Structure of *trans*-4-*tert*-Butyl-1-[*N*-ethyl-*N*-*p*-toluenesulfonylamino]-1-thioniacyclohexane Fluoroborate. Evidence for p(N)–d(S) π Bonding[1]

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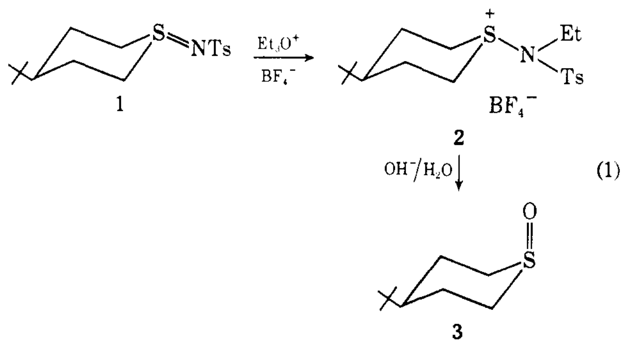
Abstract: The crystal and molecular structures of the title compound have been determined. The thiacyclohexane ring was found to be in the chair conformation with the 1 and 4 substituents equatorial. This crystallographic study provides the first unequivocal assignments of structure and stereochemistry to a geometrical sulfilimine isomer. Chemical correlations based on the title compound confirm earlier stereochemical assignments made to 4-*tert*-butylthiane 1-oxides. The SNS and SNC bond angles totaling 356° are consistent with a sp^2 hybridized nitrogen and suggest significant p–d π bonding. The conformation about the sulfonium sulfur–nitrogen bond suggests that the dihedral angle between the sp^3 lone pair on sulfur and p lone pair on nitrogen is 90° at which point lone pair–lone pair repulsion should be minimized.

In this article we report the details of the crystal and molecular structure of a representative example of a new class of sulfur compounds—aminosulfonium salts.[2] Structurally these materials are distinguished by having a fully substituted trigonal nitrogen bonded directly to a sulfonium sulfur; prior to this investigation there have been few, if any, absolute statements concerning the configuration about three-coordinated nitrogen bonded to sulfur. The spatial arrangement about such a nitrogen is of particular interest for its bearing on p–d π bonding and of current interest concerning slow rotation about nitrogen–heteroatom bonds *vs.* slow pyramidal inversion at nitrogen.[3]

These aminosulfonium salts are most directly prepared by the alkylation of sulfilimines. The example chosen for this crystal study was of further interest in that the structure would provide the first unequivocal assignment to a geometrical isomer in the sulfilimine series and could be directly related to sulfoxide stereochemistry (eq 1). Because of the intriguing conformational characteristics suggested in earlier work (axial oxygen preferred over equatorial)[4] it is of special importance to establish structures firmly in the 4-*tert*-butylthiane series.



Ts = p-$CH_3C_6H_4SO_2$
Et = C_2H_5

Discussion

A perspective drawing of the *trans*-4-*tert*-butyl-1-[*N*-ethyl-*N*-*p*-toluenesulfonylamino]-1-thioniacyclohexane cation showing bond lengths is given in Figure 1

Table I. Bond Angles for the *N*-Ethylsulfilimine Cation[a]

			Angle, deg
O(1)	S(1)	O(2)	121.1
O(1)	S(1)	N	106.3
O(1)	S(1)	C(1)	108.5
O(2)	S(1)	N	104.7
O(2)	S(1)	C(1)	110.1
N	S(2)	C(1)	104.9
C(8)	S(2)	N	105.9
C(8)	S(2)	C(12)	100.6
C(12)	S(2)	N	107.5
S(1)	N	S(2)	114.5
S(1)	N	C(17)	119.6
S(2)	N	C(17)	121.9
S(1)	C(1)	C(2)	121.2
S(1)	C(1)	C(6)	119.0
C(2)	C(1)	C(6)	119.8
C(1)	C(2)	C(3)	119.2
C(2)	C(3)	C(4)	122.3
C(3)	C(4)	C(5)	118.1
C(3)	C(4)	C(7)	121.3
C(5)	C(4)	C(7)	120.6
C(4)	C(5)	C(6)	122.3
C(5)	C(6)	C(1)	118.2
S(2)	C(8)	C(9)	107.4
C(8)	C(9)	C(10)	113.3
C(9)	C(10)	C(11)	108.4
C(9)	C(10)	C(13)	113.2
C(11)	C(10)	C(13)	111.8
C(10)	C(11)	C(12)	112.0
S(2)	C(12)	C(11)	106.0
C(10)	C(13)	C(14)	108.9
C(10)	C(13)	C(15)	109.8
C(10)	C(13)	C(16)	112.7
C(14)	C(13)	C(15)	104.8
C(14)	C(13)	C(16)	111.1
C(15)	C(13)	C(16)	109.3
N	C(17)	C(18)	111.1

[a] Standard deviations calculated from the variance–covariance matrix average 0.3° for angles involving S(1) and S(2) and 0.5° for other angles.

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[1] Part XXIV in the series "Chemistry of Sulfoxides and Related Compounds"; we gratefully acknowledge the support of the National Science Foundation (Grant No. GP-8648).

[2] C. R. Johnson, J. J. Rigau, D. McCants, Jr., J. E. Keiser, and A. Geertsema, *Tetrahedron Lett.*, 3719 (1968).

[3] For pertinent examples, see M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, 91, 6677 (1969), and previous papers.

[4] C. R. Johnson and D. McCants, Jr., *ibid.*, 87, 1109 (1965).

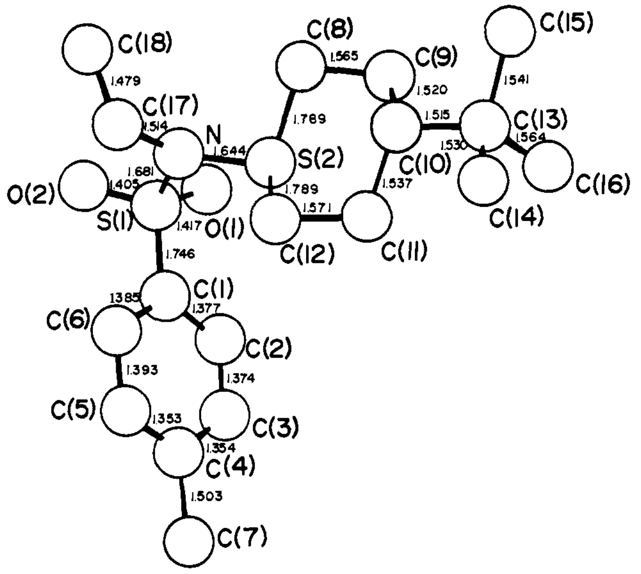

Figure 1. The *trans*-4-*tert*-butyl-1-[*N*-ethyl-*N*-*p*-toluenesulfonylamino]-1-thioniacyclohexane cation. Bond lengths (ångströms) involving sulfur have standard deviations of 0.005 Å; other bond lengths have standard deviations of 0.008 Å.

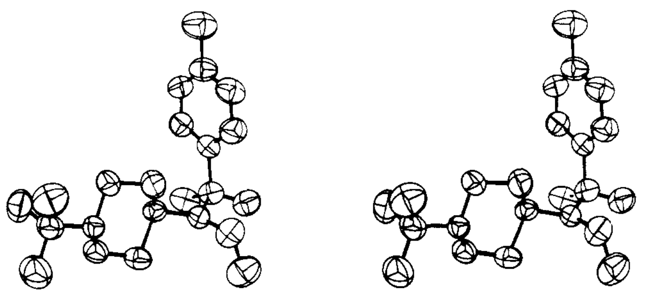

Figure 2. A stereoscopic view of the cation.

and a stereoscopic view is shown in Figure 2. Bond length and angle data for the cation are summarized in Table I; the disordered tetrahedral fluoroborate bond lengths range from 1.26 to 1.36 Å. The crystal structure reveals that structures of the sulfoxides,[4] and subsequently a sulfilimine,[5] and sulfoximines[5] in the 4-*tert*-butylthiane series were correctly assigned on the basis of chemical and physical correlations.

The thiacyclohexane ring is found in the expected chair conformation. The spatial arrangement about nitrogen is particularly noteworthy. The sum of the bond angles about nitrogen is 356°; the nitrogen lies only 0.19 Å out of the C(17)-S(1)-S(2) plane.[6] This suggests that the nitrogen is sp^2 hybridized in order to allow the remaining filled p orbital to participate more effectively in d-p π bonding with S(1) and S(2). The S-N bond lengths are shorter than the theoretically calculated 1.74 Å for a S-N single bond from Pauling's atomic radii. The S(2)-N bond (1.644 Å) is somewhat shorter than the S(1)-N bond (1.681 Å). The effectiveness of S(1), the sulfonyl sulfur, in participating in d-p π bonding with nitrogen may be somewhat diminished by involvement of S(1) in π bonding with the oxygens and aromatic ring. Kalman[7] has determined the crystal structure of a simple sulfilmine (Figure 4). In this case the O_2S-N bond distance is the shorter of the two. These differences perhaps can be accounted for by variation in the relative amounts of partial positive charge on the various sulfur atoms and/or involvement of the

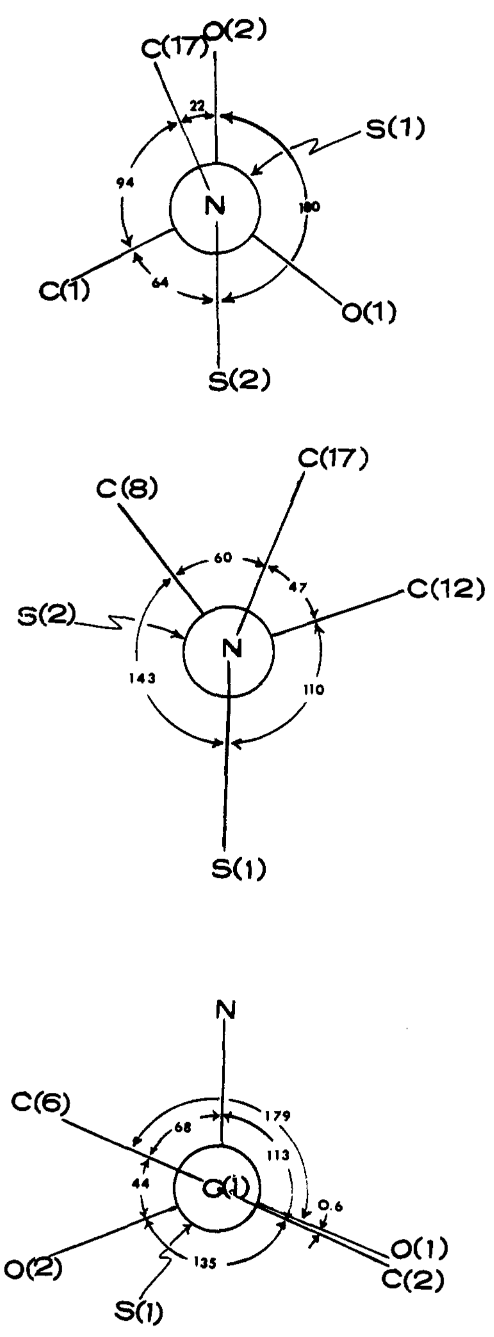

Figure 3. Selected torsional angles.

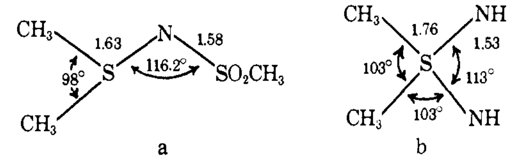

Figure 4. (a) *N*-Methanesulfonyldimethylsulfilimine (ref 5); (b) dimethyl sulfone diimine (ref 4).

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(5) C. R. Johnson and J. J. Rigau, *J. Org. Chem.*, **33**, 4340 (1968).

(6) Interesting examples of coplanar bonds about trisubstituted nitrogen bonded to phosphorus have been reported: M. D. LaPrach and C. E. Nordman, *Inorg. Chem.*, **8**, 1669 (1969), and E. D. Morris, Jr., and C. E. Nordman, *ibid.*, **8**, 1673 (1969).

(7) A. Kalman, *Acta Crystallogr.*, **22**, 501 (1967).

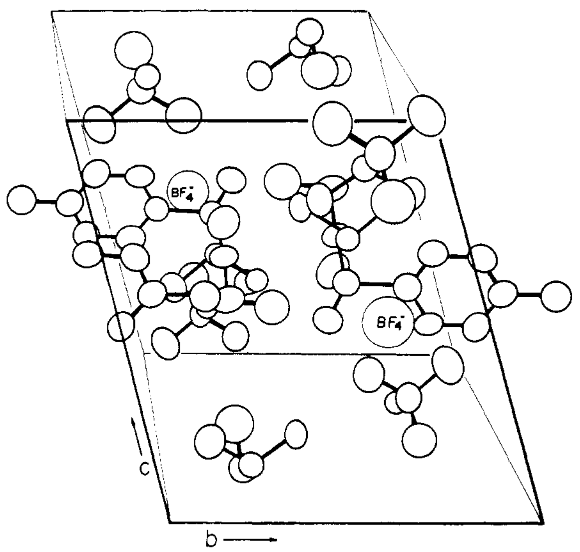


Figure 5. Molecular packing diagram of *trans*-4-*tert*-butyl-1-[*N*-ethyl-*N*-*p*-toluenesulfonylamino]-1-thioniacyclohexane fluoroborate.

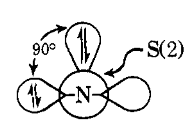
phenyl group. Webb and Glass[8] have examined the crystal and molecular structure of dimethyl sulfone diimine (Figure 4). In this instance the S–N bond distances were found to be 1.53 Å. They have tabulated pertinent distances and angles for a number of related molecules. Recently S–N bond distances averaging 1.65 Å were found for dibenzenesulfonamide[9] Further commentary on the meaning of such bond-length data is unwarranted until additional crystal structures become available.

Table II. Final Coordinates (× 10^4) and Thermal Parameters (× 10^4) for Nonhydrogen Atoms of the *N*-Ethylsulfilimine Salt[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	2743 (2)	3377 (2)	5072 (1)	153 (2)	155 (2)	95 (2)	−34 (2)	20 (2)	20 (2)
S(2)	190 (1)	3193 (1)	2986 (1)	130 (2)	125 (2)	96 (2)	−13 (1)	37 (1)	33 (1)
O(1)	2035 (1)	4280 (4)	5769 (3)	262 (7)	152 (5)	120 (5)	0 (5)	64 (5)	12 (4)
O(2)	4095 (4)	3597 (4)	5305 (4)	168 (6)	254 (7)	161 (5)	−83 (5)	−4 (5)	64 (5)
N	1835 (4)	3429 (4)	3511 (4)	128 (6)	173 (7)	98 (5)	−22 (5)	39 (4)	32 (4)
C(1)	2625 (7)	1710 (6)	5159 (5)	143 (8)	147 (8)	98 (6)	0 (6)	41 (6)	17 (6)
C(2)	1919 (6)	1442 (6)	5814 (5)	179 (9)	182 (10)	128 (7)	11 (7)	81 (7)	33 (7)
C(3)	1856 (7)	115 (7)	5860 (6)	221 (10)	178 (10)	163 (9)	−28 (8)	93 (8)	49 (8)
C(4)	2447 (7)	−951 (6)	5263 (6)	205 (10)	162 (9)	121 (7)	−16 (8)	59 (7)	39 (7)
C(5)	3133 (7)	9319 (7)	4617 (6)	251 (12)	162 (10)	157 (8)	36 (8)	102 (9)	35 (7)
C(6)	3262 (7)	644 (7)	4560 (6)	214 (11)	193 (10)	161 (8)	−2 (8)	103 (8)	49 (8)
C(7)	2308 (8)	7601 (7)	5279 (7)	391 (16)	183 (11)	226 (11)	6 (10)	171 (11)	57 (8)
C(8)	675 (6)	5693 (5)	8105 (5)	186 (9)	114 (7)	121 (7)	−19 (6)	31 (6)	34 (5)
C(9)	2217 (6)	6061 (5)	8799 (5)	172 (9)	115 (7)	144 (7)	−11 (6)	37 (6)	28 (6)
C(10)	7568 (5)	2503 (5)	362 (4)	131 (7)	111 (7)	100 (6)	−21 (5)	37 (5)	17 (5)
C(11)	8255 (6)	1478 (6)	1241 (6)	144 (8)	165 (9)	160 (8)	−8 (7)	19 (6)	59 (7)
C(12)	9857 (6)	1564 (6)	1889 (6)	150 (9)	128 (8)	198 (9)	−18 (6)	37 (7)	14 (7)
C(13)	3928 (6)	7775 (6)	470 (5)	145 (8)	147 (8)	130 (7)	−20 (6)	31 (7)	34 (6)
C(14)	4020 (7)	9205 (7)	1408 (7)	258 (12)	202 (11)	215 (10)	−45 (9)	65 (9)	−9 (9)
C(15)	4556 (7)	6751 (7)	1359 (7)	200 (11)	248 (12)	184 (10)	−24 (9)	−2 (8)	71 (9)
C(16)	4770 (7)	7693 (7)	−325 (7)	172 (10)	256 (12)	251 (11)	−41 (8)	74 (9)	51 (9)
C(17)	2561 (7)	3159 (7)	2604 (6)	186 (11)	269 (12)	141 (8)	−57 (9)	52 (8)	33 (8)
C(18)	3026 (8)	4441 (8)	2566 (7)	265 (13)	272 (13)	205 (11)	−81 (11)	76 (10)	38 (9)

[a] Standard deviations estimated by least squares are given in parentheses for the least significant digit. The anisotropic thermal parameters are of the form $\exp[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

The spatial arrangement observed about S(2)–N suggests that the angle between the direction of the sp^3 lone pair on S(2) and the p lone pair on the planar



nitrogen is in the vicinity of 90°. This is in accord with many previous suggestions that the torsional angle between bonded heteroatoms is largely determined by valence electron lone pair–lone pair repulsions.[10]

The packing diagram shown in Figure 5 indicates the position of the fluoroborate group, represented as a sphere, relative to the cation.

Solution to the Structure

A three-dimensional Patterson map of 1060 low-angle reflections revealed the apparent positions of the two sulfur atoms consistent with $P\bar{1}$; thus centrosymmetry was assumed. Least-squares refinement of the scale factor, using the sulfur positions, yielded an unweighted discrepancy factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.56. A Fourier map based on the two sulfur positions yielded the 12 atomic positions of the two rings as well as possible positions for several other atoms. These 14 positions were then used to phase a second Fourier map which resulted in the presumed determination of the remaining atomic positions.

Least-squares refinement of all positional and thermal parameters, however, only lowered the discrepancy factor R_1 to 0.171. A difference Fourier map indicated areas of large positive and negative electron density in the vicinity of the BF_4^- group, suggesting possible dis-

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(8) N. C. Webb and R. A. Glass, *Tetrahedron Lett.*, 1043 (1967).

(9) F. A. Colton and P. F. Stokely, *J. Amer. Chem. Soc.*, **92**, 294 (1970).

(10) Skewed configurations for compounds of the type $-\ddot{X}-\ddot{Y}-$ were predicted as early as 1934: W. G. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 492 (1934). For recent exemplary discussions, see A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, **90**, 4185 (1969); M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970); and M. Raban and G. W. J. Kenney, Jr., *ibid.*, 1295 (1969).

Table III. Final Coordinates ($\times 10^3$) and Thermal Parameters ($\times 10^3$) for the Fluoroborate Anion

Atom	W^a	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F(11)	0.51	−27 (5)	142 (1)	873 (6)	64 (7)	21 (2)	59 (8)	−12 (2)	48 (7)	−5 (2)
F(12)	0.59	42 (4)	347 (1)	948 (2)	69 (7)	20 (2)	18 (2)	−1 (2)	21 (2)	2 (1)
F(13)	0.39	164 (2)	176 (3)	895 (3)	36 (4)	19 (4)	78 (7)	4 (2)	21 (4)	14 (3)
F(14)	0.45	16 (3)	251 (4)	761 (2)	55 (7)	26 (4)	24 (3)	−14 (3)	24 (4)	−5 (2)
F(21)	0.54	−65 (3)	318 (2)	851 (4)	38 (4)	33 (3)	50 (7)	17 (3)	30 (4)	25 (4)
F(22)	0.54	65 (3)	166 (2)	961 (2)	47 (4)	21 (2)	16 (2)	1 (2)	13 (2)	5 (1)
F(23)	0.54	156 (1)	281 (3)	882 (2)	24 (2)	30 (4)	53 (4)	0 (2)	15 (2)	13 (3)
F(24)	0.52	9 (2)	148 (5)	760 (1)	42 (3)	37 (6)	17 (2)	−12 (2)	9 (2)	−3 (2)
B	1.00	−39 (1)	765 (1)	129 (1)	19 (1)	11 (1)	12 (1)	0 (1)	8 (1)	3 (1)

[a] W is the weighting factor of the atom.

Table IV. Final Coordinates ($\times 10^3$), Thermal Parameters, and Bond Distances for Hydrogen Atoms of the *N*-Ethylsulfilimine Salt[a]

Atom	x	y	z	B, Å^2	D, Å
H(C2)	141 (1)	213 (1)	622 (1)	3.7 (3)	0.97
H(C3)	129 (1)	000 (1)	631 (1)	4.2 (3)	0.99
H(C5)	336 (1)	859 (1)	413 (1)	6.0 (4)	0.88
H(C6)	371 (1)	92 (1)	407 (1)	6.0 (4)	1.00
H(C7)	201 (2)	752 (1)	577 (1)	5.6 (4)	0.79
H(C7′)	262 (2)	714 (2)	467 (2)	7.9 (5)	0.90
H(C7″)	342 (2)	739 (2)	573 (2)	9.0 (5)	1.10
H(C8)	26 (1)	586 (1)	868 (1)	2.6 (3)	0.92
H(C8′)	52 (1)	470 (1)	743 (1)	2.9 (3)	1.09
H(C9)	209 (2)	554 (2)	889 (2)	7.1 (4)	0.61
H(C9′)	262 (2)	592 (1)	804 (1)	6.4 (4)	1.11
H(C10)	818 (2)	226 (2)	−24 (1)	6.4 (4)	1.11
H(C11)	839 (2)	118 (2)	62 (2)	8.3 (5)	0.78
H(C11′)	801 (1)	188 (1)	208 (1)	3.9 (3)	1.09
H(C12)	948 (2)	135 (2)	219 (2)	8.9 (5)	0.72
H(C12′)	35 (1)	156 (1)	119 (1)	2.7 (3)	1.14
H(C14)	458 (2)	905 (2)	122 (1)	6.3 (4)	0.70
H(C14′)	363 (2)	996 (2)	92 (2)	8.6 (5)	1.01
H(C14″)	333 (2)	929 (2)	193 (1)	7.3 (5)	1.13
H(C15)	536 (2)	696 (2)	178 (1)	7.1 (4)	0.83
H(C15′)	469 (2)	587 (2)	74 (1)	7.1 (4)	1.03
H(C15″)	401 (2)	715 (2)	195 (2)	8.1 (5)	1.05
H(C16)	465 (1)	684 (1)	−79 (1)	4.7 (4)	0.90
H(C16′)	471 (1)	848 (1)	−60 (1)	4.5 (3)	0.92
H(C16″)	583 (2)	777 (2)	29 (2)	7.0 (4)	1.07
H(C17)	185 (1)	265 (1)	174 (1)	3.7 (3)	1.04
H(C17′)	361 (1)	276 (1)	267 (1)	4.2 (4)	1.12
H(C18)	371 (2)	491 (2)	340 (2)	7.7 (5)	0.99
H(C18′)	234 (2)	503 (1)	199 (1)	7.6 (4)	1.01
H(C18″)	364 (2)	381 (2)	192 (2)	8.7 (4)	1.20

[a] Standard deviations given in parentheses are for least significant figures. Estimated standard deviations for bond distances are about 0.10 Å for CH bond distances.

order. The positions of the disordered fluorines could not easily be identified due to large amounts of overlapping. A second difference map was run with the addition of 714 higher angle reflections in order to increase the resolution of the map. This second map gave the positions of seven distinct peaks around the boron which roughly corresponded to one BF_4^- group related to another BF_4^- group by a rotation about a common B–F bond. Least-squares refinement continued by varying the seven fluorine positions and thermal parameters, considering six fluorines as half-weight and one fluorine as full weight. The discrepancy factor would not, however, refine below 0.153 and the fluorine thermal parameters refined to values between 9 and 15. Anisotropic thermal parameters were then varied on all noncarbon atoms and reduced the R to 0.118. A third difference Fourier map located the 30 hydrogen atoms in the structure.

Owing to computer space considerations in the remaining least-squares refinement, the hydrogen contribution to the calculated structure factors was separated from the nonhydrogen contribution and each part was refined separately but with the contribution from the other portion added into the calculation. Bond distances and angles were calculated and yielded expected values, except for bond angles (81–143°) between the fluorine which was given full weight and the fluorine half-atoms. Refinement was thus continued with eight fluorine half-atoms, yielding a final R_1 of 0.068 and a weighted discrepancy factor of $\{\Sigma w(|F_o| - |F_c|)^2/w|F_o|^2\}^{1/2} = 0.068$ for 2212 observed data. All FBF angles were found to be near 109°. Final atomic parameters, with estimated standard deviations calculated from the full variance–covariance matrix,[11-13] are given in Table II.

The large overlapping thermal ellipsoids of the fluorines almost fill a sphere about the boron indicating that the group is described equally well by a freely rotating model or a disordered model. Of course, a third possibility is that the space group is $P1$ and the fluoroborate anion packs in an ordered fashion. Attempts to refine noncentrosymmetric parameters with the fluoroborate group in alternate orientations (*i.e.*, the two fluoroborate groups in the unit cell in the same orientation rather than related by the inversion center) yielded a poorer fit of the data.

Experimental Section

The preparation of *trans*-4-*tert*-butyl-1-[*N*-ethyl-*N*-*p*-toluenesulfonylamino]-1-thioniacyclohexane fluoroborate has been described.[4] Optical examination of the salt revealed large, transparent, colorless crystals with well-defined faces. Examination by X-rays, however, proved the crystals to be extremely poor diffractors. Several crystals studied in the preliminary film investigation produced no diffracted intensity. This is thought to be a result of disorder. After more than a dozen crystals were examined, a crystal was found for which diffraction was intense enough to permit data collection.

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(11) Form factors were obtained from the "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1968, pp 210–216.

(12) Calculated and observed structure factors are deposited as Document No. NAPS-01119 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting \$2.00 for microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to CCMI–NAPS.

(13) The programs used in the solving of this structure include local versions of the following programs: PICK 2, J. A. Ibers' least-squares program for lattice constants and orientation angles based on W. C. Hamilton's MODE 1; DACOR, a program for Lorentz polarization corrections and calculation of intensity standard deviations; FORDAP, A. Zalkin's Fourier program; ORFLS and ORFEE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP, C. K. Johnson's program for the drawing of crystal structures.

Even this crystal contained some disordered atoms, as described above.

The lack of symmetry in the film characterization implied space groups $P1$ or $P\bar{1}$. The final triclinic cell parameters determined from least-squares analysis of 22 reflections centered with Mo Kα_1 radiation on a Picker four-circle diffractometer were found to be a = 10.757 (8), b = 10.141 (8), c = 11.698 (9) Å, and α = 104.95 (2), β = 114.83 (2), γ = 81.33 (2). The density, assuming two chemical species per unit cell, calculated to be 1.30 g/cc which is in agreement with the observed density of 1.29 (±0.03) g/cc.

Intensity data were collected by the moving counter-moving crystal ($\theta - 2\theta$) method with scan range of 1.70° (0.75 before the peak maximum and 0.95 after) (DATA) and backgrounds of 15 sec each (BK1 and BK2). Zr-filtered Mo Kα radiation was used and the pulse height analyzer was set to accept 90% of the radiation. Data were collected in the region $+h$, $\pm k$, $\pm l$ out to 2θ of 45°. An equivalent data set was taken in the region $-h$, $\pm k$, $\pm l$ but was not used due to instrument problems which developed during the collection. Throughout the data collection, six standard reflections (004, 222, 115, 040, 500, and 422) were checked and indicated a 3.1% loss of intensity per 1000 reflections. Fourteen of the reflections in the unique set of data diffracted with intensities beyond the linear range of the detector and were rerun with an attenuator which had been standardized with reflections in the linear range. Of the 2933 data in the independent set, 2212 were found to have intensities greater than 1.5 standard deviations, where $\sigma(\mathrm{I}) = [\mathrm{DATA} + \mathrm{BK1} + \mathrm{BK2} - 0.03^2(\mathrm{DATA} - \mathrm{BK1} - \mathrm{BK2})^2]^{1/2}$. No corrections were made for the absorption of the crystal.

The Conformational Preferences of the *N*-Trimethylsilyl and *O*-Trimethylsilyl Groups[1]

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Received March 13, 1970

Abstract: *O*-Trimethylsilylcyclohexanol (I), *N*-trimethylsilylcyclohexylamine (II), and the *cis*- and *trans*-4-methyl and *cis*- and *trans*-4-*tert*-butyl derivatives of these molecules have been synthesized. Measurements at 100 and 220 MHz of the nmr chemical shifts of the α protons of the unsubstituted and *cis*- and *trans*-4-*tert*-butyl-substituted compounds were used to obtain values of 1.21 and 0.88 kcal mol^{-1} for the conformational free energy preferences (*A* values) of the $-\mathrm{NHSiMe_3}$ and $-\mathrm{OSiMe_3}$ groups, respectively. In addition, *A* values of 1.15 and 0.93 kcal mol^{-1}, respectively, for these same groups were estimated from the chemical shift data for the *cis*-4-methyl compounds, assuming an *A* value of 1.70 kcal mol^{-1} for the methyl group. The close agreement between these two methods suggests that in the present case, at least, accurate measurement of conformational preferences may be obtained by the chemical shift method. The present results are discussed in light of recent criticism of this method. An unusually large value for a HCNH proton–proton coupling of 10 Hz was observed for II.

Increasing use is being made of trimethylsilylation techniques to volatilize large molecules and polar hydrogen bonded molecules,[2] especially those of biological interest such as steroids[3] and amino acids.[4] In a recent article[3] Chambaz and Horning described the reactions of several trimethylsilylating reagents and discussed the effect of reaction conditions and the influence of steric effects on reaction rates and on the structure of products. They showed that under similar silylating conditions, the axial hydroxyl of 5β-androstan-3β-ol-17-one reacted more slowly than the equatorial hydroxyl of 5-androstan-3α-ol-17-one. Wilson and Ripley have attributed the physical behavior of $-\mathrm{OSiMe_3}$ derivatives of steroids during gas chromatographic analysis to conformational changes wrought on the steroid nucleus by conversion of a hydroxyl group to what one might anticipate to be a more bulky trimethylsilyl ether.[5,6] Eaborn[7] has summarized data which show that reaction rates and equilibria of various trialkylsilyl compounds are subject to steric effects. When a $-\mathrm{SiMe_3}$ group is bonded to a ring carbon in substituted cyclohexanes its steric influence appears to be similar to that of a *tert*-butyl group.[8,9] However, when the silicon atom is not bonded directly to a ring carbon but is separated by a nitrogen or oxygen atom, the steric requirements of the resulting silylamine or silyl ether are less certain. To clarify this situation we report in detail the determinations of the equatorial–axial free energy differences (*A* values)[10] of the $-\mathrm{OSiMe_3}$ and $-\mathrm{NHSiMe_3}$ groups by two proton nmr methods.

Method

The first approach used (method 1) is that originally described by Eliel.[11,12] In this method the nmr chemical shift of the α-proton of a conformationally mobile cyclohexyl compound is compared with the shifts of the α-protons in the corresponding conformationally rigid *cis*- and *trans*-4-*tert*-butylcyclohexyl derivatives (see Figure 1). The *A* value is then calculated from the equation[13]

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(1) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

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