assigned isotropic thermal parameters equivalent to 1.5-fold those of the attached C atom, and those included in the refinement were allowed to ride on their parent atoms. Of the two peaks $> 0.22 \text{ e } \text{\AA}^{-3}$ in the final ΔF map, the largest ($0.53 \text{ e } \text{\AA}^{-3}$) occurs at $x=0, y=0, z=1/2$, more than 2.65 \AA away from the closest atom. No attempt was made to interpret this residue, presumably an artifact related to the modeling of the disorder.

In **8b** no special treatment was applied to the 17 non-H atoms, refined anisotropically, although one of the four F atoms showed some rather anomalous U components and a short B-F distance. The coordinates of 20 H atoms (out of 23) of the asymmetric unit, as well as an individual isotropic thermal parameter for each H atom, were included among the least-squares variables. The remaining 3 H atoms, poorly resolved on the difference map, were placed at calculated positions ($\text{C-H} = 0.96 \text{ \AA}$), assigned $U(\text{H})=1.5 U(\text{C})$, and allowed to ride on their parent atom. Disorder was found also in one of the two crystallographically distinct BF_4^- groups of **11b**, located along the twofold axis at $x=1/2, z=1/4$. This was modeled by splitting each of the two independent F atoms into two equally populated positions, with no restraints on the B-F distances. All the H atoms of this structure were treated as the *tert*-butyl H atoms of **10b**. The 11 positive residues $> 0.22 \text{ e } \text{\AA}^{-3}$ in the ΔF map of **11b** were all located in the proximity ($0.9\text{-}1.2 \text{ \AA}$) of F or B atoms, indicating that disorder had been accounted for only to a first approximation.³

Crystal Data for 10a and 11c. **10a:** $C_{11}H_{23}S^+ SbCl_6^-$; crystal dimensions (mm), 0.40×0.30×0.20; space group, *Pnma*, No.62; cell dimensions (Å) at 293 K, $a=16.185(3)$, $b=12.991(3)$, $c=9.929(2)$; Z (molecules cell⁻¹), 4; volume (Å³), 2087.8(7); calcd density (g cm⁻³), 1.660; wavelength (Å), 0.71073; absorption coefficient (mm⁻¹), 2.18; reflections collected, 7824; independent, 1931; R_{int} , 0.019; decay after 120 h of exposure to X-rays, 11.8%. Data corrected for decay and absorption (max transmission 0.48, min 0.42), besides Lorentz and polarization effects.

11c: $C_{11}H_{21}S^+ PF_6^-$; crystal dimensions (mm), 0.40×0.35×0.18; space group, *Pnma*, No.62; cell dimensions (Å) at 293 K, $a=25.845(3)$, $b=9.644(1)$, $c=13.025(1)$; Z (molecules cell⁻¹), 8; volume (Å³), 3246.5(6); calcd density (g cm⁻³), 1.352; wavelength (Å), 0.71073; absorption coefficient (mm⁻¹), 0.34; reflections collected, 9909; independent, 2275; R_{int} , 0.039; decay after 92 h of exposure to X-rays, 1.52%. Data corrected for decay and Lorentz and polarization effects.

Both structures were solved using a combination of direct methods and Fourier techniques. However, although refined to R_1 indices of 0.0490 for **10a** and 0.0805 for **11c**, disorder at both anions and cations of the two structures is so extensive, and the uncertainties in atom positions so large, as to prevent any detailed discussion on the geometry of thiiranium and thiirenium ions.

Results and Discussion

X-Ray Structures. The main features of the experimental molecular geometries obtained by X-ray analysis of **8b**, **10b** and **11b** are reported in Table S2. Molecular conformations and numbering schemes for the corresponding thiiranium and thiirenium ions are shown in the

ORTEP plots⁴ of Figure S1. Experimental bond distances have been corrected for thermal motion effects, following the TLS analysis of the anisotropic displacement parameters (ADPs) proposed by Schomaker and Trueblood.⁵ The methyl atoms of the *tert*-butyl groups have been omitted from the treatment, and a satisfactory fit between calculated and observed ADPs has been obtained for the remaining six non-H atoms. In all three structures the resultant lengthening of the bond distances is larger for the S-C bonds than for the C-C bonds, and ranges between 0.009 and 0.016 Å. We have performed a similar treatment on the previously determined⁶ ADPs of **11b** at -100 °C, and compared the two sets of corrected distances, which should be the same within experimental uncertainty. The comparison indicates that corrections of the room temperature S-C distances might have been overestimated by about 0.005 Å.

Table S2 and Figure S1

In **10b** the anomalous shape of the ADPs ellipsoids (Figure S1) for atom C6 and its symmetry related C7 suggests that the crystallographic mirror symmetry probably results from an overall average of individually non-symmetric molecules. Indeed, the observed C6...C7 separation of 3.36(1) Å would imply for some H atoms of the *tert*-butyl groups contacts as short as 1.7 - 2.0 Å (vs. a 2.4 Å value for the sum of the van der Waals radii), depending on how the torsion angles of the idealized methyl groups are defined.

Differences in geometry between the thiiranium ions of **8b** and **10b** are clearly dictated by steric reasons: the relief from hindrance between the two *tert*-butyl groups of **10b** is achieved by (i) stretching the C2-C3 bond by 0.048 Å, as compared to the same bond in **8b**,

and (ii) increasing the C2-C3-C5 and C3-C2-C4 bond angles by about 10°, as compared to the corresponding angles in **8b**. Deformations in the thiiranium ion of **8b** are also related to interactions of the methyl group at sulfur with the nearest methyl of the *tert*-butyl group at C2 (see Figure 1). Here we note that (i) the S-C2-C4 angle is enlarged by more than 8° with respect to the S-C3-C5 angle; (ii) the C2-S bond is longer than the C3-S bond by 0.016 Å; (iii) the C1 methyl group is pushed away from the plane perpendicular to the ring plane, containing the S atom and bisecting the C2-C3 bond. This arrangement of the C1 methyl group is reflected in the difference by about 6° between the two exocyclic bond angles at the sulfur atom: C2-S-C1, 112.6°, and C3-S-C1, 106.8°. As a result of these deformations the shortest intramolecular distances between atoms of the two C1 and C6 methyl groups are only marginally shorter than the sum of van der Waals radii: C1...C6, 3.29(1) Å, H1B...H6B, 2.34(7) Å, and H1C...H6B, 2.37(7) Å. The presence in **8b** of a ring S-C2 bond slightly, yet significantly, longer than the S-C3 bond is worthy of note: it is the single geometrical feature that may be related to the different rearrangement rates for methyl migration from *cis* and *trans tert*-butyl groups in *trans* thiiranium ions **8** (see Table 1).

The comparison of the X-ray structures of the thiiranium ions **8b** and **10b** with the other two known X-ray structures of thiiranium cations shows that those in **4**⁷ and **5**⁸ are more sterically hindered. Indeed, the pyramidal configuration at the sulfur atom makes the non bonding interaction between the *S*-phenyl ring and the adamantylideneadamantane (in **4**) or the 1,2-dimethylacenaphthylene fragment (in **5**) much stronger than that between the *S*-methyl and the *tert*-butyl group as in **8b**. As a consequence, the endocyclic S-C bond distances in **4**, 1.909-1.937 Å, and in **5**, 1.970-1.987 Å, are substantially longer than those of **8b**, 1.845-1.867 Å before correction and 1.860-1.876 Å after correction for thermal motion. In spite of the relevant elongation of the S-C bonds in **4** and **5**, very short intramolecular contacts are

observed between atoms of the phenyl ring and those of the ring substituents: H...H separations in **4** of only 2.0 Å,⁷ and C-C separations in **5** as short as 3.04 and 3.12 Å, as calculated from the published positional parameters.⁸

A much closer agreement between *S*-phenyl- and *S*-methyothiiranium molecular dimension is observed for the ring bond angles. In particular, since in **4** the ring C-C bond length is also increased, as for the S-C bonds, by about 3% with respect to the corresponding one in **8b**, the ring bond angles of the two cations in the two structures are the same within the experimental uncertainty.

The sp² nature of the exocyclic carbon atom bonded to sulfur in **4** and **5** implies shorter S-C lengths than in **8b** and **10b**, with exocyclic sp³ carbon: **4**, 1.789 Å at 216 K; **5**, 1.784 Å at 183 K; **8b**, 1.798 Å uncorrected, 1.809 Å corrected; **10b**, 1.793 Å uncorrected, 1.807 Å corrected.

As for the overall crystal structures, the most relevant difference occurs in the anion-cation separation. While in **4** there are no interionic contacts significantly shorter than the corresponding sums of accepted van der Waals radii,⁷ and in **5** the interatomic distances between S and Cl atoms are larger than normal (3.74 Å),⁸ four S...F contacts shorter than 3.3 Å (3.21-3.24 Å) are observed in **10b**, and a separation as short as 3.122(4) Å occurs in **8b**. Furthermore, in both structures the H atoms of the *S*-methyl group are all involved in H...F contacts shorter than the sum (2.7 Å) of van der Waals radii. Similar short separations are observed also between the anion F atoms and the cation ring H atoms, with H...F contacts of 2.53(3) Å in **8b** and 2.43(1) Å in **10b**.

The molecular dimensions of the thiirenium ion in **11b** (Figure S1), determined in the present study at room temperature, were compared with those of earlier investigations⁶ at 173

K. As expected, a temperature difference of about 100°C will affect only marginally the bond angles, while significant changes (0.01 – 0.03 Å) occur in the *apparent* bond distances. Indeed, the two sets of nine bond angles at the ring atoms never differ by more than 0.3°, that is about twice the experimental uncertainty.

Other features of the thiirenium ion in **11b** are: (i) the length of the C2-C3 ring bond, 1.278 Å, even shorter than the C-C double bond in cyclopropene, 1.294 Å;⁹ (ii) the lengths of the endocyclic S-C bonds, shorter by about 0.03 Å (even if overestimated corrections are considered) than those of the thiiranium ions in **8b** and **10b**; (iii) the lengths of the C2-C4 and C3-C5 bonds < 1.50 Å, shorter by 0.02-0.03 Å than those of the thiiranium ions in **8b** and **10b**. All these features are consistent with the sp² nature of the ring C atoms.

As a final note, the crystals of thiirenium tetrafluoroborate **11b** appear to be more stable than those of the thiiranium tetrafluoroborate **8b** and **10b**: the radiation damage (see Table S1) was more serious, even with a much shorter X-ray exposure, for the latter crystals than for the former one, and also the examination of crystal samples kept for several months at -20 °C showed that only those of **11b** were still suitable for an X-ray investigation, while those of **8b** and **10b** were no longer single crystals.

References

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3. Atomic coordinates, displacement parameters and full listings of bond lengths and angles for **8b**, **10b** and **11b** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition No.s CCDC-117659, 117658, 117660, respectively. 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)336-033; e-mail: deposit@ccdc.cam.ac.uk]
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Table S1. Crystal data and structure refinement for **8b**, **10b** and **11b**.

	8b	10b	11b
empirical formula	C ₁₁ H ₂₃ B F ₄ S	C ₁₁ H ₂₃ B F ₄ S	C ₁₁ H ₂₁ B F ₄ S
formula weight	274.16	274.16	272.15
T (K)	293(2)	293(2)	291(1)
crystal size (mm)	sphere of radius 0.2	0.40x0.35x0.25	0.55x0.40x0.35
crystal system	orthorhombic	hexagonal	monoclinic
space group, no.	<i>Pbca</i> , 61	<i>P6₃/m</i> , 176	<i>P2/c</i> , 13
Unit cell dimensions (Å, deg)			
<i>a</i>	13.781(2)	12.981(1)	13.799(1)
<i>b</i>	11.702(1)	12.981(1)	8.619(1)
<i>c</i>	18.501(3)	15.966(1)	13.569(1)
α	90	90	90
β	90	90	113.37(1)
γ	90	120	90
Volume (Å ³)	2983.6(7)	2329.9(3)	1481.4(2)
Z	8	6	4
density (calcd) (g cm ⁻³)	1.221	1.172	1.220
absorption coeff (mm ⁻¹)	0.237	0.228	0.239
F(000)	1168	876	576
θ range for data collection (deg)	2.2 - 22.5	1.8 - 25.0	2.4 - 27.5
index ranges	0 < <i>h</i> < 14 -12 < <i>k</i> < 12 -19 < <i>l</i> < 19	-13 < <i>h</i> < 13 0 < <i>k</i> < 13 -18 < <i>l</i> < 0	-17 < <i>h</i> < 17 -11 < <i>k</i> < 11 -17 < <i>l</i> < 17
reflections collected	7430	4275	13588
independent reflections [<i>R</i> _{int}]	1955 (0.055)	1427 (0.035)	3403 (0.020)
decay of standards (%)	14.18	9.19	4.85
Refinement			
data/restraints/parameters	1952/0/238	1427/15/99	3403/0/180
weighting parameters (<i>a, b</i>) ^a	0.1236, 0.0	0.0994, 0.7059	0.1288, 0.0
final R indices [<i>I</i> > 2σ (<i>I</i>)]			
<i>R</i> ₁	0.0635	0.0597	0.0589
<i>wR</i> ₂	0.1740	0.1687	0.1841
R indices (all data)			
<i>R</i> ₁	0.0966	0.0946	0.0759
<i>wR</i> ₂	0.1953	0.1938	0.1950
goodness of fit	1.001	1.056	1.090
largest Δρ peak, hole (e Å ⁻³)	0.41, -0.22	0.53, -0.23	0.63, -0.24

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

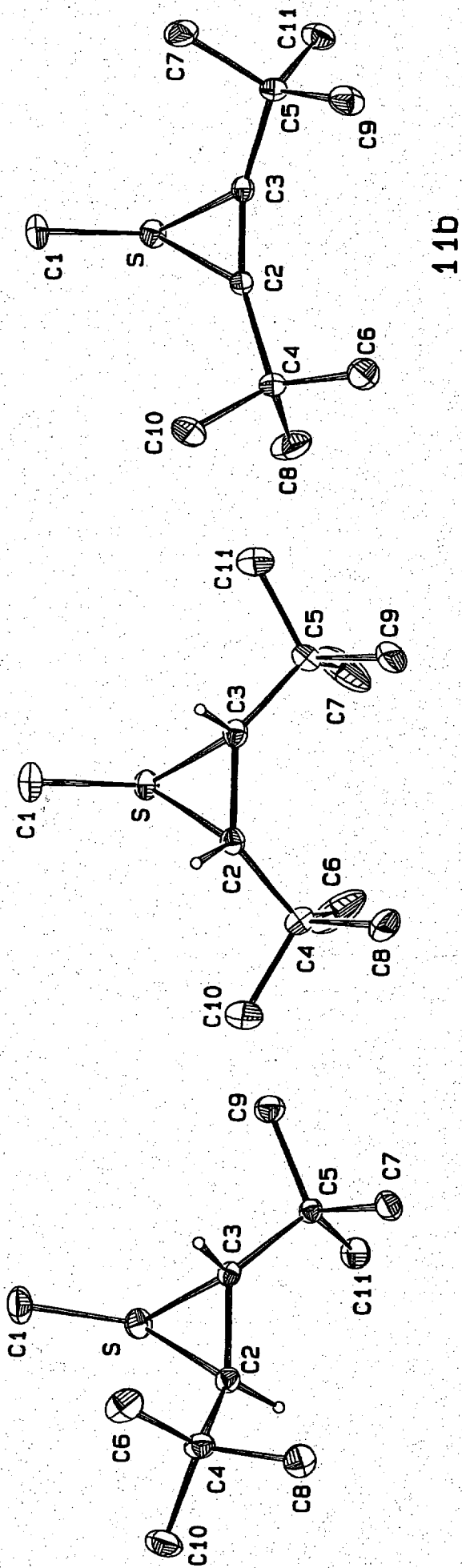


Figure S1

Table S2. Some relevant bond lengths^a (Å) and angles (deg) for **8b**, **10b** and **11b**, obtained by X-ray analysis.^b

	8b	10b	11b
C1 - S	1.809(8)	1.807(4)	1.817(2)
C2 - S	1.876(4)	1.859(3)	1.831(1)
C3 - S	1.860(4)	1.859(3)	1.831(2)
C2 - C3	1.452(6)	1.500(6)	1.278(3)
C2 - C4	1.518(5)	1.531(4)	1.497(3)
C3 - C5	1.527(6)	1.531(4)	1.496(3)
C2 - S - C3	45.7(1)	47.6(2)	40.85(9)
S - C2 - C3	66.6(2)	66.21(9)	69.5(1)
S - C3 - C2	67.7(2)	66.21(9)	69.6(1)
S - C2 - C4	125.1(2)	119.2(2)	134.0(1)
S - C3 - C5	117.1(3)	119.2(2)	133.3(1)
C3 - C2 - C4	127.0(3)	135.4(2)	156.4(2)
C2 - C3 - C5	125.5(3)	135.4(2)	157.1(1)

^a Corrected for thermal motion effects after TLS analysis (ref. 5).

^b Standard uncertainties in parentheses.