Title
SYNTHESIS AND STEREOSTRUCTURE OF A BICYCLIC SULFONIUM SALT

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SYNTHESIS, STEREOSTRUCTURE, PYRAMIDAL INVERSION, AND ALKYLATION OF 1-THIONIABICYCLO[4.4.0]DECANE SALTS[1]

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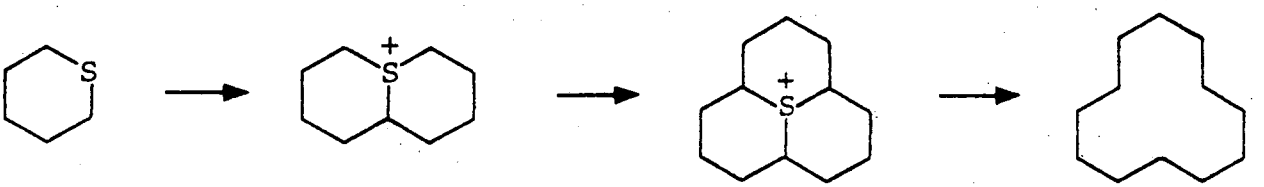
INTRODUCTION

The synthesis of multifunctional macrocycles such as the macrolide antibiotics[3] confronts the chemist with two vexing problems: formation of the macrocycle and stereospecific introduction of a number of chiral centers on the conformationally mobile ring. Both these problems can be circumvented if the macrocycle is constructed as the periphery of a rigid polycyclic system of smaller rings. Proper relative chirality may be imparted to the various centers by taking advantage of the rigidity of the intermediate polycycle, after which appropriate bond cleavages will yield the macrocycle. Various versions of this strategy have been studied.[4] In our version of this approach, the macrocycle would be constructed in several steps around a template atom, which would be removed in a penultimate step. As the template, we selected sulfur, since it could provide activation for carbon-carbon bond formation, and might be more easily removable

than other atoms. This approach is illustrated below for the possible synthesis of a simple macrocycle, cyclododecane. The method



i *ii* *iii* *iv*

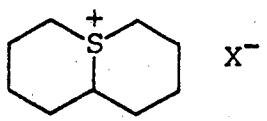
would be applicable to the synthesis of rings of virtually any size, given the required starting cyclic sulfides, which themselves might be available by carbon-sulfur bond cleavage at the bicyclic stage.

ii *v*

However, several fundamental questions must be answered before this approach can be utilized in complex synthesis. First, an efficient annelation[5] technique (e.g., *i* → *ii*, *ii* → *iii*) must be developed. Second, bicyclic and tricyclic salts such as *ii* and *iii* may each exist in two diastereomeric forms. One must know something of their relative stability and ease of interconversion. Third, one must know something of the stereochemistry of alkylation of rigid salts such as *ii*. Finally, the practicality of working with intermediate salts such as *ii* and *iii* must be examined. In this paper, we present the results of our initial steps toward answering some of these questions.

Synthesis of Bicyclic Sulfonium Salts

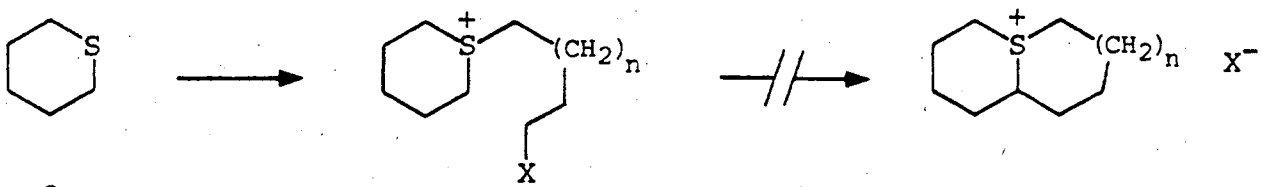
In 1959, Eastman and Kritchevsky reported the synthesis of salt 1,[8] which seemed an ideal model for our purposes. However, in Eastman's synthesis of 1, the bicyclic salt is formed by closure of



1

both rings starting with a symmetrical dihydroxythiol. This procedure is not sufficiently general for the purpose we have in mind, which is to construct the two rings consecutively and thus have access to both symmetrical and unsymmetrical bridgehead sulfonium salts.

We first examined the approach to such salts which is outlined below. The S-3-iodopropyl- and S-4-iodobutylthianium salts 3 and 4 are produced in 60% and 50% yield, respectively, upon allowing thiane (2) to react with the appropriate diiodide at 25° C for eight days.



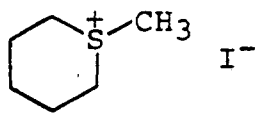
2

3: n = 0, X = I
4: n = 1, X = I
5: n = 0, X = Cl
6: n = 1, X = Cl

1: n = 1

Alternatively, chloroalkylsulfonium salts 5 and 6 may be obtained in about 50% yield by treating thiane with the appropriate dialkoxycarbonium tetrafluoroborate[9] in methylene chloride for 20 h at 25° C.

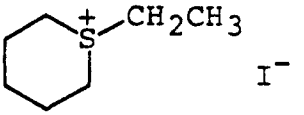
Unfortunately, we were not able to induce ring closure to occur by treating salts 3-6 with bases under a variety of conditions. Although we were not able to identify any of the products from reaction of 3-6 with bases (they seem to be polymeric salts), it is clear from spectra of the crude product that Eastman's salt (1) is not formed in attempted cyclization of 4 or 6. It occurred to us that the failure of salts 3-6 to cyclize might be due to the fact that the exocyclic methylene groups are more acidic than the ring methylenes. However, Fava and co-workers had found that at 35° C the methylene protons in 7 exchange at approximately the same rate as those in the acyclic salt 8.[10,11] Even so, we examined the rates of exchange of the two types of



7

$(CH_3CH_2)_2\overset{+}{S}CH_3\ I^-$

8



9

methylene groups in salts 7 and 9 with NaOD in D_2O at 25° C. Surprisingly, the exocyclic methylene protons in salt 9 were found to exchange *much more rapidly* than the ring methylene protons. Data are summarized in Table I. For comparison, the Fava data for salt 7 have been extrapolated to the appropriate temperature and included in Table I. Our experimental procedure differs from theirs in that we used solutions 0.1 M in salt while they measured exchange on 1.0 M solutions; both sets of experiments employed 5.0 M NaOD. Comparison of the rates of exocyclic methylene exchange in 9 and ring methylene exchange in 7 reveals that the exocyclic protons are removed 75 times more rapidly. The reason for this substantial difference in relative acidity is probably related to the so-called "*gauche* effect".[12]

TABLE I. Rates of Proton Exchange of Sulfonium Salts 7 and 9[a]

Salt	$10^5\ k_{CH_3}^{25°}$ ($sec^{-1}\ M^{-1}$)	$10^7\ k_{CH_2}^{35°}$ ($sec^{-1}\ M^{-1}$)
7	7.3[b,c]	0.37[b,d]
	14	0.46
9	--	35[e]

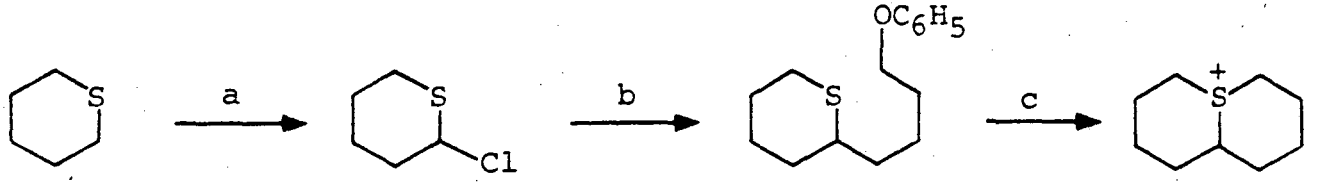
[a] Statistically corrected to a per-proton basis; [b] Reference 10; [c] Extrapolated to 25° C; [d] Extrapolated to 35° C; [e] Exchange of exocyclic protons

Bernardi *et al.* have recently reported *ab initio* calculations of $^{+}SH_2CH_2^{-}$ which show a mininum energy structure for the ylide when the lone pairs on carbon and sulfur are orthogonal, with maxima at lone pair-lone pair dihedral angles of 0° and 180° (11.0 and 7.6 kcal $mole^{-1}$ respectively).[13] Using Dreiding stereomodels,[14] it can be seen that the dihedral angles formed between the sulfur lone pair and the ring methylene protons in the two chair conformations of 9 are 55° and 175° with ethyl equatorial, and 55° and 60° with ethyl axial. Because the S-ethyl group is freely rotating, it is possible for the ylide to be formed in a conformation with the lone pairs orthogonal.[15] Although this consideration might explain the *relative* acidities of the two types of methylene protons in 9, the question of why the exocyclic methylene protons are exchanged some 120 times faster than those in salt 8 remains. The difference may be steric in origin; since two of the alkyl groups in 9 are pinned back into a ring, the exocyclic methylene

protons may be more accessible to the base, resulting in enhanced kinetic acidity. Whatever the explanation for the phenomenon, it is clear that, as a consequence, cyclizations of salts 3-6 are untenable, especially since the inductive effect of the halogen substituent will exacerbate the difference in acidity between the ring and side-chain protons.

To circumvent this problem, we developed the alternate synthesis outlined in Chart I, which produces 1 ($X^- = Br^-$) in 30-40% overall yield. The 6-methoxycarbonyl analog 17 ($X^- = I^-$) was prepared in 16% overall yield, as outlined in Chart II.

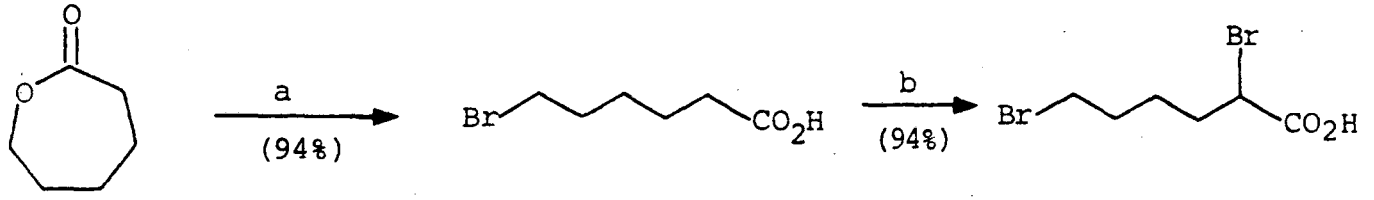
CHART I



2 10 11 1

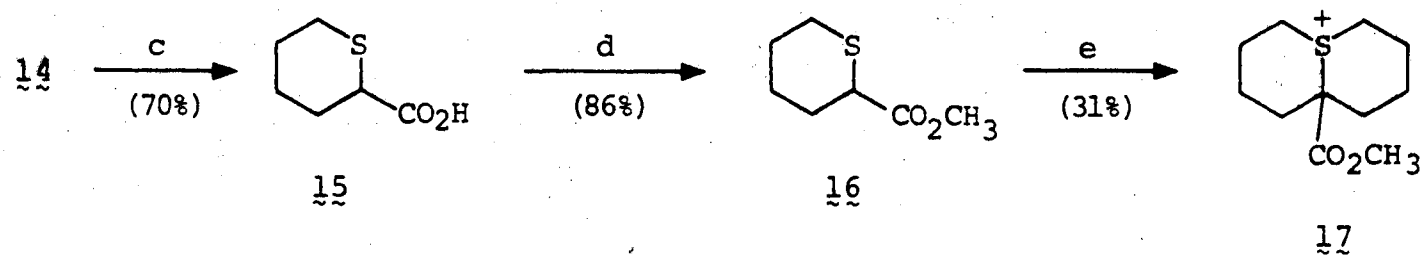
a) N-chlorosuccinimide, benzene b) $C_6H_5OCH_2CH_2CH_2CH_2MgCl$
c) HBr, $(CH_3CO)_2O$

CHART II



12 13 14

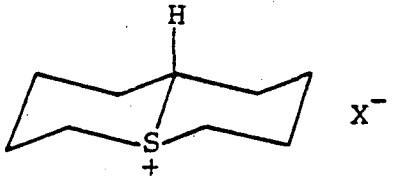
CHART II [continued]



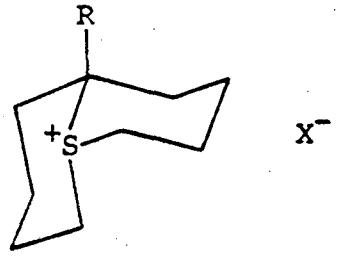
a) HBr, H_2SO_4 b) PCl_3, Br_2 c) 1. $NaHCO_3$ 2. $Na_2S \cdot 9\,H_2O$ d) CH_3OH, H^+
e) 1. LDA 2. $ICH_2CH_2CH_2CH_2I$

Stereostructure

Bicyclic sulfonium salt 1, prepared either by Eastman's method[8] or by the method outlined in Chart I, is formed as a 1:1 mixture of stereoisomers 1a and 1b, as shown by its ^{13}C-NMR spectrum. Thermal equilibration of the mixture of tetrafluoroborate salts in $CHCl_3$ or CH_2Cl_2 at 110° C for 24 h affords an equilibrium mixture (70% 1a, 30% 1b) from which pure 1a ($X^- = BF_4^-$) may be obtained by recrystallization. Pure diastereomer 1b ($X^- = BF_4^-$) is obtained by treating the 1:1 mixture of 1a and 1b with *n*-butyllithium in THF at -23°, allowing the resulting mixture of ylides to equilibrate for 2 h, then quenching with fluoboric acid. Salt 17 is obtained from the synthesis outlined in Chart II



1a

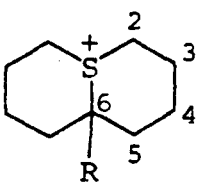


1b: R = H
17: R = CO_2Me

as a single stereoisomer, subsequently shown to have the "*cis*-thioniadecalin" configuration (*vide infra*).

The ^{13}C-NMR chemical shifts of salts 1a, 1b, and 17 ($X^- = BF_4^-$) are tabulated in Table II. It is noteworthy that each carbon in sulfonium salt 1a resonates downfield of the analogous carbon in its less stable stereoisomer 1b, a situation parallel to that found in *trans*- and *cis*-decalins.[18] The last two columns in Table II are $\Delta\delta$ between stereoisomers 1a and 1b and the 6-methoxycarbonyl analog 17. For comparison, we list in Table III the ^{13}C-NMR chemical shifts for pentane (18)[19] and methyl hexanoate (19),[20] along with $\Delta\delta$'s for the

TABLE II. ^{13}C-NMR Chemical Shifts of Salts 1a, 1b, and 17[a]

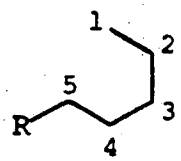


X^-

Carbon	1a (R = H)[b]	1b (R = H)[b]	17 (R = CO_2Me)[c]	$\delta_{1a}-\delta_{17}$	$\delta_{1b}-\delta_{17}$
2	38.3	30.7	32.2	+6.0	-1.6
3	23.9	20.0	19.5	+4.4	+0.5
4	23.5	19.9	19.5	+4.0	+0.4
5	30.7	26.1	29.7	+1.0	-3.6
6	53.3	42.6	59.3	-6.0	-16.7
CH_3	--	--	54.6	--	--
carbonyl	--	--	169.9	--	--

[a] Data are presented in ppm downfield from internal trimethylsilane.
[b] Spectra were determined on ca. 25% solutions in $CDCl_3$.
[c] ca. 5% solution in $CDCl_3$.

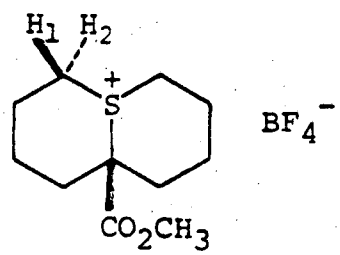
TABLE III. ^{13}C-NMR Chemical Shifts of Pentane and Methyl Hexanoate



Carbon	18 (R = H)[19]	19 (R = CO_2CH_3)[20]	$\delta_{18}-\delta_{19}$
1	13.7	14.3	- 0.7
2	22.6	23.4	- 0.8
3	34.5	32.2	+ 2.3
4	22.6	25.5	- 2.9
5	13.7	33.9	-20.2

five corresponding carbons. Comparison of the $\delta_{18}-\delta_{19}$ values in Table III with the $\Delta\delta$ values in Table II clearly indicates that sulfonium salts 1b and 17 have the same stereostructure. Considering the fact that 1b and 17 are cyclic structures with only two stable ring conformations each, while 18 and 19 are acyclic, with many possible conformations, the correspondence in $\Delta\delta$'s between the two cases is remarkable.

Stereostructures for 1a, 1b, and 17 may confidently be assigned on the basis of the 360-MHz ^1H-NMR spectra of the three tetrafluoroborates in D_2O.[21] Pertinent resonances for salts 1a and 1b have been



17

discussed elsewhere.[1] For salt 17, the protons next to sulfur (H_1 and H_2) appear as a complex multiplet in the region around δ 3.5. This region of the spectrum was simulated using the Nicolet ITRCAL program (as the AB part of ABXYZ pattern), and was found to consist of two resonances with δ = 3.48 ppm (J = -13.8, 8.9, 3.3, and 0 Hz) and δ = 3.56 ppm (J = -13.8, 7.0, 3.4, and 0.9 Hz). The higher field resonance was assigned to H_2 in analogy to the results of Barbarella, *et al.*[22] The -13.8 Hz splitting is obviously the geminal constant, while the 3.3 and 3.4 Hz splittings are weighted averages of J_{ae} and J_{ea} with a proton on C_3. The 8.9 and 7.0 splittings are too small for J_{aa} and too large for J_{ae} or J_{ee}, and must be weighted averages of J_{aa} and J_{ee}. Thus, the ^{1}H-NMR results also indicate that this salt has the "*cis*-decalin" configuration 17.

The *cis* configuration of 17 was confirmed by determination of the crystal structure of its iodide salt by X-ray diffraction. The crystals of $C_{11}H_{19}IO_2S$ are monoclinic, space group $P2_1/n$; a = 8.890(3) Å, b = 20.120(7) Å, c = 8.150(3) Å, β = 110.17(4)°, Z = 4, d_{calcd} = 1.661 g/cm^3, d_{obs} = 1.665 g/cm^3, t = 20° C. Atomic coordinates are listed in Table IV, bond distances in Table V, and bond angles in Table VI. Carbon-hydrogen distances (not listed) range from 0.83 to 1.05 Å with standard deviations of about 0.1 Å, values typical of X-ray diffraction determinations in the absence of correction for the electronic polarization of the hydrogen atom. Other bond lengths are within a standard deviation or two of accepted values for aliphatic compounds. The molecular structure of the cation, shown in Fig. 1, has both rings in chair conformations and approximately at a right angle to each other, the same as found for *cis*-decalin in the gas phase by Bastiansen and Hassel.[23] These ions are packed in the crystal as

Table IV. Atomic coordinates in 6-methoxycarbonyl-1-thioniabicyclo-[4.4.0]decane iodide.

Atom	x	y	z
I	.14544(8)	.11472(3)	.20623(9)
S	.0786(2)	.2990(1)	.2743(3)
O(1)	-.2249(6)	.3450(3)	.2312(7)
O(2)	-.1852(6)	.4552(2)	.2439(7)
C(1)	.291(1)	.3001(5)	.306(1)
C(2)	.312(1)	.3407(5)	.160(2)
C(3)	.264(1)	.4140(5)	.165(2)
C(4)	.090(1)	.4229(5)	.146(1)
C(5)	.042(1)	.3886(4)	.290(1)
C(6)	.070(1)	.2655(5)	.477(1)
C(7)	.150(1)	.3078(5)	.636(1)
C(8)	.094(1)	.3794(5)	.619(1)
C(9)	.134(1)	.4159(4)	.473(1)
C(10)	-.139(1)	.3929(4)	.251(1)
C(11)	-.356(1)	.4635(5)	.213(2)
H(1)	.30(1)	.254(4)	.28(1)
H(2)	.34(1)	.323(5)	.42(1)
H(3)	.24(1)	.321(4)	.05(1)
H(4)	.42(1)	.340(5)	.17(1)
H(5)	.33(1)	.433(4)	.27(1)
H(6)	.27(1)	.431(4)	.07(1)
H(7)	.03(1)	.402(4)	.05(1)

Table IV. Atomic coordinates in 6-methoxycarbonyl-1-thioniabicyclo-[4.4.0]decane iodide. (Continued)

Atom	x	y	z
H(8)	.06(1)	.470(4)	.15(1)
H(9)	.11(1)	.228(5)	.48(1)
H(10)	-.04(1)	.265(4)	.45(1)
H(11)	.15(1)	.281(5)	.74(1)
H(12)	.25(1)	.304(3)	.67(1)
H(13)	.15(1)	.397(4)	.72(1)
H(14)	-.03(1)	.380(5)	.60(1)
H(15)	.26(1)	.416(4)	.50(1)
H(16)	.11(1)	.460(4)	.46(1)
H(17)	-.38(1)	.504(5)	.19(1)
H(18)	-.42(1)	.445(5)	.10(1)
H(19)	-.37(1)	.454(6)	.32(2)

TABLE V. Bond Distances (Å)

I -S	3.825(3)	C(5) -C(9)	1.54(1)
S -C(1)	1.81(1)	C(6) -C(7)	1.51(1)
S -C(6)	1.81(1)	C(7) -C(8)	1.52(1)
S -C(5)	1.85(1)	C(8) -C(9)	1.54(1)
C(1)-C(2)	1.51(1)	C(5) -C(10)	1.52(1)
C(2)-C(3)	1.54(1)	C(10)-O(1)	1.21(1)
C(3)-C(4)	1.51(1)	C(10)-O(2)	1.32(1)
C(4)-C(5)	1.55(1)	C(11)-O(2)	1.46(1)

TABLE VI. Bond Angles (deg.)

C(1)-S -C(5)	100.3(5)	C(4)-C(5) -C(10)	111.5(7)
C(1)-S -C(6)	104.2(6)	C(9)-C(5) -C(10)	110.6(6)
C(5)-S -C(6)	103.6(5)	S -C(6) -C(7)	114.6(5)
S -C(1)-C(2)	107.5(6)	C(6)-C(7) -C(8)	114.5(8)
C(1)-C(2)-C(3)	112.5(9)	C(7)-C(8) -C(9)	111.4(8)
C(2)-C(3)-C(4)	113.2(9)	C(5)-C(9) -C(8)	113.1(7)
C(3)-C(4)-C(5)	114.2(8)	O(1)-C(10)-O(2)	125.4(6)
S -C(5)-C(4)	106.3(4)	O(1)-C(10)-C(5)	123.8(6)
S -C(5)-C(9)	111.5(4)	O(2)-C(10)-C(5)	110.7(6)
S -C(5)-C(10)	103.9(4)	C(10)-O(2)-C(11)	114.2(7)
C(4)-C(5)-C(9)	112.6(7)		

shown in Fig. 2. Each iodide ion is surrounded by six cations, and its nearest neighbors are thirteen hydrogen atoms at distances ranging from 3.1 to 3.8 Å. It has a sulfur atom at 3.82 Å as its closest heavy atom neighbor. This contact is indicated by a line in Fig. 2, and the structure can be regarded as a molecular packing of these ion pairs.[21]

Pyramidal Inversion

The 1:1 mixture of salts 1a and 1b ($X^- = BF_4^-$) was thermally equilibrated at 110° C in several solvents. In each case the "*trans*" diastereomer 1a was found to be slightly more stable than the "*cis*" isomer 1b, the equilibrium constants being: $CHCl_3$, 2.33; CH_2Cl_2, 2.33; THF, 1.50; CH_3CN, 1.70; D_2O, 1.50. Rates of equilibration were determined in CD_2Cl_2 and $CDCl_3$ over the range 90.07-105.80° C; data are summarized in Table VII. Application of the Eyring equation to these data gives $\Delta H^{\ddagger} = 28.0 \pm 0.9$ kcal mole^{-1} and $\Delta S^{\ddagger} = -3.1 \pm 2.5$ e.u. The calculated rate at 100° C, 6.5×10^{-5} sec^{-1}, compares well with that obtained by Fava, 8.1×10^{-5} sec^{-1}, for equilibration of 1,3,3-trimethylthianium perchlorate.[24]

TABLE VII. Rates of Inversion, 1b $\rightleftharpoons$ 1a

Temperature (° C)	Solvent	10^5 k (sec^{-1})	Corr. Coeff.
90.07 ± 0.02	CD_2Cl_2	2.24 ± 0.03	0.9983
96.30 ± 0.02	CD_2Cl_2	4.77 ± 0.01	0.9968
104.05 ± 0.02	$CDCl_3$[a]	9.8 ± 0.2	0.9944
105.80 ± 0.02	CD_2Cl_2	12.1 ± 0.1	0.9995

[a] The sulfonium salt partially separates as an oil at this temperature, although it is soluble in $CDCl_3$ at 25° C.

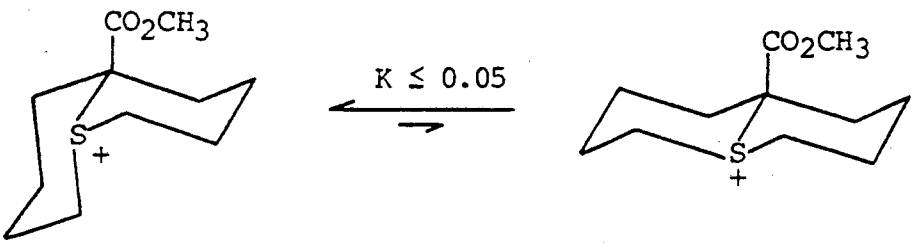
The $\Delta G°$ for the equilibrium $\underset{\sim}{1b} \rightleftharpoons \underset{\sim}{1a}$ is -0.64 kcal mole^{-1} at 110° C. For comparison, *trans*-decalin is 2.7 kcal mole^{-1} more stable than *cis*-decalin in the range 268-378° C.[25] The observed difference in stability has been ascribed to the fact that *cis*-decalin contains three more *gauche*-butane interactions than the *trans*-isomer.[26] However, Eliel and Willer have recently shown that $\Delta G°$ for S-CH_3 in 1-methylthianium salts is small (0.0-0.3 kcal mole^{-1}), suggesting that *gauche* interactions of the type C-C-$\overset{+}{S}$-C are much smaller than *gauche*-butane interactions.[27] In salts $\underset{\sim}{1a}$ and $\underset{\sim}{1b}$, the *gauche* four-atom interactions may be divided into three types, C-C-C-C, C-C-C-S, and C-C-S-C, as shown in Table VIII. If, for a first approximation, we ignore the C-C-S-C interactions on the basis of the work of Eliel and Willer,[27] then the difference in energy between the "*trans*-" and "*cis*-" diastereomers $\underset{\sim}{1a}$ and $\underset{\sim}{1b}$ should be one *gauche*-butane interaction (0.85 kcal mole^{-1}) plus $\Delta S°$, which should favor diastereomer $\underset{\sim}{1b}$, since it has two equivalent chair-chair conformations, while $\underset{\sim}{1a}$ has only one. For the equilibrium *trans*-decalin $\rightleftharpoons$ *cis*-decalin, $\Delta S°$ has been reported to be 0[28] or 0.55 ± 0.3 e.u.[25] Thus, at 110° C, $\Delta G°$ for the equilibrium

TABLE VIII. *Gauche* Four-Atom Interactions in $\underset{\sim}{1a}$ and $\underset{\sim}{1b}$

Interaction	$\underset{\sim}{1a}$	$\underset{\sim}{1b}$
C-C-C-C	4	5
C-C-C-S	4	4
C-C-S-S	4	6
TOTAL	12	15

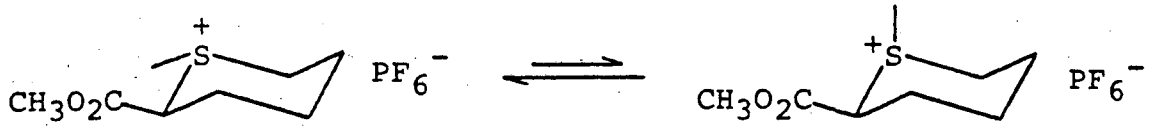
1b ⇌ 1a should be -0.52 to -0.85 kcal mole^{-1}, in good agreement with the experimental value of -0.64 kcal mole^{-1}.

In an attempt at thermal equilibration of salt 17 ($X^- = BF_4^-$), a $CDCl_3$ solution was heated at 110° C for 72 h; no isomerization was observed. Since the half-life for conversion of 1b to 1a under these conditions is approximately 1 h, equilibration of 17 with its "*cis*" diastereomer 20 should occur under the conditions of our experiment. The attempted equilibration was monitored by ^{13}C-NMR under conditions adequate to detect as little as 2-3% of another diastereomer. If we make the conservative assumption that we could detect no less than 5% of isomer 20, then $\Delta G°$ for the equilibrium must be ≥ 2.2 kcal mole^{-1}.



17 20

We realize the danger implicit in drawing conclusions on the basis of negative experiments such as the foregoing. For example, one might argue that the methoxycarbonyl group in 17 might significantly increase the pyramidal inversion barrier in 17 relative to that in 1b. However, it has been found that $\Delta G^{\ddagger}$'s for pyramidal inversion of ethylmethylphenacylsulfonium perchlorate and benzylethylmethylsulfonium perchlorate at 100° C are 27.3 and 26.9 kcal mole^{-1}, respectively.[29] In order to provide a further check on this point, we prepared the analogous thianium salts 21 and 22 by methylation of thiane 16. Upon heating for 10 h at 110° C in 1:1 acetone/$CHCl_3$, a 9:1 mixture of 21 and 22 equilibrates to a 7:3 mixture of the two isomers; heating for



21 22

an additional 62 h produces no further change in composition. Thus, it would seem that the barrier for inversion of salt 17 should be comparable to that for inversion of salt 1a, and that 17 is indeed substantially more stable than 20.

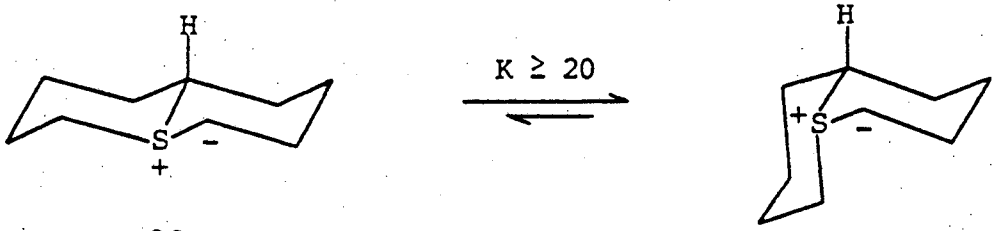
If it is accepted that 17 is more than 2.2 kcal mole^{-1} more stable than 20, then replacement of angular hydrogen by methoxycarbonyl disfavors the *trans*-1-thioniabicyclo[4.4.0]decane configuration by at least 2.2 + 0.6 = 2.8 kcal mole^{-1}, relative to the *cis* configuration. A similar phenomenon is observed with the decalins. While *trans*-decalin is 2.7 kcal mole^{-1} more stable than is *cis*-decalin, 9-methyl-*trans*-decalin is estimated to be only 0.3 kcal mole^{-1} more stable than 9-methyl-*cis*-decalin at 250° C.[30,31] The effect has been ascribed to the fact that replacement of the C_9-H by CH_3 adds four new *gauche*-butane interactions in the *trans*-isomer and only two in the *cis*-isomer.[30] The same explanation may be offered for the effect of substitution at C_6 in compound 1. However, the A value for the methoxycarbonyl group on a cyclohexane ring is only 1.3 kcal mole^{-1}.[33] Even allowing for the possibility that the A value for a tertiary methoxycarbonyl may be as high as 1.55 kcal mole^{-1},[34] the group seems to be exerting too large an effect in destabilizing isomer 17 by at least 2.8 kcal mole^{-1}.

The reason for this larger-than-expected apparent "size" of an angular substituent in the thioniadecalin system originates in the small C-S-C bond angles (100-104°; see Table VI). This has the effect of tilting the axial bonds at C_2 and C_{10} toward that at C_6, thus

increasing 1:3 diaxial interactions. This question was addressed by carrying out molecular mechanics calculations on 1a, 1b, and their 6-methyl analogs using the Allinger 1973 force field.[35] Preliminary calculations were performed on salt 7 (for which an X-ray structure is known[36]) and eight pairs of diastereomeric S-methylthianium ions (for which equilibrium constants have been determined[27]). Using Allinger's equilibrium C-S^+-C bond angle of 94.3°, it was found that the computed bond angles in salt 7 are about four degrees too small and that the stability of the equatorial S-methyl diastereomers is over-estimated by 0.9 to 1.2 kcal $mole^{-1}$. By employing an equilibrium C-S^+-C angle of 101°, we were able to adequately reproduce the bond distances (within 0.02 Å), bond angles (within one degree), and torsion angles (within three degrees) in salt 7. Furthermore, the Allinger program reproduces the experimental enthalpies of equilibration for the eight pairs of diastereomeric S-methylthianium ions by 0.15 ± 0.2 kcal $mole^{-1}$, with the stability of equatorial S-methyl groups still being slightly exaggerated. The force field predicts *trans*-isomer 1a to be 0.84 kcal $mole^{-1}$ more stable than *cis*-isomer 1b (compared to the experimental value of 0.64 kcal $mole^{-1}$). On the other hand, the 6-methyl derivative of 1b is predicted to be 2.8 kcal $mole^{-1}$ more stable than its *trans* counterpart.[37]

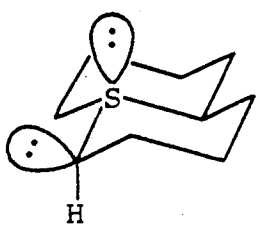
Pyramidal Inversion of Unstabilized Sulfonium Ylides

As mentioned earlier, pure diastereomer 1b may be obtained by forming the sulfonium ylide from the 1:1 mixture of salts 1a and 1b ($X^- = BF_4^-$) with *n*-butyllithium in THF at -23°, followed by a fluoboric acid quench after 2 h at this temperature. Ylides 23 and 24 presumably interconvert by pyramidal inversion at sulfur, with diastereomer 24

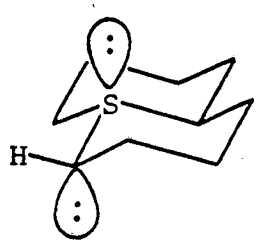


23 24

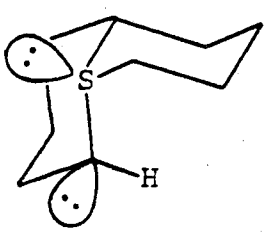
being at least 1.5 kcal mole^{-1} more stable than 23. It is interesting to speculate as to the reason for the preponderance of *cis*-ylide 24 at equilibrium. Interaction of vicinal lone pairs may again be involved. If we assume that both sulfur and the carbanion are pyramidal, then there are two conformations of ylide 23 (23a,b) and four of ylide 24 (24a-24d) which must be considered (Fig. 3). Using Dreiding scale models[13,14] and assuming a perfect tetrahedral geometry for the carbanion, one may estimate θ, the dihedral angle between the axes of the



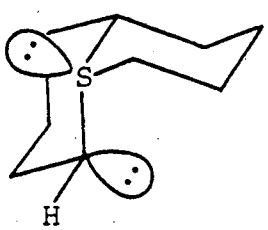
23a



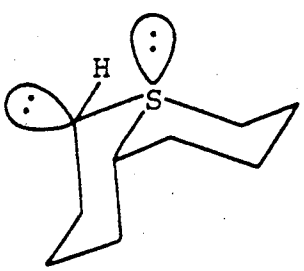
23b



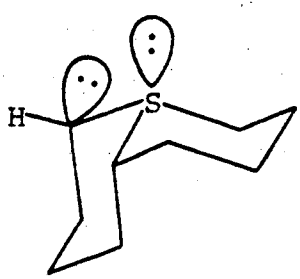
24a



24b



24c



24d

FIG. 3 Possible Conformations of Ylides 23 and 24

TABLE IX. Values of θ for Structures 23a-24d

Structure:	23a	23b	24a	24b	24c	24d
θ^a	50°	170°	46°	168°	50°	75°
θ^b	--	--	44°	176°	51°	76°

[a] Dihedral angle between the axes of the lone pairs, measured from Dreiding scale stereomodels.[13]

[b] Dihedral angles calculated between the sulfur lone pair and the appropriate C-H bonds calculated from the atomic coordinates of salt 17. The lone pair axis was assumed to pass through the midpoint of the triangle described by C_2, C_6, and C_{10}.

two lone pairs in structures 23a,b and 24a-24d; values are summarized in Table IX, along with the dihedral angles calculated from the atomic coordinates of salt 17. Clearly, structure 24d allows the lone pairs to approach orthogonality with the least structural reorganization. Attempts to obtain experimental evidence for the relative disposition of the lone pairs in ylide 24 by deuteration were unsuccessful. Best results were obtained by inverse quench of the equilibrated ylide mixture with DCl in ether or D_2SO_4 in CH_3OD, but even under these conditions a mixture of 15% d_2, 70% d_1, and 15% d_0 products was obtained.

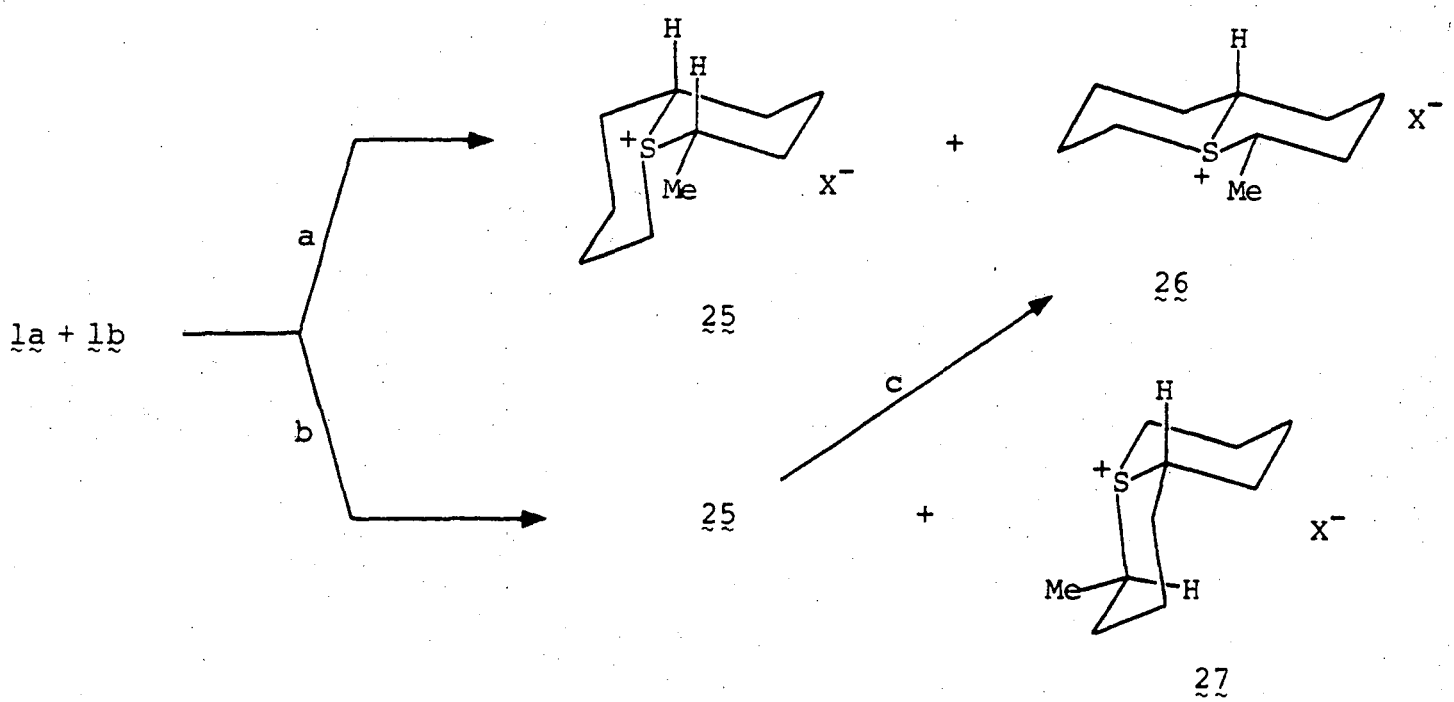
Activation parameters for pyramidal inversion of ylide 23 have been discussed elsewhere.[1] Experimental details will be found in the experimental section.

Alkylation of Ylides 23 and 24

Since one of our main goals in this study was to obtain information regarding the stereochemistry of alkylation of bicyclic sulfonium ylides, we examined the methylation of ylides 23 and 24. We first formed a mixture of the ylides by slow addition of *n*-butyllithium to a 1:1 mixture of salts 1a and 1b in THF at -72° C, and allowed the

ylides to react with methyl iodide at -72° C. After conversion to tetrafluoroborate salts, ^{13}C-NMR spectroscopy showed the product formed under these conditions to consist mainly of two isomers, subsequently shown to be 25 and 26, present in nearly equal amount. When this mixture is heated at 110° C in $CHCl_3$, the amount of isomer 26 increases, while that of isomer 25 decreases. Pure isomer 26 (X^- = picrate) may be obtained by recrystallization of the picrate salts. When the ylide mixture is equilibrated at -23° C for 2 h, then methylated at -72° C, the alkylation product consists of isomer 25 and a new isomer (27) in a ratio of 3:2; isomer 26 is not produced under these conditions. Thermal equilibration of this mixture affords a 3:2 mixture of isomers 26 and 27 (see Chart III).

CHART III



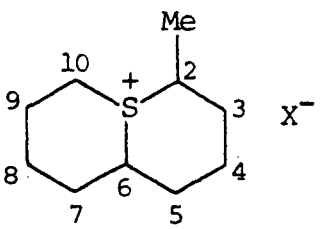
a) *n*-BuLi, THF, -72°; MeI, THF, -72°

b) *n*-BuLi, THF, -72°; -23°, THF, 2 h; MeI, THF, -72°

c) $CHCl_3$, 110°, 96 h

Stereostructures were assigned to salts 25, 26, and 27 on the basis of their ^{13}C-NMR spectra, which are tabulated in Table X. First, it is clear that isomer 26 has the *trans*-1-thioniabicyclo[4.4.0]decane structure, from the values of $\Delta\delta$ given in the second column of Table X. The equatorial disposition of the methyl group is shown by the fact that C_{10} is shifted upfield (γ-*gauche* interaction),[38] while C_4 and C_6 resonate at nearly the same frequency as in salt 1a. The large shifts of C_2 and C_3 result from the expected α and β effects.[38] Since isomer 25 is converted to isomer 26 by pyramidal inversion of sulfur, it must have the stereostructure indicated, and since isomer 27 is produced

TABLE X. ^{13}C-NMR Chemical Shifts of Salts 25, 26, and 27[a]



Carbon	26	$\delta_{26}-\delta_{1a}$	25	27
2	49.6	11.0	45.3	38.6
3	35.9	12.0	26.1	31.5
4	23.8[b]	0.3	23.3	18.5
5	30.9[c]	0.2	22.1	28.4
6	53.4	0.0	44.7	43.9
7	30.9[c]	0.2	29.2	(24.5)[d]
8	23.8[b]	0.3	16.8	(23.6)[d]
9	23.8[b]	-0.1	22.9	(21.5)[d]
10	33.3	-5.3	22.7	30.7
CH_3	17.4	--	17.7	18.0

[a] Spectra were determined on *ca.* 5% solutions of the picrates in $CDCl_3$; data are presented in ppm downfield from internal TMS.

[b] Triple intensity peak [c] Double intensity peak [d] These assignments are uncertain

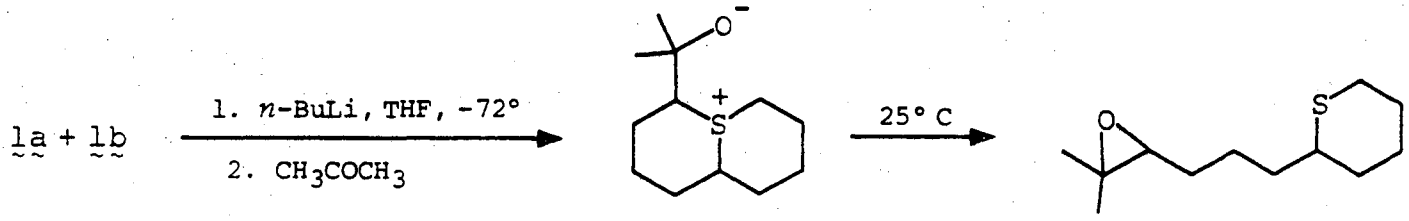
after equilibration of the ylides to the "*cis*" form, it must be the remaining *cis*-isomer, as indicated. Assignment of resonances to 25 and 27 was made on the basis of consideration of the number of α, β, and γ-*gauche* interactions in these isomers, relative to the spectrum of the parent salt 1b. The chemical shifts of the various carbons in isomers 25 and 27 do not correspond as closely to those in the parent unmethylated salt 1b, mainly due to the fact that 1b has two equivalent conformations, while 25 and 27 probably exist primarily in the conformation in which the methyl is equatorial, with a resultant change in the number of effective γ-*gauche* interactions.[39]

The stereochemistry of these methylations is of interest. When methylation is carried out without allowing the ylide mixture to warm above -70° C (path a in Chart III), the equatorial methylated salts 25 and 26 are produced in a ratio close to that of the starting salts 1a and 1b. Furthermore, these products are precisely those expected for replacement of the proton most nearly orthogonal to the lone pair in each isomer (1a and 1b).[40] It is noteworthy that isomer 27 is not produced in this reaction, although it *is* produced after the ylides are allowed to equilibrate. These results are consistent with the hypothesis that 23a is the kinetic ylide derived from 1a, 24d is the kinetic ylide derived from 1b, and that these ylides do not undergo stereomutation, either at sulfur *or at carbon* at -72° C. Upon warming to -23° C for 2 h prior to methylation, the ylides equilibrate by pyramidal inversion at both sulfur and carbon, giving a mixture of ylides 24d and either 24a or 24c (which are chair-chair conformers).

The foregoing hypothesis demands that $\Delta G^{\ddagger}$ for pyramidal inversion of the carbanion exceed $\Delta G^{\ddagger}$ for methylation (or reaction with acetone, *vide infra*). Calculations of the inversion barrier for methyl anion range from 1.7 to 25.2 kcal mole^{-1},[41] with the most sophisticated

calculations giving a value of 9.9 kcal mole^{-1}.[42] However, the adjacent sulfonium group should raise the barrier,[43] although the magnitude of this effect is unknown.[44]

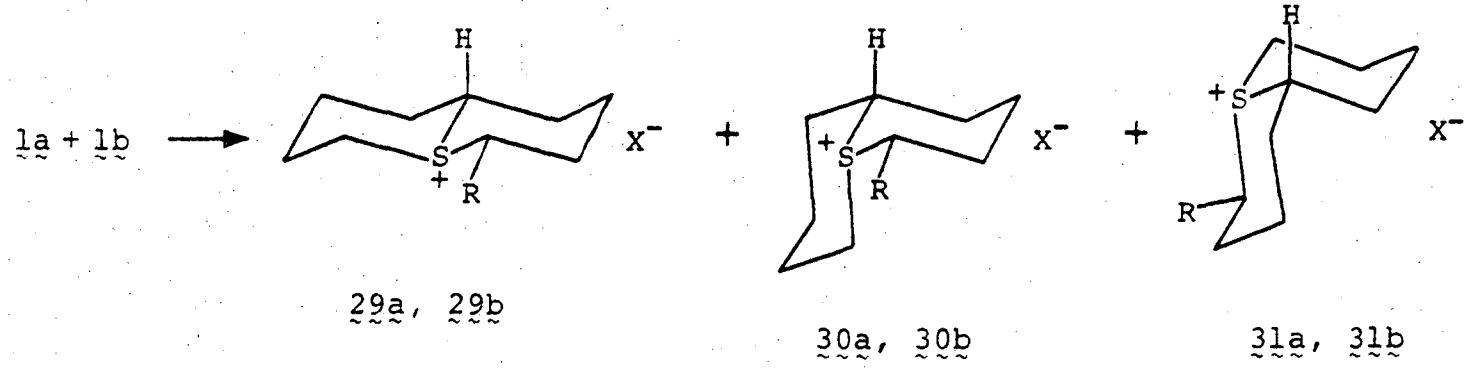
The reactions of ylides 23 and 24 with acetone are qualitatively similar to the methylations. If the intermediate zwitterion is allowed to warm to room temperature, epoxy sulfide 28 is produced. However, the zwitterion can be trapped by quenching at -72° C with fluoboric



28

acid or ethyl chloroformate (Chart IV). When the zwitterion is quenched with HBF_4, salts 29a and 30a are produced in roughly equal amounts. A trace of the other *cis*-isomer 31a may be seen in the ^{13}C-NMR spectrum of the crude product. Pure salt 30a ($X^- = BF_4^-$) may be isolated by recrystallization of the product. Thermal equilibration ($CDCl_3$, 110° C, 5 h) of the crude product provides essentially pure

CHART IV



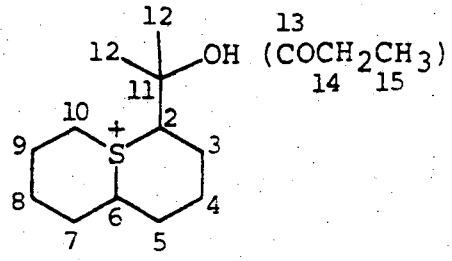
29a, 29b 30a, 30b 31a, 31b

a: $R = C(CH_3)_2OH$ b: $R = C(CH_3)_2OCOC_2H_5$

trans salt 29a. When the zwitterion is trapped with ethyl chloroformate, an equimolar mixture of carbonates 29b and 30b is produced. When the ylide mixture is allowed to thermally equilibrate at -23° before formation of the zwitterion at -72°, which is then trapped with ethyl chloroformate, *cis* sulfonium salts 30b and 31b are produced in a ratio of 3:1.

Stereostructures were assigned to salts 29-31 on the basis of arguments analogous to those used for assignments of methylated salts 25-27.[39] Table XI summarizes the ^{13}C-NMR chemical shifts.

TABLE XI. ^{13}C-NMR Chemical Shifts of Salts 29, 30, and 31[a]



Carbon	29a	29b	30a	30b	31b
2	66.7	61.9	63.4	60.4	55.0
3	24.4	19.5	d	19.3	24.2
4	23.9[b]	c	d	e	16.9
5	31.5[b]	23.4[b]	30.4	e	34.1
6	54.6	44.6	54.3	45.0	44.6
7	31.0[b]	29.9	31.0	30.1	c
8	23.9[b]	17.6	d	18.6	c
9	23.7[b]	23.5[b]	d	e	21.8
10	42.6	c	37.8	25.4	35.3
11	73.5	72.1	84.2	82.5	84.4
12	27.8, 28.3	27.5, 28.9	27.6, 29.3	26.8, 27.5	28.0, 28.3
13	--	--	151.4	151.8	151.5
14	--	--	63.0	63.4	62.6
15	--	--	13.5	13.5	13.5

[a] Spectra were determined on ca. 5% solutions of the tetrafluoroborate salts in $CDCl_3$; data are presented in ppm downfield from internal TMS.

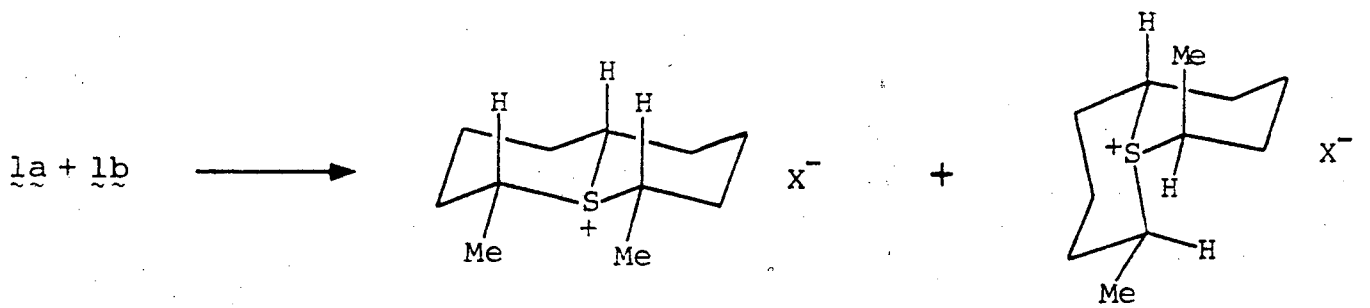
[b] These assignments are considered to be slightly uncertain.

[c] Resonance not found; assumed to coincide with another peak.

[d] These resonances could be either 20.1 or 23.0; the 23.0 peak is large enough for at least three carbons.

[e] Could be either 22.8 or 23.9.

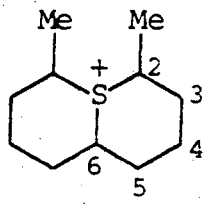
We have also briefly examined the formation and alkylation of sulfonium ylide anions. When the 1:1 mixture of salts 1a and 1b is treated with 2.5-3.0 equivalents of *t*-butyllithium in THF under careful conditions so that the temperature is maintained at -76 ± 2° C, and the resulting solution then treated with excess methyl iodide, an equimolar mixture of salts 32 and 33 (X^- = picrate) is isolated in 12% yield. If the ylide anion solution is kept at -65° to -70° C for 1 h before methylation, the sole product is salt 33, isolated in 12% yield. Attempted thermal equilibration of the 1:1 mixture of 32 and 33 ($CHCl_3$, 110°, 10 h) produces no change in composition.



32 33

The ^{13}C-NMR chemical shifts of salts 32 and 33 are summarized in Table XII. The correspondence in chemical shifts between isomer 32 and the analogous resonances in salts 26 (Table X) and 1a (Table II) is striking and clearly supports the assigned stereostructure. The alternative *trans*-1-thioniabicyclo[4.4.0]decane structure having one methyl axial is ruled out by symmetry (eleven resonances would result). The "*trans*" salt having both methyls axial is eliminated by the lack of γ-*gauche* shifts on C_4 and C_6, and also because this isomer would thermally equilibrate to "*cis*" isomer 33. Isomer 33 is assigned the indicated stereostructure first on symmetry grounds. Since this

TABLE XII. ^{13}C-NMR Chemical Shifts of Salts 32 and 33[a]



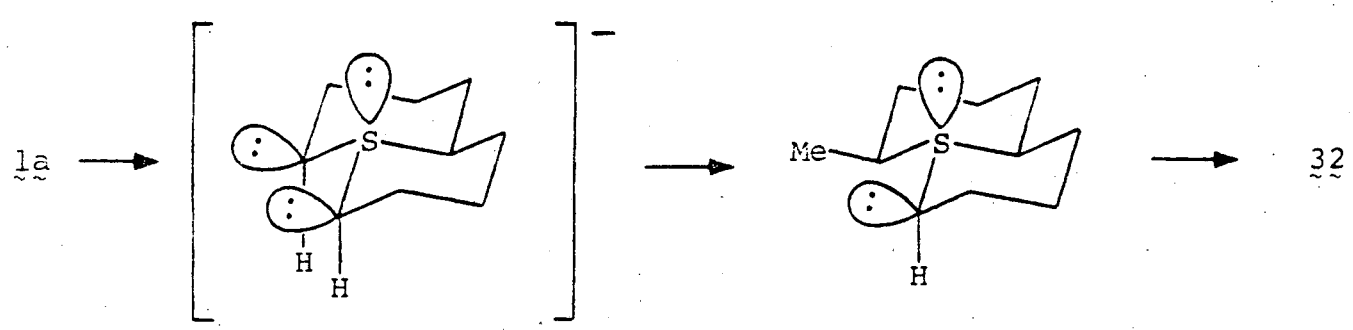
Carbon	32	$\delta_{32}-\delta_{1a}$	33	$\delta_{33}-\delta_{1b}$
2	50.2	11.6	41.0	10.3
3	34.9	11.0	28.4	8.4
4	23.7	0.2	17.2	-2.7
5	31.0	0.3	26.5	0.4
6	53.9	0.5	42.2	-0.4
CH_3	20.5	--	18.0	--

[a] Spectra were determined on ca. 5% solutions of the picrate salts in $CDCl_3$; data are presented in ppm downfield from internal TMS.

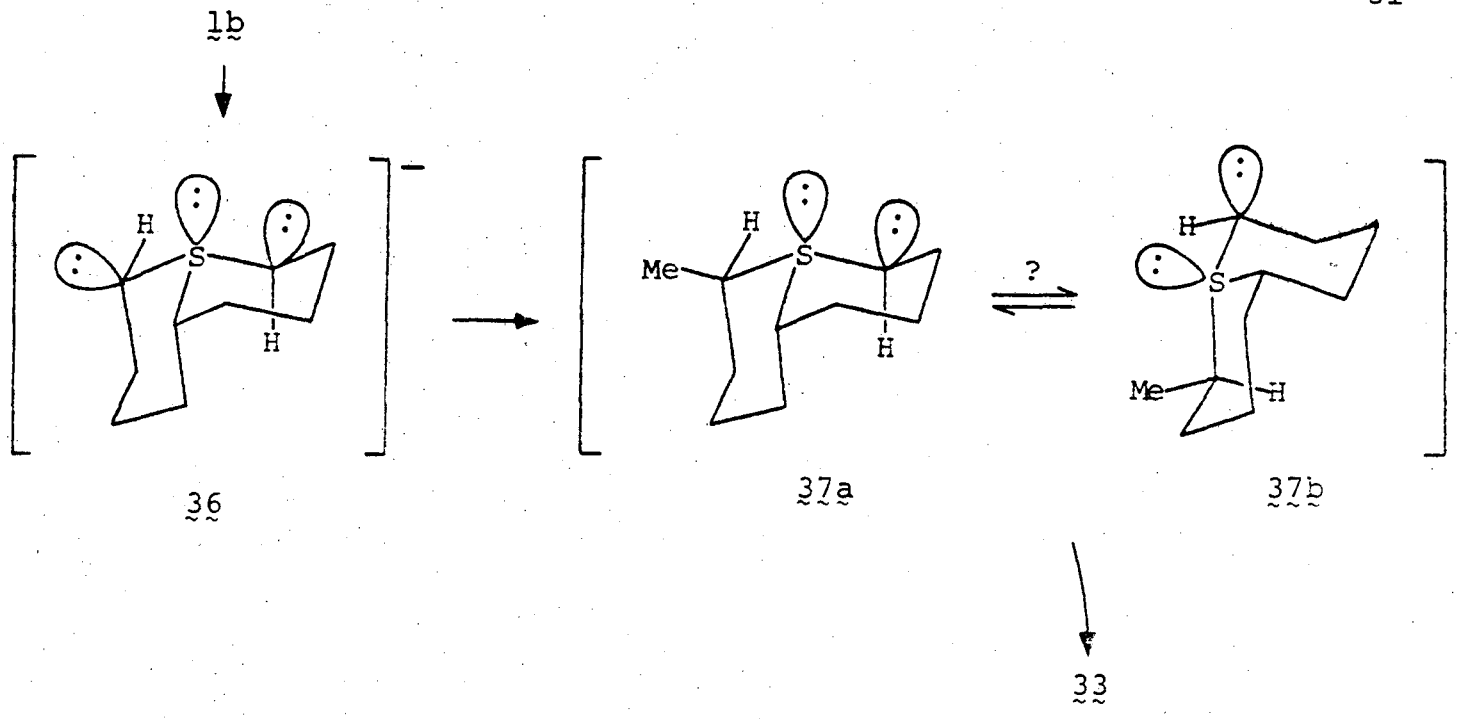
isomer has two equivalent conformations, the molecule has average C_s symmetry and should show only six resonances, as is observed. The alternative structure having both methyls equatorial would show eleven resonances. The isomer having both methyls *trans* to the angular hydrogen would also show average C_s symmetry, but should thermally equilibrate to isomer 32. The spectrum of 33 may be most profitably compared to that of its parent unmethylated salt 1b, since both exist as a mixture of two enantiomeric chair-chair conformers. In addition to the expected large downfield shifts of C_2 and C_3 (α and β effects), C_4 experiences a moderate upfield shift in 33, resulting from the fact that this carbon experiences a new γ-*gauche* interaction in one of its

two conformations. The γ-*gauche* effect expected on C_6 is not observed, perhaps because of the greater length of the C_2-S and C_6-S bonds.

Although the isolated yields in the alkylations leading to 32 and 33 are low at this point, it is interesting to consider the stereochemistry of these reactions. First, it definitely appears that the ylide anion undergoes stereomutation at sulfur with a considerably lower barrier than that for ylide 23.[44] It also seems that the stable structure of this species is one having a *cis*-1-thioniabicyclo[4.4.0]-decane structure, as in the case of the ylide itself. The most reasonable hypothesis is that the "*trans*" salt 1a gives an ylide anion 34 in which both carbanion lone pairs are *gauche* to the sulfur lone pair; after the first methylation, the product ylide 35 is formed. The *cis* salt 1b might afford ylide anion 36, which would probably react first on the more basic carbon lone pair (e.g., the one having the most unfavorable interaction with the sulfur lone pair) to give 37, which might exist either in conformation 37a or 37b, depending on whether the unfavorable lone-pair interactions in 37b or the axial methyl group in 37a are more important. Of course, since the precursors of products 32 and 33 are not neutral species, they may exist as ion pairs or aggregates, or may even be C-lithiated ylides.



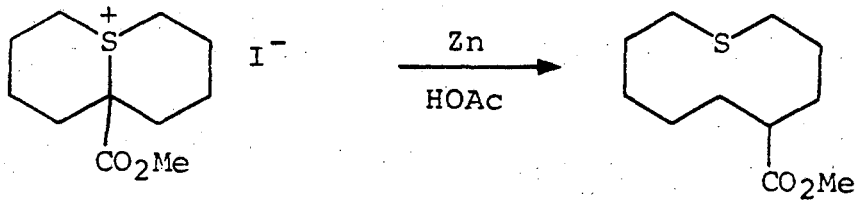
34 35



Finally, we should point out that these reaction intermediates are apparently the first known sulfonium ylide anions, although analogous species derived from ammonium and phosphonium salts have been previously described.[45] Dianions derived from sulfones[46] and nitroalkanes[47] have also been studied.

Conversion of Salt 17 to 6-Methoxycarbonylthiacyclodecane

In the Introduction, we considered the possibility that the sulfur-template approach might be employed to synthesize cyclic sulfides with ring sizes not conveniently accessible by direct cyclization. Bicyclic salt 17 provided us with an excellent opportunity to test this hypothesis. In fact, treatment of 17 with zinc dust in refluxing acetic acid affords the ten-membered cyclic sulfide 38 in 96% yield, thus establishing the feasibility of this approach to large-ring sulfides.



17 38

Conclusions

The present study has provided answers to a number of our original questions regarding the feasibility of a sulfur template approach to macrocycles. Bicyclic sulfonium salts *can* be prepared and their ylides alkylated stereoselectively. At this point, yields are not exceptional, but additional research may remedy this problem. The greatest obstacle we have encountered thus far stems from the difficulty with handling the sulfonium salts (they are usually produced as oils, often highly hygroscopic), and with separating mixtures of salts. In the future, use of ion-exchange or reverse-phase high-pressure liquid chromatography may alleviate these problems.

Experimental Section

The ^{1}H-NMR spectra were determined on a Varian T-60 NMR spectrometer or on a Bruker HXS-360 (Stanford Magnetic Resonance Laboratory). The ^{13}C-NMR spectra were measured at 25.14 MHz with a Nicolet TT-23 spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane (TMS) or sodium trimethylsilylpropionate (TSP). Significant ^{1}H-NMR data are tabulated in order (number of protons, multiplicity, proton assignment). Infrared spectra were determined on a Perkin-Elmer 137 infrared spectrophotometer. Mass spectra were obtained with Atlas MS-12 and Consolidated 12-110B mass spectrometers. Melting points (Pyrex capillary) and boiling points are uncorrected. Microanalyses were performed by the College of Chemistry Microanalytical Laboratory, University of California, Berkeley. Ether solvents were distilled from $LiAlH_4$ or sodium/benzophenone prior to use. All reactions involving ylides were performed under a nitrogen atmosphere.

1-(3-Iodopropyl)-thianium Iodide (3). A solution of 2.6 mL (25 mmol) of pentamethylene sulfide (Aldrich Chemical Co.) and 11.5 mL (0.10 mmol) of 1,3-diiodopropane is stirred for 6 days. The solid is filtered and recrystallized from ethanol to give pure salt 3 (9.0 g, 60%); mp 151-152°. ^{1}H-NMR (D_2O, external TMS) δ 1.6-2.6 (8H,m), 3.2-3.8 (8H, m). Anal. Calcd. for $C_8H_{16}I_2S$: C, 24.14; H, 4.05; S, 8.05; I, 63.76. Found: C, 23.88; H, 3.96; S, 7.88; I, 63.82.

1-(3-Iodobutyl)-thianium Iodide (4). A solution of 24 mL (0.20 mol) of 1,4-diiodobutane and 10.4 mL (0.10 mol) of pentamethylene sulfide is stirred for 5 days. Filtration and recrystallization (methanol/tetrahydrofuran) gives 20 g (50%) of 4; mp 147-148° C.

^{1}H-NMR (D_2O, external TMS) δ 1.4-2.2 (10H,m), 3.0-3.6 (8H,m). Anal. Calcd. for $C_9H_{18}I_2S$: C, 26.23; H, 4.40; I, 61.59; S, 7.78. Found: C, 26.28; H, 4.56; I, 61.38; S, 7.72.

Ethylthianium Tetrafluoroborate. Approximately 76 mmol of diethoxycarbonium tetrafluoroborate is prepared by the method of Borch[48] and immediately mixed with 20 mL of methylene chloride (distilled from P_2O_5) and 7.4 mL (76 mmol) of pentamethylene sulfide. After stirring for 20 h, the methylene chloride is removed and the product is triturated with anhydrous ether. The crude salt, obtained in quantitative yield, is extremely hygroscopic. The ^{1}H-NMR spectrum is identical to that of ethylthianium iodide. ^{1}H-NMR (D_2O, external TMS) δ 1.2 (3H,t, J=7, CH_3), 1.4-2.2 (6H,m), 3.1 (2H,q, J=7, $\overset{+}{S}CH_2$), 2.6-3.6 (4H, m).

1-[4-Chlorobutyl]thianium Tetrafluoroborate (6). To a solution of 1.71 g (5.11 mmol) of 4-chlorobutylorthoformate in 2 mL of dry CH_2Cl_2, cooled to -30° C, is added 0.75 mL (6.0 mmol) of $BF_3 \cdot Et_2O$ over a 5-min period. The mixture is stirred for 15 min at -30° C and the CH_2Cl_2 is then decanted from the salt by syringe. After washing the carbonium salt with 2 mL of CH_2Cl_2, a solution of 0.6 mL (6 mmol) of pentamethylene sulfide in 2 mL of dry ether is added at -72° C. The mixture is slowly warmed to room temperature and the clear supernatant layer is decanted from the oily lower layer. The oil is washed several times with ether. After evacuation to remove remaining traces of solvent, a crystalline solid is obtained. This material is recrystallized from ethanol to obtain 753 mg (53%) of 6; mp 140-142° C. ^{1}H-NMR (D_2O, external TMS) δ 1.9 (10H, m), 3.0-3.6 (8H,m). Anal. Calcd for $C_9H_{18}BClF_4S$: C, 38.53; H, 6.47. Found: C, 38.74; H, 6.53.

4-Chloro-1-phenoxybutane. To a solution of 120 g (3.0 mol) of

sodium hydroxide dissolved in 1 L of water is added 282 g (3.0 mol) of phenol. To this solution is added 381 g (3.0 mol) of 1,4-dichlorobutane. The heterogeneous mixture is refluxed until it becomes nearly neutral (several days). Ether (300-500 mL) is added and the aqueous layer is separated and extracted again with 500 mL of ether. The combined ether extracts are washed with 5% sodium hydroxide and saturated brine, and dried with $MgSO_4$. The solvent is evaporated *in vacuo* and the residue is distilled through a 30-cm Vigreaux column to yield 390 g (77%) of pure chloro ether (bp 86-87° C/0.5 Torr). IR (neat) 1600, 1580, 1500, 1460, 1250 cm^{-1}; ^{1}H-NMR (CCl_4) δ 1.78 (4H,m), 3.38 (2H,t, J=6), 3.78 (2H,t, J=6), 6.80 (3H,m), 7.02 (2H,m). Anal. Calcd. for $C_{10}H_{13}ClO$: C, 65.04; H, 7.09; Cl, 19.20. Found: C, 65.05; H, 7.02; Cl, 19.24.

2-[4-phenoxybutyl]-pentamethylene Sulfide (11) is prepared by the method of Tuleen and Bennett.[49] In a two-liter flask, 25 g (1.0 g-atom) of magnesium turnings is stirred under nitrogen with 250 mL of dry ether. A solution of 174 g (0.95 mol) of 4-chloro-1-phenoxybutane in 300 mL of dry ether is added dropwise so as to maintain a gentle reflux. The reaction mixture is refluxed an additional hour after the addition of chloride is complete. In a 500-mL inversion addition flask is placed 48.5 g (475 mmol) of pentamethylene sulfide in 250 mL of benzene. The solution is cooled to 10° C and 63.0 g (475 mmol) of N-chlorosuccinimide (NCS) is added in portions so as to maintain the temperature below 20° C. The mixture is stirred for an additional hour after the final addition of NCS and is then filtered into the Grignard reaction mixture at a rate so as to keep the temperature between 10-15° C. After stirring overnight at room temperature, CO_2 is bubbled through the reaction mixture to remove excess Grignard reagent, and

a 10% HCl solution is added dropwise. The aqueous layer is separated and extracted with ether. The combined ether layers are washed with 10% NaOH and saturated brine and dried over potassium carbonate. Removal of the solvents gives crude sulfide 11 which is used without further purification. In a similar reaction, a sample was purified by distillation (bp 145-150° C/0.2 Torr). ^{1}H-NMR (CCl_4) δ 1.6 (12H, m), 2.6 (3H,m), 3.90 (2H,t, J=6, OCH_2), 6.8 (3H,m), 7.0 (2H,m). Anal. Calcd. for $C_{15}H_{22}OS$: C, 71.95; H, 8.86. Found: C, 71.70; H, 8.79.

1-Thioniabicyclo[4.4.0]decane Bromide (1, $X^- = Br^-$). To 300 mL of acetic anhydride, cooled with an ice bath, is added 300 mL of 48% HBr. The crude sulfide 11 is added slowly, while cooling with an ice bath. This reaction mixture is refluxed for 6-10 h, and is then cooled and extracted with benzene (2 × 250 mL). The aqueous layer is evaporated *in vacuo* to near dryness and triturated with THF. Recrystallization from THF/ethanol yields an off-white product (30-40%). An analytical sample is obtained by an additional recrystallization; mp 264-265° C (dec) (lit.[8] mp 266-267° C). ^{1}H-NMR (D_2O, external TMS) δ 1.5-2.2 (12H,m), 2.8-3.6 (5H,m); ($CDCl_3$) δ 1.7-2.4 (12H,m), 3.8-4.6 (5H,m). ^{13}C-NMR ($CDCl_3$) *trans:* δ 23.3 (double intensity), 30.5, 38.0, 50.8; *cis:* δ 19.6, 19.9, 26.0, 31.5, 42.5. Anal. Calcd. for $C_9H_{17}BrS$: C, 45.57; H, 7.23; Br, 33.69; S, 13.52. Found: C, 45.51; H, 7.12; Br, 33.38, S, 13.42.

1-Thioniabicyclo[4.4.0]decane Tetrafluoroborate (1, $X^- = BF_4^-$).

Method A. To a solution of 5.5 mL (50 mmol) of trimethylorthoformate in 6 mL of dry methylene chloride, cooled to -72°, is added 7.3 mL (56 mmol) of boron trifluoride etherate, and the resulting mixture is stirred at -72° for 0.5 h and at 0° for 0.5 h. To the dimethoxycarbonium tetrafluoroborate reaction mixture is added 3.88 g

(16.4 mmol) of sulfonium bromide 1. After stirring overnight at room temperature, several milliliters of ethanol are added and the mixture is stirred for 1 h. Removal of the solvents and trituration with ether gives 1 ($X^- = BF_4^-$) in quantitative yield. Recrystallization from ethanol yields 3.41 g (85%) of pure salt; mp 174-175° C.

Method B. To a cold solution of 125 mL of acetic acid and 125 mL of 48% fluoboric acid is added crude 2-[4-phenoxybutyl]-pentamethylene sulfide (11), prepared from 245 mmol of pentamethylene sulfide. This mixture is refluxed for 4 days, and is then cooled and neutralized with sodium hydroxide. The resulting mixture is extracted three times with ether. The water is removed *in vacuo* and the sulfonium salt is removed from the sodium tetrafluoroborate by extraction with methylene chloride. Removal of the solution and trituration with THF yields 10 g (17%) of sulfonium salt 1 ($X^- = BF_4^-$). ^{1}H-NMR (360-MHz, 1% in D_2O) *trans:* δ 1.67 (4H,m), 1.85 (2H, br d, J=14), 1.97 (2H, br d, J=15), 2.12 (2H, br d, J=15), 2.31 (2H, br d, J=15), 3.16 (2H, ddd, J = 11.8, 13.3, 2.5), 3.27 (1H, tt, J= 11.9, 2.3), 3.56 (2H, br d, J = -11.8, 2.3); *cis:* δ 1.60 (2H,m), 1.94 (6H,m), 2.13 (4H,m), 3.23 (2H, ddd, J = -13, 9, 3.3), 3.48 (2H, dddd, J = -13, 7, 3.4, 0.9), 3.69 (1H, tt, J = 7.8, 3.9). ^{13}C-NMR ($CDCl_3$) *trans:* 23.5, 23.9, 30.7, 38.3, 53.3; *cis:* 19.9, 20.0, 26.1, 30.7, 42.6. Anal. Calcd. for $C_9H_{17}BF_4S$: C, 44.28; H, 7.02; S, 13.14. Found: C, 44.19; H, 6.98; S, 12.89.

Thermal Equilibration of 1-Thioniabicyclo[4.4.0]decane Tetrafluoroborate (1). A solution of 495 mg of salt 1 (1:1 mixture of 1a/1b) dissolved in 10 mL of $CDCl_3$ (or ethanol-free $CHCl_3$) is heated at 110° C (sealed tube) for 21 h to give a 70:30 mixture of 1a/1b. The ratios are determined by 360-MHz ^{1}H-NMR (by comparing the resonance of δ 3.69 of the *cis* isomer to the resonance at δ 2.31 of the *trans* isomer) and

^{13}C-NMR (by comparing resonance of 1a to the corresponding resonances of 1b and using the average of the values obtained). Further heating does not change this ratio. Salt 1 is equilibrated in other solvents in the same manner and the ratios determined by ^{13}C-NMR. Pure *trans* salt (1a) is obtained by dissolving the equilibrated salt (1a/1b = 7:3) in a minimum amount of hot ethanol. THF is added and the solution is allowed to cool. The 1:1 mixture of 1a and 1b preciptates and is removed by filtration. The filtrate is evaporated to dryness and the process repeated. After three crystallizations of the molecular compound 1a/1b, the concentrated filtrate (*ca.* 25% yield) is pure 1a, as shown by its ^{13}C-NMR spectrum. The pure salt is obtained as a clear glass; we have not attempted to crystallize it.

6-Bromohexanoic Acid (13) was prepared from commercially available 6-hydroxyhexanoic acid lactone (Aldrich Chemical Co., Inc.) by the method of Brown and Partridge[50] (94% distilled yield; bp 130-132° C/ 1 Torr). ^{1}H-NMR (CCl_4) δ 1.4-2.2 (6H,m), 2.37 (2H, t, J=7), 3.40 (2H, t, J=7), 12.0 (1H,s).

2,6-Dibromohexanoic Acid (14) was prepared in 94% yield by Hell-Vollhard-Zelinsky bromination of 13 after the method of Clarke and Taylor[51]; mp 45-47° C (lit.[52] oil at room temperature). ^{1}H-NMR (CCl_4) δ 1.6-2.4 (6H,m), 3.42 (2H, t, J=7), 4.25 (1H, t, J=7), 12.1 (1H,s). Anal. Calcd. for $C_6H_{10}Br_2O_2$: C, 26.30; H, 3.68; Br, 58.24. Found: C, 26.56; H, 3.73; Br, 58.12.

2-Carboxypentamethylene Sulfide (15). A mixture of 14 g (164 mmol) of $NaHCO_3$, 45 g (164 mmol) of 2,6-dibromohexanoic acid, and 40 g (167 mmol) of finely ground $Na_2S \cdot 9\,H_2O$ in 200 ml of water is kept at room temperature for 20 hrs. Conc. HCl (40 ml) is added and the aqueous mixture is extracted with ether. The extract is dried and evaporated

to yield 16.5 g (70%) of crude acid 15, which may be used in the subsequent esterification. The analytical sample was obtained by distillation (bp 103-105°/1 torr). IR (neat) ν_{max} 3000 (broad), 1710 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.6-2.2 (6H,m), 2.7 (2H,m), 3.62 (1H, dd, J=4 and 6), 12.0 (1H,s).

Anal. Calcd. for $C_6H_{10}O_2S$: C, 49.29; H, 6.85; S, 21.93. Found: C, 48.98; H, 6.64; S, 21.74.

2-Methoxycarbonylpentamethylene Sulfide (16). A solution of 16.5 g (113 mmol) of crude acid 15, and 1 ml of conc. H_2SO_4 in 100 ml of CH_3OH is stirred overnight. Sodium carbonate is added and the CH_3OH removed under vacuum. The residue is taken up in ether, washed with aqueous Na_2CO_3, satd. brine, and then dried. Removal of the solvent affords an oil which is distilled under vacuum to obtain pure ester 16 (15.4 g, 86%). IR (neat) ν_{max} 1740 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.8-2.2 (6H,m), 2.7 (2H,m), 3.45 (1H, dd, J=4 and 6), 3.70 (3H,s).

Anal. Calcd. for $C_7H_{12}O_2S$: C, 52.47; H, 7.55; S, 20.01. Found: C, 52.66; H, 7.57; S, 19.97.

6-Methoxycarbonyl-1-thioniabicyclo[4.4.0]decane Iodide (17). To a solution of 11.2 ml (78 mmol) of diisopropylamine in 100 ml of dry tetrahydrofuran, cooled to 0°, is added 78 mmol of a solution of *n*-butyllithium in hexane. After 30 min at room temperature, the lithium diisopropylamide solution is cooled to -76° in a bath of dry ice/acetone and 12.5 g (78 mmol) of ester 16 is added. The cold enolate solution is added to a solution of 12 ml (90 mmol) of 1,4-diiodobutane in 50 ml of dry tetrahydrofuran, which has been precooled to -76°. After 3 hrs at -76° and 2 hrs at room temperature, the solvent and diisopropylamine are removed under vacuum and the residue is parti-

tioned between ether and water. The ether layer is separated and the aqueous layer extracted again with ether. The combined ether extracts are quickly dried by filtration through a column of anhyd. $MgSO_4$ and then refluxed for 3 days. The resulting salt is removed by filtration and the mother liquors are again refluxed for 3 days, yielding more insoluble salt. The combined salts are recrystallized from ethanol to obtain 8.64 g (31%) of analytically pure 17; mp 144-145°. ^{1}H-NMR (60 MHz, $CDCl_3$) δ 1.6-3.0 (12H,m), 3.8-6.2 (m), 3.95 (s). ^{13}C-NMR ($CDCl_3$) δ 19.0, 29.5, 32.9, 54.2, 58.7, 169.4.

Anal. Calcd. for $C_{11}H_{19}IO_2S$: C, 38.61; H, 5.60; S, 9.36; I, 37.08. Found: C, 38.74; H, 5.57; S, 9.24; I, 36.98.

The fluoborate salt (mp 121-122° C) is prepared by adding one equivalent of $AgBF_4$ to a methylene chloride solution of the iodide salt (100%). IR ($CHCl_3$) ν_{max} 1740, 1050 cm^{-1}. ^{1}H-NMR (360 MHz, D_2O, external Me_4Si) δ 1.68 (2H,m), 1.94 (4H,m), 2.18 (4H,m), 2.48 (2H, ddd, J = 15, 9, and 2.5), 3.48 (2H, ddd, J = 13.8, 8.9, and 3.3), 3.56 (2H, dddd, J = 13.8, 7.0, 3.4, and 0.9), 3.95 (3H,s). ^{13}C-NMR ($CDCl_3$) δ 19.5, 29.7, 32.3, 54.6, 59.3, 169.9.

Anal. Calcd. for $C_{11}H_{19}BF_4O_2S$: C, 43.72; H, 6.34. Found: C, 43.46; H, 6.31.

6-Methoxycarbonylthiacyclodecane (37). Zinc dust (3.5 g) is added to a solution of 426 mg (1.24 mmol) of salt 17 ($X^- = I^-$) in 20 ml of acetic acid. The heterogeneous mixture is refluxed for 20 hrs, and is then diluted with 100 ml of water. The excess zinc is removed by filtration and the filtrate is extracted with ether (4 × 50 ml). The combined ether extracts are washed with satd. $NaHCO_3$ solution until the washings are neutral and then with satd. brine. After drying, the ether is removed under vacuum and the resulting oily

product is purified by bulb-to-bulb distillation. In this way, 257 mg (96%) of analytically pure 37 is obtained. IR (neat) ν_{max} 1740 cm^{-1}. ^{1}H-NMR (CCl_4) δ 1.4-2.0 (13H,m), 2.3-2.8 (5H,m), 3.58 (3H,s).

Anal. Calcd. for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32. Found: C, 61.43; H, 9.19. HRMS: Found, 216.1189.

X-ray Diffraction. Crystals of the iodide of 17 were found as plates and needles. The plate-like crystals seemed less perfect, and Weissenberg photographs indicated many to be multiple crystals. The needles appeared to be single under the microscope with optical extinction approximately parallel with the long direction (c axis). One of these (0.174 × 0.070 × 0.030 mm) was glued to a glass fiber for examination by Weissenberg and diffractometer technique. Cell dimensions were determined from setting angles for twelve reflections (2θ in the range 25° to 32°) with a Picker FACS-I diffractometer with MoKα radiation (λ 0.70926 Å for $K\alpha_1$). Intensity data were measured by θ-2θ scans (2θ from 0.5° below $K\alpha_1$ to 0.5° above $K\alpha_2$) with 10 sec background counts (20 sec at some of the higher angles) near each end of the scan. Three standard reflections, measured at intervals of 200 reflections, indicated a linear decrease in intensity of 10% in the course of the measurements, and a compensating correction was applied. Absorption corrections ($\mu = 22.99$ cm^{-1}) were calculated using dimensions of the crystal which were adjusted to minimize the variation of intensity with azimuthal angle for several test reflections. The corrections ranged from 1.07 to 1.18. Measurements were made of 5499 reflections not excluded by the space group in the hemisphere ±h, +k, ±l; the maximum 2θ was 50°. Averaging of equivalent reflections yielded 2426 unique ones, of which 1432 with $F^2 > 2\sigma$ were used in the least-squares refinement.

The structure was solved by the heavy atom method. A Patterson function revealed the position of the iodine atom. Other non-hydrogen atoms were found in a ΔF map. After some refinement by least squares, another ΔF map revealed the hydrogen atoms. With isotropic thermal parameters for hydrogen and anisotropic ones for other atoms, refinement reduced $R = \Sigma|\Delta F|/\Sigma|F_o|$ to 0.042 for 1432 reflections stronger than 2σ and 0.089 including zero-weighted data; $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2} = 0.042$. The goodness of fit was 0.97. Scattering factors for spherical hydrogen from Stewart, Davidson, and Simpson,[53] for other atoms from Doyle and Turner,[54] and dispersion corrections from Cromer and Liberman[55] were used. Calculations were made with the CDC-7600 computer and programs listed elsewhere.[56]

Kinetics of Equilibration of 1-Thioniabicyclo[4.4.0]decane Tetrafluoroborate (1). The 1:1 mixture of 1a and 1b was dissolved in deuteriochloroform or deuteriomethylene chloride (0.33 to 0.57 g per mL). The solution was sealed in an NMR tube, which was placed in a constant temperature bath (±0.02° C) and periodically cooled to room temperature to analyze the isomer ratio by ^{13}C-NMR. Several values were corroborated by 360-MHz ^{1}H-NMR, and analyses by the two methods corresponded within 2-3%. Rate constants were obtained using the equation:

$$\ln[1-F_t(1+{}^1/_K)] - \ln[1-(F_t)_o(1+{}^1/_K)] = -kt$$

where F_t is the mole fraction of *trans* salt 1a, $(F_t)_o$ is the initial mole fraction of 1a (0.50), and K is the equilibrium constant (2.33 ± 0.03). Data were analyzed by plotting $\ln[1+F_t(1+{}^1/_K)]$ versus time; the negative slope of the resulting line is the rate constant, k. Results are summarized in Table VII.

2-Methoxycarbonyl-1-methylthianium Hexafluorophosphate (21 + 22). A mixture of 2.94 g (14.3 mmol) of trimethyloxonium hexafluorophosphate (Aldrich Chemical Co., Inc.) and 2.52 g (15.7 mmol) of 2-methoxycarbonylpentamethylene sulfide in 10 mL of dry ether is stirred for 7 h at room temperature. Filtration of the mixture gives a 9:1 mixture of 21 and 22 in quantitative yield. Recrystallization from ethanol provides an analytical sample; mp 102-104° C. ^{1}H-NMR (D_2O/DMSO-d_6, internal TSP) δ 1.8-2.6 (6H,m), 2.86 (minor, s, $\overset{+}{S}$-CH_3), 3.00 (major, 3H, s, $\overset{+}{S}$-CH_3), 3.2-3.8 (2H,m), 3.84 (3H,s, OCH_3). Anal. Calcd. for $C_8H_{15}F_6O_2PS$: C, 30.00; H, 4.72. Found: C, 30.14; H, 4.92.

A sample of the 9:1 mixture of 21 and 22 is dissolved in a 1:1 mixture of acetone-d_6 and $CDCl_3$ and heated in a sealed NMR tube for 10 h at 110° C. After this period of time, the ratio of 21/22 is 7:3; further heating at 110° for 62 h does not alter this ratio.

Kinetics of Inversion of Ylide 23. In three separate flasks were placed a 1:1 mixture of sulfonium salts 1a and 1b and sufficient dry THF to make a 0.34 (± 0.01) M solution. The solutions were cooled to -72°C (internal temperature) and a slight excess (5%) of *n*-butyllithium was added simultaneously to each flask over a 15-min period. By this slow addition there was no noticeable temperature rise. The reaction mixtures were stirred for 1 h at -70°C to ensure complete formation of the ylide. The three flasks were placed in the constant temperature bath (±1°) and allowed to warm to the desired temperature. When the internal temperature reached that of the constant temperature bath, one reaction mixture was quenched by addition of aqueous fluoboric acid for an initial ratio (t = 0). The remaining two reaction flasks were kept at constant temperature and quenched after an appropriate amount of time. The solvents were removed *in vacuo* and the isomer

TABLE XIII

Temperature (°C)	% 1a	Time (hrs)
-23	34.9	0
	20.1	1.0
	12.3	2.0
-33	50.0	0
	33.0	4
	28.8	5

ratios were determined by comparing the ^{13}C resonances of the *trans* isomer to the corresponding ^{13}C resonances of the *cis* isomer. Data are tabulated in Table XIII. Rate constants were determined in the same manner as that used for equilibration of salt 1a (*vide supra*).

2-Methyl-1-thioniabicyclo[4.4.0]decane Salts (25, 26, 27). To a slurry of 102.6 mg (0.420 mmol) of 1-thioniabicyclo[4.4.0]decane tetrafluoroborate (1a/1b = 1:1) in 1 mL of dry THF, cooled to -72° C, is added a 10% excess of *n*-butyllithium. After stirring for 1.5 h at -72°, 0.5 mL (8 mmol) of methyl iodide is added, giving an immediate precipitate. The reaction mixture is allowed to stir at -72° for 0.5 h, then allowed to warm to room temperature over a 1-h period. The solvents are removed and chloroform is added. After filtration, the chloroform is evaporated to obtain 106.9 mg (85-99%, mixture of iodide and tetrafluoroborate salts) of a mixture of salts 25 and 26, shown by ^{13}C-NMR to be present in an approximate equimolar ratio. ^1H-NMR ($CDCl_3$) δ 1.58 (minor, 3H, d, J=6.8, CH_3), 1.65 (major, 3H, d, J=6.6, CH_3), 1.5-2.8 (12H,m), 3.5-4.8 (5H,m). The product was converted to the picrate[8] for analysis. Anal. Calcd. for $C_{16}H_{21}N_3O_7S$: C, 48.11; H, 5.30; N, 10.52. Found: C, 47.82; H, 5.16; N, 10.59.

Isomer 26: In a similar alkylation, employing 4.08 mmol of salt 1, the reaction mixture was filtered and a hot solution of 1 g of picric acid in 75 mL of water was added. Filtration yielded 383.4 mg (24%) of a mixture of 25 and 26 (mp 155-159°). The solvents were removed from the filtrate and the resulting oil was re-dissolved in THF and treated with hot aqueous picric acid as above to obtain 180.0 mg (11%) of pure salt 26. ^{1}H-NMR (360-MHz, $CDCl_3$) δ 1.50 (3H,d, J=6.6, CH_3), 1.6 (2H,m), 1.9 (5H,m), 2.2 (3H,m), 2.32 (1H,d, J=15), 2.44 (1H, broad d, J=10), 3.45 (1H, broad d, J=-11.5, 2.3), 3.94 (1H, ddd, J = -11.5, 12.5, 3), 4.04 (1H, tt, J = 12.5, 2), 4.25 (qdd, J = 12, 6.5, 3). ^{13}C-NMR ($CDCl_3$) δ 53.4, 49.6, 35.9, 33.3, 30.9 (double intensity), 23.8 (triple intensity), 17.4.

Isomers 25 and 27: A slurry of 189.9 mg (0.778 mmol) of salt 1 ($X^- = BF_4^-$, 1a/1b = 1:1) in 2 mL of dry THF is cooled to -23° C. *n*-Butyllithium (20% excess) is added and the mixture is stirred for 2 h at -23° C. The ylide solution is cooled to -76° C and 1 mL (16 mmol) of methyl iodide is added. After several h of stirring, approximately 5 mmol of dimethoxycarbonium tetrafluoroborate[48] is added and the mixture is stirred at room temperature for 4 h. A few mL of methanol is added and the mixture is stirred for 1 h. The solvents are removed and the product is triturated with THF and filtered. The lithium salts are removed by adding chloroform and filtering. ^{13}C-NMR (D_2O, external TMS): major isomer (60%) δ 45.1, 44.6, 28.8, 25.4, 22.9 (double height) 21.5 (double intensity), 17.3, 16.0; minor isomer (40%) δ 43.8, 38.4, 31.0, 30.7, 28.0, 23.8, 22.3 (double intensity), 18.1, 17.3.

The product is converted to the picrate by adding a hot picric acid solution containing a 10-20% excess of picric acid. ^{13}C-NMR ($CDCl_3$): major isomer δ 45.3, 44.7, 29.2, 26.1, 23.3, 22.9, 22.7, 22.1,

17.7, 16.8; minor isomer δ 43.9, 38.6, 31.5, 30.7, 28.4, 24.5(?), 23.6(?), 21.5(?), 18.5, 18.0.

The foregoing mixture of tetrafluoroborate salts 25 and 27 is dissolved in $CHCl_3$ and heated at 110° C (sealed tube) for 4 days. The solvent is removed and the product analyzed by ^{13}C-NMR. The ^{13}C-NMR resonances of the major isomer are nearly identical with those of salt 26 (X^- = picrate). ^{13}C-NMR ($CDCl_3$): major isomer (60%) δ 53.45, 49.90, 35.87, 32.73, 31.08, 30.33, 23.79, 23.50, 23.26, 16.85; minor isomer (40%) δ 43.59, 38.20, 31.05, 28.39, 24.28, 21.51, 18.35, 17.73.

2-[4-Epoxy-5-methylhexyl]-thiane (28). A slurry of 93.3 mg (0.382 mmol) of 1-thioniabicyclo[4.4.0]decane tetrafluoroborate in 1 mL of dry THF is cooled to -72° C. A 20% excess of *n*-butyllithium is added and the solution is stirred for 1 h at -72° C. To the ylide solution is added 1 mL (14 mmol) of purified acetone. The reaction mixture is allowed to slowly warm up to room temperature and is added to 100 mL of water. After extraction with ether (2 × 100 mL), the organic layers are combined and washed with a saturated salt solution then dried over K_2CO_3. Removal of the solvents and bulb-to-bulb distillation yields 48.4 mg (59%) of sulfide 28. ^1H-NMR (CCl_4) δ 1.22 (3H,s, CH_3), 1.25 (3H,s, CH_3), 1.2-2.3 (12H,m), 2.4-2.8 (3H,m). Anal. Calcd. for $C_{12}H_{22}OS$: C, 67.21; H, 10.34. Found: C, 67.25; H, 10.61.

2-[2-Hydroxyisopropyl]-1-thioniabicyclo[4.4.0]decane Tetrafluoroborate (29a, 30a). To a slurry of 758.3 mg (3.11 mmol) of 1 in 5 mL of dry THF, cooled to -72° C, is added a 20% excess of *n*-butyllithium. After stirring for 1 h at -72° C, a large excess of acetone is added and the solution is stirred for 5 min; the reaction is then quenched by addition of aqueous fluoboric acid. The solvents are removed and the salt dried *in vacuo* overnight. Chloroform is added and the lithium

salts are filtered. The $CHCl_3$ is removed and the product is dissolved in THF, leaving behind 24.0 mg (0.10 mmol) of starting material. Evaporation of solvent yield an equimolar mixture of 29a and 30a. ^{13}C-NMR ($CDCl_3$): 29a, δ 73.45, 66.65, 54.57, 42.58, 31.46, 31.02, 28.26, 27.78, 24.38, 23.88 (double height), 23.74; 30a, δ 72.14, 61.85, 44.61, 29.85(?), 28.94(?), 27.47(?), 23.49, 23.39, 19.47, 17.62. Crystallization of this mixture from THF yields 303.2 mg (32%) of analytically pure 30a; mp 178.5-179.0° C. ^1H-NMR ($CDCl_3$) δ 1.32 (3H,s, CH_3), 1.45 (3H,s, CH_3), 1.4-2.6 (13H,m), 3.4-4.3 (4H,m). Anal. Calcd. for $C_{12}H_{23}BF_4OS$: C, 47.76; H, 7.57. Found: C, 47.40; H, 7.67.

A solution of 189 mg of the 1:1 mixture of salts 29a and 30a ($X^- = BF_4^-$) is dissolved in $CDCl_3$ and heated at 110°C (sealed NMR tube) for 5 h. The ^{13}C-NMR spectrum showed that isomer 30a had disappeared. ^{13}C-NMR ($CDCl_3$) δ 73.59, 66.65, 54.51, 42.52, 31.70, 31.30, 28.34, 28.05, 24.55, 23.89 (triple intensity).

2-[2-Oxyethoxycarbonylisopropyl]-1-thioniabicyclo[4.4.0]decane Tetrafluoroborate (29b, 30b, 31b). Method A: To a flask containing 219.3 mg (0.897 mmol) of salt 1 ($X^- = BF_4^-$) and 3 mL of dry THF, cooled to -72°C, is added an equivalent amount of *n*-butyllithium. The reaction mixture is stirred at -72°C for 2 h, at which time 0.75 mL (10 mmol) of acetone is added. After stirring for 5 min, 1 mL (10 mmol) of ethyl chloroformate (distilled from potassium carbonate) is added. The solution is allowed to stir for 0.5 h at -72°C, then allowed to warm to room temperature. The resulting salt is dissolved in water and extracted with ether. The water is removed at reduced pressure. Chloroform is added and any undissolved material is removed by filtration. Removal of the $CHCl_3$ yields 261.5 mg (78% as BF_4^-, 90% as Cl^-) of product. The product was converted to the tetrafluoroborate by

ion exchange and recrystallized from THF to give analytically pure carbonate; mp 155-157° C. ^{1}H-NMR (360 M-Hz, $CDCl_3$) δ 1.28 (3H, m, CH_3), 1.62 (3H, s, CH_3, major isomer), 1.67 (3H, s, CH_3, minor isomer), 1.70 (3H, s, CH_3, minor isomer), 1.72 (3H, s, CH_3, major isomer), 1.8-2.0 (6H, m), 2.0-2.4 (6H, m), 3.16 (1H, m, minor isomer), 3.57 (1H, broad t, J=13, minor isomer), 3.83 (1H, m), 4.13 (3H, m), 4.35 (1H, broad d, J=12, major isomer). ^{13}C-NMR ($CDCl_3$), 29b: δ 151.37, 84.23, 63.40, 63.01, 54.32, 37.76, 27.62, 25.97, 24.07, 22.97, 20.10; 30b: δ 151.75, 82.54, 63.41, 60.40, 45.00, 30.12, 27.51, 26.75, 25.42, 23.92, 23.29, 22.81, 19.26, 18.61, 13.45; 31b: δ 151.50, 84.41, 62.62, 54.96, 44.63, 35.28, 34.10, 28.31, 28.02, 24.18, 21.76, 16.87. Anal. Calcd. for $C_{15}H_{27}BF_4O_3S$: C, 48.14; H, 7.27. Found: C, 48.18; H, 7.18.

Method B: A slurry of 891.0 mg (3.65 mmol) of salt 1 ($X^- = BF_4^-$) in 5 mL of dry THF is cooled to -23° C. *n*-Butyllithium (10% excess) is added and the mixture is stirred for 2 h keeping the temperature between -20° and -23° C. The reaction mixture is cooled to -72° C and 2.7 mL (37 mmol) of acetone is added. After 5 min of stirring at -72° C, 0.4 mL (4 mmol) of ethyl chloroformate is added; the solution is stirred for 0.5 h and allowed to warm to room temperature. The solvents are removed at reduced pressure and CH_2Cl_2 is added. Any material that does not dissolve is removed by filtration. The CH_2Cl_2 is evaporated and the product is triturated with ether. The product is dried *in vacuo* to yield 880 mg (65-75%). IR ($CHCl_3$) ν_{max} 1730, 1000-1100 cm^{-1}; ^{13}C-NMR ($CDCl_3$), 30b (75%): δ 151.75, 82.54, 63.41, 60.40, 45.00, 30.12, 29.24, 27.51, 26.75, 25.42, 23.92, 23.29, 22.81, 13.45; 31b (25%): δ 151.50, 84.41, 62.62, 54.96, 44.63, 35.28, 34.10, 28.31, 28.02, 25.67, 21.76, 18.61, 16.87.

1,10-Dimethyl-1-thioniabicyclo[4.4.0]decane Picrate (32 + 33). Method A: To a slurry of 212.4 mg (0.870 mmol) of salt 1 ($X^- = BF_4^-$) in 2 mL of dry THF, cooled to -76° C, is slowly added 3 equiv of *tert*-butyllithium. After stirring for 1 h at -76° C, 2 mL (32 mmol) of methyl iodide is added and the mixture is stirred for 0.5 h at -72° C. The solvents are evaporated and the crude product is converted to the picrate to yield 42.4 mg (12%) of dimethyl isomers 32 and 33. ^{1}H-NMR (D_2O, external TMS, 60-MHz) δ 1.54 (d, J=7, CH_3), 1.60 (d, J=6, CH_3), 1.5-2.4 (m), 3.5-4.2 (m); ^{1}H-NMR (360-MHz, D_2O) δ 1.54 (3H,d, J=7.0, CH_3), 1.60 (3H, d, J=6.5, CH_3), 1.6-2.3 (12H, m), 3.46 (1H,m), 3.78 (1H,m), 3.88 (1H, tt, J=7.8, 3.9, *cis*), 3.95 (1H, t, J=7); ^{13}C-NMR ($CDCl_3$), 32: δ 53.9, 50.2, 34.9, 31.0, 23.7, 20.5; 33: 42.2, 41.0, 28.4, 26.5, 18.0, 17.2. Anal. Calcd. for $C_{17}H_{23}N_3O_7S$: C, 49.38; H, 5.61; N, 10.16. Found: C, 49.12; H, 5.39; N, 10.17.

Method B: A slurry of 281.3 mg (1.15 mmol) of salt 1 ($X^- = BF_4^-$) in 2 mL of dry THF is cooled to -72° C and 3 equiv of *tert*-butyllithium are added. After stirring at -65° to -70° C for 1 h, an excess (2 mL) of methyl iodide is added and the mixture is stirred for 15 min. Several drops of 48% fluoboric acid is added and the solvents are removed. A hot picric acid solution is added to yield 58.8 mg (12%) of salt 32. ^{13}C-NMR ($CDCl_3$) δ 42.2, 41.0, 28.4, 26.5, 18.0, 17.2.

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Supplementary Material Available: Tables of thermal parameters and structure factors for compound 17; 360-MHz ^{1}H-NMR spectra of compounds 1a, 1b, and 17 (fourteen pages). Ordering information is given on any current masthead page.

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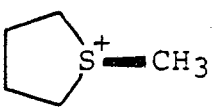
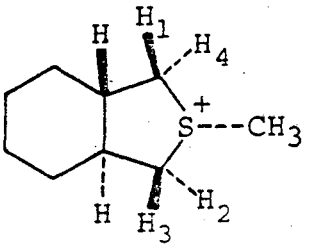
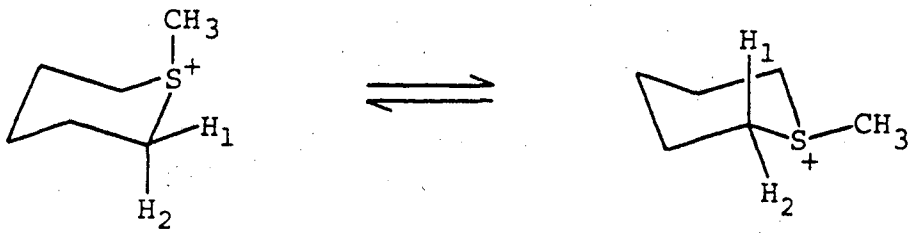


vi



vii

four ring protons in vii are: H_1, 1; H_2, 700; H_3, *ca.* 90; and H_4, *ca.* 90.[17b] Because the NMR signals of H_3 and H_4 overlap, separate exchange rates were not determined, although it is asserted that they appear to exchange at about the same rate. Examination of a scale model of vii[14] reveals the relevant dihedral angles to be: H_1, 5°; H_2, 100°; H_3, 20°; H_4, 125°. Thus, it is clear that H_2 should exchange most rapidly and H_1 least rapidly, with H_3 and H_4 being of intermediate acidity. Since Fava and co-workers have shown that the more flexible salt vi exists in a conformation with maximum puckering at C_3-C_4 and minimum puckering at C_2-S-C_5,[17a] the same argument may be used to explain the enhanced acidity of the protons *syn* to methyl



7a ⇌ 7b

in this salt. Furthermore, this argument serves to explain why H_2 in *viii* and the *syn* protons in *vi* are more acidic than either ring proton in salt 7.[16a] For compound 7, which may exist in conformations 7a and 7b ($\Delta G° = 0.0$ kcal mole^{-1}),[16b] estimated dihedral angles for the C_1-H and C_2-H bonds are 55°, 60° and 55°, 175°, respectively. Experimental dihedral angles for the analogous 4-tert-butyl salts[16b] are 51°, 64° and 57°, 175°, respectively.

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FIGURE CAPTIONS

Fig. 1. Stereo (ORTEP) drawing of the bicyclic sulfonium anion. Hydrogen atoms are drawn with fictitious spherical thermal parameters of 0.5 $\AA^2$.

Fig. 2. The unit cell, viewed along the c axis. The long axis is b. A line connects each iodide ion with its nearest sulfur neighbor.

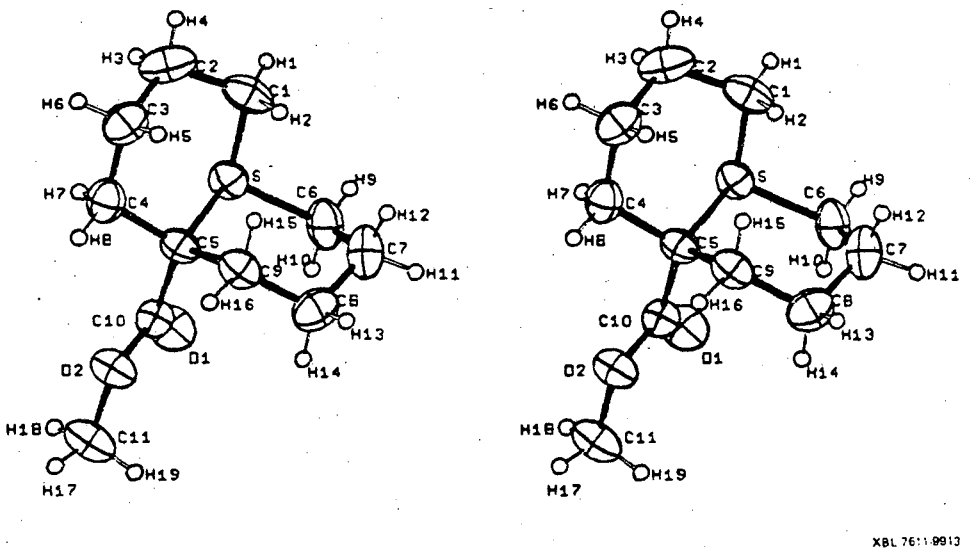
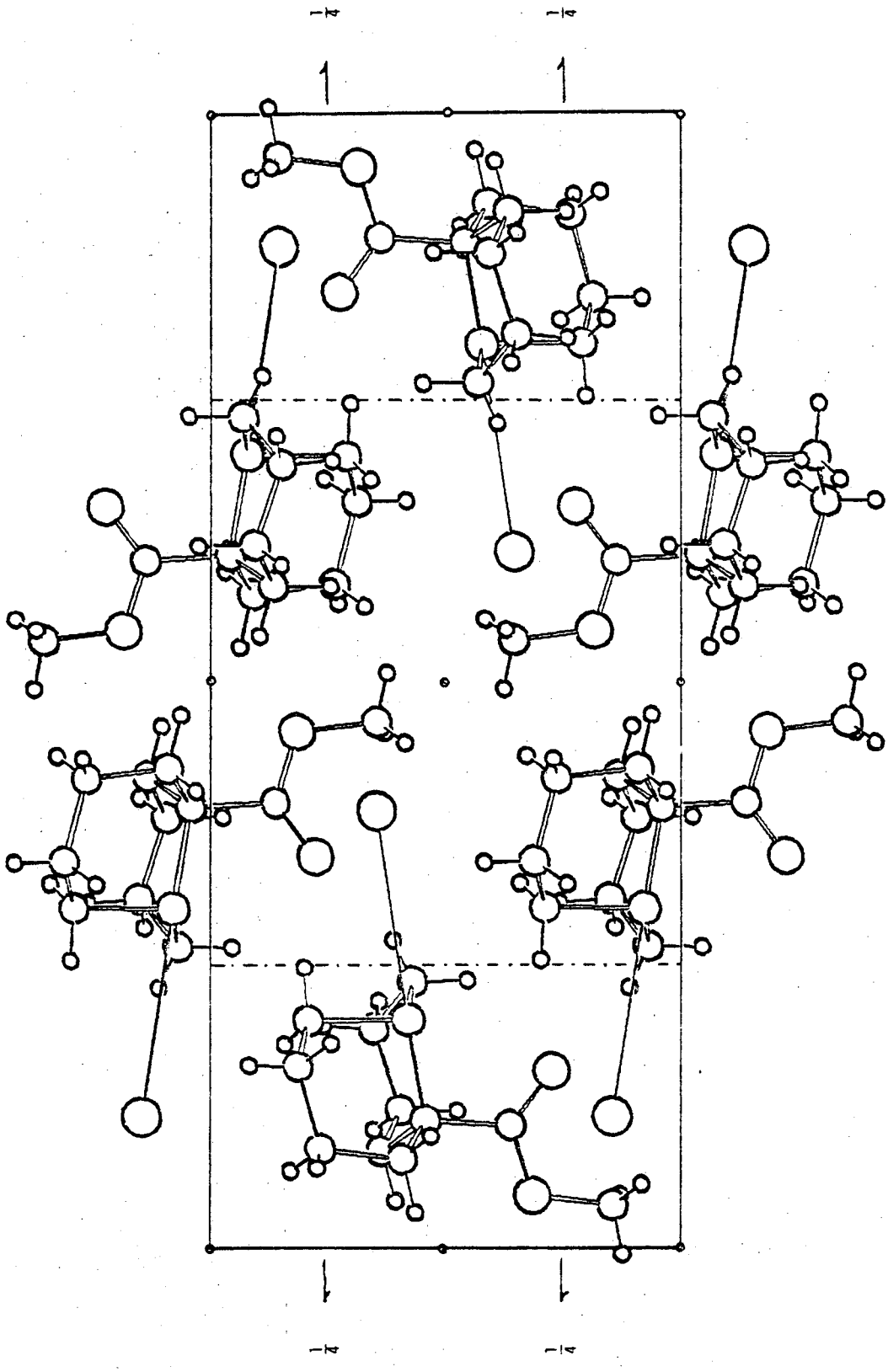

H4
H3
C2
H1
C1
H6
C3
H2
H5
S
C6
H9
H7
C4
H12
H15
C5
C7
H8
H10
H11
C9
H16
C8
C10
H13
O1
O2
H14
H18
C11
H19
H17
XBL 7611-9913

Fig. 1



XBL 7611-9912

Fig. 2

SUPPLEMENTARY MATERIAL

for

SYNTHESIS AND STEREOSTRUCTURE OF A BICYCLIC SULFONIUM SALT

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Thermal parameters for $C_{11}H_{19}IO_2S$

ATOM	B11	B22	B33	B12	B13	B23
I	4.75(3)	3.87(2)	5.51(3)	.02(3)	1.40(2)	-.45(3)
S	3.36(9)	2.38(7)	3.38(9)	-.03(7)	.99(7)	-.29(6)
O1	3.3(3)	3.2(2)	5.4(3)	-.8(2)	1.1(2)	-.1(2)
O2	2.9(3)	2.9(2)	5.2(3)	.1(2)	1.2(2)	-.1(2)
C1	3.3(4)	2.9(4)	6.1(6)	.6(3)	1.2(4)	-.9(4)
C2	4.4(5)	5.0(5)	5.8(6)	-.9(4)	3.1(5)	-1.4(4)
C3	4.5(5)	4.9(5)	4.6(5)	-.5(4)	2.3(4)	.2(4)
C4	4.3(5)	3.2(4)	3.8(4)	-.2(3)	1.5(3)	.5(3)
C5	2.5(3)	2.0(3)	3.6(3)	-.0(3)	.9(2)	-.2(3)
C6	5.2(6)	2.9(4)	4.3(4)	-.1(4)	1.2(4)	1.0(3)
C7	4.3(5)	4.9(5)	3.6(4)	-.3(4)	.1(4)	.9(4)
C8	4.6(5)	4.5(4)	3.5(4)	-.6(4)	1.4(4)	-1.1(4)
C9	3.3(4)	2.4(3)	3.9(4)	-.1(3)	.7(3)	-.6(3)
C10	2.6(3)	2.9(3)	2.9(3)	-.4(3)	.9(3)	-.1(3)
C11	3.2(4)	3.9(4)	6.5(6)	1.0(4)	.9(4)	.1(5)
H1	3.2(16)					
H2	7.1(25)					
H3	4.4(21)					
H4	5.3(23)					
H5	2.5(16)					
H6	2.4(16)					
H7	3.6(20)					
H8	3.3(16)					
H9	6.1(25)					
H10	3.6(19)					
H11	5.2(22)					
H12	.5(12)					
H13	4.8(23)					
H14	7.9(27)					
H15	4.3(19)					
H16	3.1(16)					
H17	3.3(19)					
H18	7.3(29)					
H19	8.0(35)					

OBSERVED STRUCTURE FACTORS, STANDARD DEVIATIONS, AND DIFFERENCES (ALL X 4.0)

$C_{11}H_{19}IO_2S$ F(0,0,0) = 2727

FOB AND FCA ARE THE OBSERVED AND CALCULATED STRUCTURE FACTORS.
SG = ESTIMATED STANDARD DEVIATION OF FOB. DEL = /FOB/ - /FCA/.
* INDICATES ZERO WEIGHTED DATA.

L	FOB	SG	DEL
H,K=	0,	0	
21	096	28	-51
4	398	10	-1
6	34	40	14*
8	17	34	12*
H,K=	0,	1	
1	193	10	-5
2	348	10	-7
3	189	7	1
4	232	8	-7
5	230	7	-4
6	48	36	27*
7	116	5	-5
8	30	18	24*
9	45	13	-5
H,K=	0,	2	
0	0122		-36*
1	90	18	11
2	40	52	-4*
3	76	9	-5
4	32	17	11*
5	60	8	-3
6	7	42	-3*
7	46	9	-5
8	30	32	16*
9	73	9	11
H,K=	0,	3	
1	262	8	8
2	501	13	-5
3	336	9	-7
4	367	10	-11
5	213	7	-8
6	191	7	-4
7	96	5	-13
8	74	10	-4
9	58	8	6
H,K=	0,	4	
0	924	24	32
1	151	7	3
2	593	15	18
3	213	6	2
4	108	5	-2
5	82	9	-4
6	15	34	-3*
7	37	12	24*
8	52	9	12
H,K=	0,	5	
1	103	12	-7
2	204	6	2
3	182	6	-4
4	118	5	-8
5	195	6	-4
6	95	7	-4
7	97	5	0
8	21	26	4*
H,K=	0,	6	
0	353	12	-3
1	841	21	15
2	25	28	-3*
3	389	10	-0
4	82	9	-3
5	113	9	-6
6	41	32	17*
7	39	10	16
8	36	12	24*
H,K=	0,	7	
1	22	50	-11*
2	229	6	2
3	99	6	2
4	285	8	3
5	0	34	-17*
6	147	5	-7
7	15	26	4*
8	83	7	-0
H,K=	0,	8	
0	282	8	7
1	257	7	1
2	220	7	9
3	160	5	5
4	78	10	-3
5	13	38	-1*
6	18	28	-10*
7	30	17	25*
8	46	15	-2*
H,K=	0,	9	
1	266	7	7
2	80	13	11
3	372	10	2
4	130	6	3
5	276	8	-10
6	105	5	-8
7	129	6	-2
8	63	6	4
H,K=	0,	10	
0	434	12	5
1	379	10	2
2	307	9	2
3	122	5	9
4	119	8	2
5	0	53	-16*
6	20	29	-1*
7	40	18	-0*
8	14	31	8*
H,K=	0,	11	
1	0	35	-22*
2	137	7	-0
3	10	29	-11*
4	110	6	-1
5	20	24	12*
6	82	7	3
7	19	29	-3*
8	21	32	5*
H,K=	0,	12	
0	410	11	15
1	223	7	-3
2	379	11	-3
3	32	36	-29*
4	143	6	5
5	18	27	6*
6	45	12	-0
7	36	18	4*
H,K=	0,	13	
1	138	6	-5
2	19	37	-10*
3	358	10	-8
4	64	11	2
5	188	6	-7
6	29	15	-4*
7	104	6	2
H,K=	0,	14	
0	275	8	-9
1	150	6	0
2	230	7	3
3	25	41	-4*
4	106	4	1
5	52	11	-6
6	35	21	11*
7	53	11	-1
H,K=	0,	15	
1	14	50	8*
2	124	8	-2
3	80	7	9
4	129	5	-4
5	35	20	16*
6	101	6	3
7	37	10	18
H,K=	0,	16	
0	111	8	1
1	258	8	-5
2	81	11	-8
3	135	5	-1
4	6	31	4*
5	27	23	2*
6	0	31	-7*
H,K=	0,	17	
1	54	8	-21
2	29	15	2*
3	130	5	-8
4	54	10	5
5	85	6	-1
6	68	7	2
H,K=	0,	18	
0	138	6	1
1	201	6	-1
2	140	5	3
3	121	5	3
4	59	7	4
5	28	22	4*
6	37	16	31*
H,K=	0,	19	
1	16	35	15*
2	93	7	-4
3	75	10	-6
4	110	5	1
5	42	11	-5
H,K=	0,	20	
0	51	10	7
1	134	6	-1
2	73	10	-3
3	58	8	-1
4	56	9	-5
5	40	22	14*
H,K=	0,	21	
1	22	30	1*
2	0	41	-2*
3	68	7	-11
4	29	32	15*
H,K=	0,	22	
0	198	7	4
1	48	15	2*
2	172	6	0
3	48	10	9
H,K=	0,	23	
1	16	28	-12*
2	24	46	-19*
H,K=	1,	0	
5	62	9	-8
6	58	10	-12
7	97	11	3
8	348	10	-9
9	111	8	1
10	444	12	35
11	606	16	-48
12	28	20	11*
13	70	8	-3
14	111	5	-13
H,K=	1,	1	
9	28	43	23*
H,K=	0,	17	
8	125	6	-7
7	43	17	-8*
6	229	7	-12
5	62	10	-1
4	188	6	-0
-3	155	5	3
-2	69	16	4
-1	538	14	20
0	10	63	-16*
1	445	12	2
2	277	8	-13
3	406	11	-15
4	223	6	-17
5	203	7	-9
6	150	6	2
7	34	19	9*
8	18	43	1*
H,K=	1,	2	
-9	30	26	6*
-8	38	13	0*
-7	25	34	19*
-6	283	8	-6
-5	24	30	20*
-4	557	14	-2
-3	46	16	-0*
-2	750	19	35
-1	14	49	11*
0	330	10	3
1	238	7	3
2	330	9	-7
3	162	6	-3
4	34	36	23*
5	121	7	8
6	139	7	-5
7	31	35	-8*
8	92	6	-4
H,K=	1,	3	
-9	56	10	16
-8	109	6	-1
-7	122	5	-3
-6	198	7	-10
-5	209	7	-2
-4	204	7	-2
-3	179	6	-4
-2	51	29	-2*
-1	211	6	10
0	0	47	-45*
1	536	14	12
2	95	11	-4
3	480	12	-12
4	150	6	-1
5	182	7	-9
6	77	7	-10
7	41	12	-1*
8	41	15	26*
H,K=	1,	4	
-9	34	20	14*
-8	11	32	2*

STRUCTURE FACTORS CONTINUED FOR $C_{11}H_{19}IO_2S$

L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
-7	20	28	0*	-6	38	41	20*	-3	295	8	6	4	224	6	0	0	156	11	-7
-6	39	19	-4*	-5	208	6	0	-2	388	10	4	5	25	29	9*	1	47	10	-7
-5	197	7	-2	-4	32	33	22*	-1	405	11	-2	6	63	8	5	2	198	9	-8
-4	88	5	1	-3	190	6	-1	0	415	11	4	7	22	37	11*	3	63	8	3
-3	371	10	1	-2	62	17	-8	1	341	9	4	H,K=	1,	14		4	138	10	-2
-2	343	10	10	-1	238	8	2	2	113	8	-1	-7	33	33	7*	5	31	25	0*
-1	636	16	12	0	339	9	2	3	212	6	1	-6	37	39	4*	6	51	30	8*
0	367	10	1	1	444	11	3	4	74	7	-0	-5	91	6	-10	H,K=	1,	18	
1	355	9	6	2	212	6	1	5	58	8	-1	-4	149	5	6	-6	22	40	10*
2	287	8	-2	3	442	12	11	6	103	6	-6	-3	150	5	-2	-5	54	18	-9*
3	45	9	3	4	160	6	-3	7	24	28	22*	-2	112	5	4	-4	15	37	7*
4	81	7	-5	5	214	6	-3	H,K=	1,	11		-1	134	5	-7	-3	113	13	-3
5	168	7	-11	6	26	17	15*	-8	15	39	8*	0	135	5	4	-2	35	16	2*
6	36	14	6*	7	50	15	2*	-7	66	10	-9	1	87	7	-1	-1	121	5	-2
7	121	10	-11	8	10	31	4*	-6	2	31	-2*	2	10	34	2*	0	33	22	-2*
8	12	42	-7*	H,K=	1,	8		-5	57	16	4	3	19	34	0*	1	60	9	4
H,K=	1,	5		-8	23	34	1*	-4	42	15	-10*	4	93	5	1	2	33	65	4*
-9	42	17	1*	-7	64	7	10	-3	197	6	10	5	55	10	-3	3	22	28	16*
-8	41	19	-11*	-6	105	8	-4	-2	26	31	9*	6	101	7	-5	4	0	31	-5*
-7	60	7	4	-5	174	5	1	-1	321	9	4	7	48	22	-11*	5	48	16	-26*
-6	85	12	-9	-4	84	6	1	0	60	10	5	H,K=	1,	15		H,K=	1,	19	
-5	102	6	-5	-3	340	9	-1	1	381	10	-0	-7	82	8	-3	-5	111	11	-12
-4	23	30	14*	-2	80	7	-3	2	105	11	5	-6	0	32	-28*	-4	64	12	-11
-3	89	5	8	-1	314	8	8	3	342	9	4	-5	92	7	-1	-3	73	7	-3
-2	213	8	3	0	97	9	6	4	33	40	-14*	-4	35	16	3*	-2	65	10	0
-1	28	44	17*	1	232	11	4	5	192	6	-9	-3	32	25	-14*	-1	26	33	20*
0	336	9	3	2	43	10	-2	6	23	31	21*	-2	100	6	1	0	8	27	-26*
1	226	7	9	3	29	20	26*	7	56	11	-6	-1	123	6	4	1	105	10	-5
2	447	12	7	4	104	8	-10	H,K=	1,	12		0	47	73	-39*	2	31	33	12*
3	229	7	1	5	126	6	-6	-8	48	17	16*	1	209	6	-4	3	112	8	-7
4	284	8	-8	6	97	7	-12	-7	18	29	11*	2	99	15	-8	4	42	22	-2*
5	125	6	-3	7	98	6	-11	-6	88	6	3	3	200	6	-3	5	70	10	3
6	108	6	-10	8	48	19	-7*	-5	102	5	2	4	25	28	9*	H,K=	1,	20	
7	28	33	-8*	H,K=	1,	9		-4	200	6	-1	5	148	8	2	-5	46	15	12*
8	28	39	22*	-8	78	10	-2	-3	183	7	-2	6	6	32	-12*	-4	126	10	-6
H,K=	1,	6		-7	70	6	8	-2	196	7	6	H,K=	1,	16		-3	48	15	-13*
-9	19	32	13*	-6	157	5	-10	-1	199	6	-1	-7	23	41	12*	-2	133	6	-2
-8	14	38	-14*	-5	95	8	-5	0	141	5	-4	-6	52	31	3*	-1	33	20	-10*
-7	20	34	16*	-4	191	8	-2	1	134	15	-2	-5	103	7	2	0	134	6	-5
-6	77	9	10	-3	89	12	-9	2	0	37	-38*	-4	172	6	-1	1	25	33	8*
-5	59	8	-8	-2	17	29	-6*	3	133	6	5	-3	150	5	-0	2	34	37	6*
-4	356	9	12	-1	125	5	4	4	74	7	-3	-2	294	9	-4	3	22	34	-21*
-3	277	8	4	0	121	8	-9	5	28	15	8*	-1	162	5	6	4	19	41	-15*
-2	548	14	18	1	3	29	-18*	6	94	7	8	0	296	9	-8	H,K=	1,	21	
-1	251	9	0	2	359	10	-1	7	0	33	-20*	1	103	13	-7	-4	22	35	3*
0	582	15	13	3	26	31	23*	H,K=	1,	13		2	112	52	-36*	-3	99	7	2
1	269	7	3	4	250	8	5	-7	15	33	-5*	3	74	6	5	-2	13	40	5*
2	256	7	9	5	27	38	12*	-6	161	7	-17	4	59	12	33	-1	82	8	-14
3	83	7	5	6	94	7	-7	-5	30	22	5*	5	23	37	16*	0	80	8	-2
4	31	17	7*	7	13	31	6*	-4	181	6	-9	6	12	38	1*	1	112	7	-8
5	25	33	2*	8	29	35	26*	-3	91	5	-4	H,K=	1,	17		2	93	6	3
6	69	8	3	H,K=	1,	10		-2	117	7	-0	-6	31	49	-2*	3	78	16	-7
7	44	11	-5	-8	31	25	29*	-1	38	11	2*	-5	25	34	7*	H,K=	1,	22	
8	39	42	5*	-7	16	29	10*	0	129	6	-5	-4	48	10	24	-3	98	7	3
H,K=	1,	7		-6	66	14	-4	1	15	36	-1*	-3	17	33	11*	-2	10	33	-8*
-8	25	38	23*	-5	133	5	6	2	207	7	9	-2	73	7	5	-1	141	9	-7
-7	169	6	-7	-4	247	8	4	3	33	33	19*	-1	32	12	22*	0	0	48	-17*

STRUCTURE FACTORS CONTINUED FOR $C_{11}H_{19}IO_2S$

L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
1	95	9	-9	H,K=	2,	3		H,K=	2,	6		-7	24	32	-25*	-1	205	7	-8
2	18	32	-3*	-9	0	34	-10*	-9	32	39	17*	-6	51	9	4	0	0	30	-4*
3	36	59	-24*	-8	87	8	0	-8	29	33	-14*	-5	36	42	11*	1	37	52	-26*
H,K=	1,	23		-7	33	40	-13*	-7	55	13	-5	-4	20	35	-8*	2	110	18	-19
-2	35	19	-0*	-6	132	6	2	-6	77	10	18	-3	129	7	8	3	69	16	-4
-1	66	15	3	-5	78	7	8	-5	226	9	1	-2	36	22	21*	4	96	10	-2
0	11	32	8*	-4	128	5	7	-4	178	6	0	-1	371	10	0	5	75	7	1
1	103	11	10	-3	83	6	10	-3	447	12	19	0	64	23	8*	6	77	9	12
2	41	13	17*	-2	212	8	10	-2	146	5	5	1	362	10	-3	7	54	11	10
H,K=	2,	0		-1	474	12	1	-1	256	7	3	2	24	28	15*	H,K=	2,	13	
-8	58	11	24	0	497	15	-6	0	58	10	3	3	227	8	8	-8	14	33	3*
-6	84	7	-3	1	368	10	2	1	25	27	-19*	4	24	32	-8*	-7	27	33	-11*
-4	425	11	7	2	310	8	13	2	75	7	1	5	49	16	-3*	-6	13	30	12*
-2	757	19	43	3	72	9	-1	3	193	6	1	6	13	31	-10*	-5	38	11	3*
0	335	9	1	4	129	6	-1	4	126	6	5	7	31	32	30*	-4	43	20	41*
2	94	5	-1	5	47	12	1	5	143	8	-11	H,K=	2,	10		-3	56	37	1*
4	231	8	-7	6	21	34	7*	6	41	30	3*	-8	21	32	5*	-2	68	8	4
6	89	6	5	7	47	14	8	7	74	10	-9	-7	43	17	-6*	-1	258	7	7
8	51	21	3*	8	30	38	-6*	8	37	23	-2*	-6	32	35	16*	0	43	10	15
H,K=	2,	1		H,K=	2,	4		H,K=	2,	7		-5	178	7	-5	1	317	9	7
-9	21	42	-10*	-9	36	37	11*	-9	40	43	30*	-4	55	16	7	2	22	37	-8*
-8	54	11	4	-8	76	10	-1	-8	46	20	-18*	-3	297	8	6	3	127	6	5
-7	20	36	14*	-7	0	34	-2*	-7	52	13	5	-2	49	13	1	4	5	33	-0*
-6	92	12	-13	-6	183	6	-1	-6	90	8	-6	-1	228	7	0	5	26	46	-7*
-5	42	11	9	-5	17	28	13*	-5	2	45	0*	0	65	7	6	6	46	12	32
-4	37	37	10*	-4	391	10	3	-4	53	14	-3	1	0	27	-11*	H,K=	2,	14	
-3	339	9	12	-3	112	10	-4	-3	115	5	-3	2	193	8	-5	-7	83	8	14
-2	187	8	8	-2	420	11	13	-2	265	7	8	3	144	6	7	-6	123	9	2
-1	543	14	6	-1	17	34	-21*	-1	301	8	4	4	138	7	2	-5	100	6	-7
0	684	18	-22	0	224	8	-1	0	517	19	5	5	104	6	-0	-4	167	6	-10
1	447	16	-15	1	31	41	13*	1	262	7	0	6	73	8	8	-3	248	7	-7
2	401	10	-9	2	160	6	3	2	301	8	4	7	57	13	-16	-2	186	6	4
3	228	7	-10	3	43	12	13	3	92	8	4	H,K=	2,	11		-1	159	7	-3
4	213	7	-7	4	169	6	-4	4	148	6	-3	-8	67	12	-6	0	49	12	-6
5	39	17	-7*	5	52	21	-1*	5	64	9	-0	-7	39	13	29*	1	371	03	-29*
6	52	13	-13	6	133	5	-9	6	24	33	20*	-6	37	24	-8*	2	49	23	-1*
7	0	31	-2*	7	31	43	3*	7	27	39	19*	-5	30	31	23*	3	87	6	-2
8	33	30	16*	8	71	10	11	H,K=	2,	8		-4	58	25	-6*	4	94	6	5
H,K=	2,	2		H,K=	2,	5		-9	57	12	6	-3	0	31	-5*	5	59	11	0
-9	38	24	-10*	-9	70	9	5	-8	87	8	-2	-2	390	11	-3	6	85	8	9
-8	55	12	2	-8	30	36	-7*	-7	121	6	6	-1	80	8	1	H,K=	2,	15	
-7	141	8	-7	-7	50	9	8	-6	209	7	-4	0	517	13	2	-7	22	50	10*
-6	110	8	-1	-6	36	17	27*	-5	255	7	9	1	31	41	7*	-6	44	15	-7*
-5	385	10	9	-5	69	11	8	-4	317	9	3	2	416	11	4	-5	39	46	-27*
-4	226	7	2	-4	55	9	18	-3	259	7	2	3	50	11	12	-4	19	27	14*
-3	537	14	26	-3	466	12	20	-2	309	8	0	4	186	7	-2	-3	123	11	-2
-2	138	11	8	-2	184	6	8	-1	325	9	-8	5	0	36	-8*	-2	184	7	-1
-1	371	10	9	-1	599	18	-4	0	32	25	17*	6	72	12	9	-1	156	6	5
0	101	9	-1	0	122	8	1	1	97	5	-4	7	0	32	-4*	0	237	8	-7
1	244	7	-3	1	592	18	-1	2	88	8	3	H,K=	2,	12		1	94	12	-5
2	39	14	5*	2	260	7	9	3	25	28	4*	-8	15	43	9*	2	208	6	0
3	265	7	-14	3	365	10	3	4	168	6	1	-7	78	10	-14	3	96	7	-1
4	0	36	-6*	4	93	6	-5	5	74	9	0	-6	60	14	-7	4	59	23	2*
5	229	7	-10	5	172	7	-2	6	120	8	-4	-5	172	6	5	5	62	9	10
6	36	36	-2*	6	39	14	12*	7	57	10	5	-4	117	6	-5	6	58	20	46*
7	109	8	-9	7	51	11	2	H,K=	2,	9		-3	286	8	-1	H,K=	2,	16	
8	0	36	-22*	8	36	32	30*	-8	41	20	12*	-2	160	9	4	-7	27	35	23*

L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
-6	32	39	7*	2	28	41	-7*	-5	72	9	4	-2	405	11	1	1	160	5	0
-5	74	9	-2	3	50	18	-18*	-4	303	8	17	-1	235	7	-0	2	113	7	-5
-4	65	12	-13	4	33	36	-5*	-3	165	7	12	0	363	10	-6	3	189	6	5
-3	119	5	1	H,K=	2,	21		-2	192	7	14	1	117	5	-0	4	64	19	6*
-2	75	10	-4	-4	17	31	-3*	-1	71	16	-3	2	240	7	7	5	111	6	2
-1	66	9	-9	-3	44	27	-1*	0	20	42	11*	3	94	7	5	6	39	26	-11*
0	0	39	-25*	-2	85	7	7	1	94	6	-1	4	0	32	-3*	7	23	37	14*
1	25	33	-8*	-1	94	7	6	2	248	7	-1	5	48	9	4	H,K=	3,	9	
2	104	8	-0	0	83	7	12	3	35	19	10*	6	47	20	9*	-8	0	36	-8*
3	95	7	-6	1	109	7	6	4	191	8	2	7	35	23	-4*	-7	50	17	-10*
4	83	7	8	2	102	7	-4	5	47	9	-10	H,K=	3,	6		-6	119	6	6
5	84	9	9	3	37	47	-17*	6	85	14	-8	-9	0	43	-13*	-5	54	19	-14*
H,K=	2,	17		H,K=	2,	22		7	19	35	2*	-8	61	25	6*	-4	311	9	-3
-6	21	42	2*	-3	0	47	-2*	H,K=	3,	3		-7	79	7	2	-3	130	6	4
-5	5	32	-4*	-2	14	32	-28*	-9	0	44	-18*	-6	135	6	3	-2	424	11	2
-4	0	30	-11*	-1	0	33	-3*	-8	0	34	-7*	-5	112	6	3	-1	131	7	-3
-3	106	7	11	0	19	36	14*	-7	39	13	-2*	-4	117	6	4	0	408	11	-2
-2	13	26	-1*	1	0	32	-9*	-6	66	9	-5	-3	231	7	11	1	100	6	-1
-1	263	8	2	2	31	40	-15*	-5	239	7	5	-2	37	11	6	2	206	6	7
0	34	40	14*	H,K=	2,	23		-4	212	6	4	-1	44	15	2*	3	12	43	2*
1	251	7	2	-2	79	10	2	-3	382	10	16	0	250	7	-2	4	27	21	26*
2	0	39	-22*	-1	48	13	-2	-2	305	8	9	1	21	27	-19*	5	65	7	2
3	182	7	6	0	125	7	8	-1	539	14	-9	2	393	10	8	6	68	15	-9
4	39	16	7*	1	50	16	10*	0	305	8	-0	3	89	6	9	7	39	19	2*
5	54	20	-14*	H,K=	3,	0		1	394	10	-7	4	307	9	13	H,K=	3,	10	
H,K=	2,	18		-9	63	9	5	2	144	5	2	5	40	12	3*	-8	61	11	-4
-6	132	7	14	-7	194	6	3	3	124	5	-9	6	118	8	4	-7	57	12	-12
-5	32	28	10*	-5	152	7	5	4	12	35	6*	7	33	37	29*	-6	102	6	-6
-4	126	8	-1	-3	32	15	18*	5	14	35	-3*	H,K=	3,	7		-5	94	7	6
-3	22	33	-26*	-1	319	9	-4	6	71	9	-2	-9	0	33	-9*	-4	159	6	2
-2	124	6	-4	1	405	11	-9	7	36	23	-13*	-8	44	27	1*	-3	69	11	15
-1	67	12	-6	3	449	12	-9	H,K=	3,	4		-7	19	34	-7*	-2	44	37	12*
0	45	22	0*	5	297	9	-5	-9	78	17	-1	-6	55	18	-14*	-1	82	6	-3
1	0	39	-15*	7	110	8	10	-8	43	19	37*	-5	119	8	8	0	88	7	1
2	24	37	7*	H,K=	3,	1		-7	185	6	-1	-4	39	12	12*	1	144	8	-10
3	0	56	-14*	-9	57	11	3	-6	34	36	23*	-3	312	8	-3	2	205	6	4
4	39	22	-8*	-8	50	10	7	-5	251	8	6	-2	84	6	-1	3	212	7	4
5	37	25	17*	-7	34	24	26*	-4	62	7	1	-1	414	11	-12	4	163	5	1
H,K=	2,	19		-6	73	15	-2	-3	178	5	8	0	167	5	-2	5	133	6	10
-5	14	43	-20*	-5	123	6	3	-2	74	18	-4	1	372	10	-3	6	65	9	4
-4	6	44	-1*	-4	182	7	2	-1	90	16	7	2	82	7	5	H,K=	3,	11	
-3	68	8	12	-3	332	9	14	0	179	5	-4	3	84	9	9	-8	41	20	27*
-2	78	8	-5	-2	424	11	7	1	251	7	4	4	0	32	-9*	-7	0	38	-36*
-1	74	8	-10	-1	163	8	1	2	262	7	-2	5	41	17	-5*	-6	36	15	-6*
0	110	6	-2	0	362	9	-4	3	355	10	10	6	33	19	18*	-5	82	10	14
1	82	7	-1	1	282	8	-4	4	146	6	-2	7	64	27	3*	-4	36	43	5*
2	86	8	0	2	194	6	3	5	173	6	-2	H,K=	3,	8		-3	181	7	-5
3	22	32	2*	3	113	7	-4	6	73	13	-6	-9	82	10	23	-2	47	13	3
4	45	12	26	4	45	10	10	7	40	41	-20*	-8	49	13	-1	-1	283	8	-9
H,K=	2,	20		5	54	8	2	H,K=	3,	5		-7	161	6	7	0	41	27	12*
-5	101	9	11	6	99	7	-5	-9	30	34	8*	-6	97	7	9	1	232	7	4
-4	77	9	2	7	12	36	3*	-8	67	9	3	-5	220	7	2	2	0	31	-24*
-3	157	9	-5	H,K=	3,	2		-7	15	30	-4*	-4	63	11	-0	3	130	6	0
-2	66	9	5	-9	29	36	19*	-6	27	36	-11*	-3	197	6	-6	4	6	30	0*
-1	77	8	0	-8	110	9	-3	-5	121	6	-4	-2	30	34	-15*	5	21	34	17*
0	0	40	-1*	-7	0	33	-20*	-4	185	6	6	-1	85	6	-3	6	0	36	-15*
1	0	39	-23*	-6	263	8	7	-3	128	9	-6	0	23	36	-11*	H,K=	3,	12	

STRUCTURE FACTORS CONTINUED FOR $C_{11}H_{19}IO_2S$

L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
-8	52	12	2	4	27	34	23*	1	0	39	-30*	3	244	8	2	6	42	43	4*
-7	68	13	3	5	0	33	-26*	2	62	14	4	4	34	36	29*	H,K=	4,	6	
-6	120	7	1	H,K=	3,	16		3	8	35	-14*	5	54	9	14	-9	81	9	-1
-5	101	6	-10	-7	51	11	3	H,K=	3,	21		6	15	32	-7*	-8	0	32	-8*
-4	72	8	-6	-6	39	19	1*	-4	70	8	6	7	44	18	24*	-7	134	7	-5
-3	23	30	7*	-5	81	7	-3	-3	48	25	7*	H,K=	4,	3		-6	19	36	-9*
-2	28	22	9*	-4	57	8	-5	-2	98	6	-1	-9	46	13	20	-5	142	6	6
-1	70	12	16	-3	49	19	2*	-1	71	10	7	-8	61	13	6	-4	59	14	3
0	84	7	-1	-2	44	17	6*	0	109	7	-2	-7	68	8	2	-3	102	5	-3
1	211	7	5	-1	20	33	14*	1	20	36	-20*	-6	149	8	7	-2	99	5	-1
2	108	6	8	0	118	6	-8	2	77	7	7	-5	201	6	5	-1	336	9	-13
3	222	7	5	1	63	16	-15	H,K=	3,	22		-4	399	11	11	0	180	6	-2
4	95	8	-8	2	188	6	2	-3	26	29	23*	-3	398	10	5	1	410	11	-9
5	147	6	18	3	85	7	1	-2	17	32	16*	-2	280	8	-5	2	104	8	6
6	58	10	12	4	142	7	0	-1	48	14	-6	-1	410	11	-9	3	273	9	4
H,K=	3,	13		5	49	15	-7*	0	9	55	-15*	0	133	7	-11	4	99	6	7
-8	3	53	-1*	H,K=	3,	17		1	108	8	-6	1	170	7	-2	5	145	8	-0
-7	55	12	12	-6	33	18	27*	H,K=	4,	0		2	26	34	-7*	6	18	37	-17*
-6	83	8	8	-5	45	32	-14*	-8	106	8	-5	3	37	21	24*	H,K=	4,	7	
-5	30	36	-8*	-4	99	11	6	-6	201	8	-1	4	71	12	-1	-9	20	33	2*
-4	251	8	6	-3	78	7	-5	-4	54	9	10	5	42	31	-9*	-8	77	9	10
-3	42	23	7*	-2	136	7	-1	-2	251	7	-1	6	79	9	1	-7	24	39	13*
-2	284	8	-8	-1	96	5	1	0	551	14	2	7	57	17	20*	-6	188	6	1
-1	0	38	-6*	0	167	7	-8	2	374	10	-3	H,K=	4,	4		-5	8	39	-8*
0	266	9	-8	1	75	7	-5	4	237	9	-7	-9	65	14	7	-4	353	10	-4
1	0	31	-16*	2	86	8	5	6	111	7	-2	-8	68	12	-9	-3	67	9	-2
2	138	8	3	3	48	12	-1	H,K=	4,	1		-7	68	10	5	-2	409	11	-12
3	0	49	-5*	4	0	42	-26*	-9	15	33	-9*	-6	107	13	4	-1	67	7	6
4	16	32	-0*	H,K=	3,	18		-8	25	45	22*	-5	95	7	11	0	231	7	-3
5	28	31	22*	-6	29	31	22*	-7	93	6	9	-4	47	13	17	1	66	10	-4
6	68	14	-0	-5	108	7	-6	-6	50	16	14*	-3	27	19	25*	2	80	6	7
H,K=	3,	14		-4	24	30	18*	-5	247	7	1	-2	220	7	-11	3	92	6	3
-7	84	13	-7	-3	60	15	-6	-4	127	5	6	-1	25	34	10*	4	62	6	9
-6	93	10	-10	-2	46	21	2*	-3	420	11	4	0	318	9	-12	5	53	13	11
-5	112	6	-3	-1	21	35	-9*	-2	85	5	-3	1	88	10	2	6	58	10	-3
-4	81	8	1	0	59	9	10	-1	548	14	-0	2	232	7	0	H,K=	4,	8	
-3	85	9	2	1	80	10	3	0	167	5	6	3	100	8	-0	-9	32	41	11*
-2	61	10	-9	2	101	9	10	1	207	6	-1	4	154	8	14	-8	46	15	7*
-1	0	40	-23*	3	93	9	8	2	169	6	-0	5	59	11	-10	-7	16	29	-9*
0	0	32	-16*	4	64	11	-13	3	29	29	4*	6	35	20	-3*	-6	77	8	-5
1	73	15	-7	H,K=	3,	19		4	161	7	-0	7	45	24	15*	-5	31	20	20*
2	44	17	36*	-5	70	12	16	5	49	13	-15	H,K=	4,	5		-4	17	41	12*
3	94	6	-6	-4	43	36	-6*	6	49	12	-7	-9	0	50	-17*	-3	60	11	-2
4	69	8	7	-3	126	6	4	7	32	35	-5*	-8	0	39	-8*	-2	144	6	-11
5	71	11	-0	-2	60	8	3	H,K=	4,	2		-7	29	34	-12*	-1	140	7	-1
H,K=	3,	15		-1	154	8	3	-9	52	31	6*	-6	57	15	-9	0	231	7	-8
-7	0	48	-14*	0	62	9	2	-8	25	41	21*	-5	185	7	6	1	110	8	-1
-6	45	23	10*	1	105	7	1	-7	56	11	-12	-4	150	5	-5	2	212	7	4
-5	94	9	1	2	0	32	-5*	-6	49	18	19*	-3	259	7	1	3	39	21	-13*
-4	33	34	11*	3	34	23	17*	-5	109	6	9	-2	159	8	-3	4	86	6	-5
-3	189	6	0	H,K=	3,	20		-4	74	11	9	-1	192	6	-0	5	25	29	-0*
-2	0	36	-22*	-5	58	9	6	-3	66	7	-4	0	113	11	-8	6	21	43	-4*
-1	238	7	1	-4	46	11	-9	-2	147	6	10	1	47	13	2	H,K=	4,	9	
0	50	10	15	-3	69	7	-2	-1	351	9	-8	2	44	9	18	-8	20	35	17*
1	181	7	-3	-2	40	16	-8*	0	89	6	5	3	96	10	-1	-7	57	16	-1
2	0	39	-3*	-1	47	11	-3	1	424	11	-14	4	0	30	-20*	-6	81	7	4
3	92	7	4	0	19	32	-26*	2	0	28	-11*	5	118	8	-6	-5	215	7	-3

STRUCTURE FACTORS CONTINUED FOR $C_{11}H_{19}IO_2S$

L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
-4	92	10	-8	5	19	42	16*	-6	55	17	5*	3	53	27	-8*	-6	56	15	15
-3	325	9	-1	H,K=	4,	13		-5	70	9	0	5	40	30	15*	-5	139	8	-0
-2	174	6	-3	-8	0	36	-36*	-4	49	11	12	H,K=	5,	1		-4	64	9	-6
-1	237	7	-3	-7	69	10	-1	-3	117	6	4	-9	32	43	-18*	-3	278	8	-14
0	95	6	-2	-6	42	29	-1*	-2	0	32	-36*	-8	36	39	-11*	-2	90	5	5
1	57	10	-5	-5	176	7	-4	-1	45	11	-8	-7	156	8	2	-1	388	11	-12
2	39	21	-22*	-4	60	10	1	0	0	30	-17*	-6	110	6	8	0	132	7	-5
3	62	14	14	-3	310	9	-13	1	35	40	30*	-5	214	7	6	1	277	9	-10
4	21	31	17*	-2	54	8	4	2	0	42	-8*	-4	122	6	7	2	132	6	4
5	68	9	0	-1	237	7	-11	3	59	13	1	-3	133	6	4	3	94	11	-5
6	35	26	9*	0	61	8	4	4	27	38	16*	-2	109	6	2	4	37	14	11*
H,K=	4,	10		1	122	6	-4	H,K=	4,	18		-1	70	11	5	5	45	11	37
-8	50	20	-2*	2	37	15	-21*	-6	26	33	8*	0	22	29	15*	6	27	39	14*
-7	80	8	-8	3	39	14	31*	-5	51	11	19	1	169	7	2	H,K=	5,	5	
-6	65	7	9	4	32	21	13*	-4	30	43	22*	2	172	7	4	-9	31	38	8*
-5	51	10	8	5	3	33	-10*	-3	38	15	27*	3	182	8	9	-8	81	7	2
-4	24	36	-16*	H,K=	4,	14		-2	86	7	-3	4	128	7	-1	-7	53	11	-9
-3	40	44	-12*	-7	29	32	5*	-1	57	25	-3*	5	145	6	12	-6	152	6	5
-2	79	12	-5	-6	28	41	3*	0	98	7	1	6	70	10	2	-5	134	8	8
-1	224	7	-6	-5	25	36	5*	1	53	11	-6	H,K=	5,	2		-4	160	9	10
0	242	7	8	-4	16	32	-0*	2	108	6	8	-9	14	33	-11*	-3	117	5	-2
1	161	7	-1	-3	57	12	16	3	51	28	-12*	-8	27	36	22*	-2	102	7	-1
2	236	7	-0	-2	105	8	-6	H,K=	4,	19		-7	39	14	7*	-1	43	31	-3*
3	89	8	-9	-1	91	7	0	-5	40	32	-21*	-6	106	7	-2	0	83	8	-4
4	177	8	2	0	183	6	2	-4	152	6	5	-5	81	8	-11	1	55	11	-12
5	34	35	-1*	1	90	5	8	-3	109	7	1	-4	218	8	-7	2	249	7	-4
6	80	15	2	2	175	7	-1	-2	175	7	-3	-3	77	8	7	3	125	6	-1
H,K=	4,	11		3	36	21	26*	-1	78	8	-4	-2	409	11	-6	4	205	7	22
-8	39	16	18*	4	81	13	-5	0	95	9	-8	-1	66	8	-2	5	67	20	-1
-7	17	31	10*	5	0	32	-14*	1	57	19	-19*	0	443	12	-8	6	81	11	-2
-6	80	8	1	H,K=	4,	15		2	24	32	-9*	1	29	40	21*	H,K=	5,	6	
-5	39	15	19*	-7	39	17	25*	3	28	33	1*	2	310	9	0	-9	28	37	21*
-4	167	6	-2	-6	74	10	-3	H,K=	4,	20		3	17	33	-8*	-8	69	9	-7
-3	30	20	2*	-5	10	34	4*	-4	0	32	-1*	4	60	15	-13	-7	13	30	-1*
-2	209	7	-4	-4	150	6	2	-3	30	33	-11*	5	31	44	15*	-6	35	39	-15*
-1	34	19	7*	-3	20	29	-5*	-2	19	40	-5*	6	43	18	8*	-5	54	16	1
0	78	13	-7	-2	198	6	-5	-1	101	8	9	H,K=	5,	3		-4	28	31	11*
1	29	33	25*	-1	39	21	12*	0	29	32	-2*	-9	41	19	7*	-3	118	6	3
2	104	8	3	0	96	8	6	1	113	7	5	-8	31	32	-2*	-2	147	8	-5
3	27	35	12*	1	36	13	5*	2	3	36	-7*	-7	137	6	-4	-1	65	8	-0
4	136	7	10	2	40	14	-2*	H,K=	4,	21		-6	66	12	-5	0	224	7	-4
5	34	30	20*	3	45	16	27*	-4	22	31	14*	-5	212	7	7	1	72	9	3
6	101	10	10	4	90	8	4	-3	63	14	-4	-4	96	6	9	2	175	7	-1
H,K=	4,	12		H,K=	4,	16		-2	0	47	-18*	-3	261	9	4	3	33	25	21*
-8	47	16	-11*	-7	87	12	6	-1	37	30	-5*	-2	109	6	-1	4	53	12	18
-7	49	30	17*	-6	51	15	2*	0	23	36	-12*	-1	65	8	-7	5	0	36	-3*
-6	86	8	5	-5	37	38	-11*	1	0	40	-7*	0	96	5	0	6	52	21	50*
-5	30	21	-11*	-4	23	36	-27*	H,K=	4,	22		1	22	31	6*	H,K=	5,	7	
-4	80	6	4	-3	27	35	20*	-2	34	44	-9*	2	22	30	-2*	-9	34	29	1*
-3	64	9	7	-2	43	10	2	-1	24	40	17*	3	105	7	8	-8	43	14	-2*
-2	97	6	-3	-1	136	7	-3	H,K=	5,	0		4	8	36	-10*	-7	118	8	5
-1	119	6	1	0	110	6	8	-9	113	8	5	5	51	11	9	-6	54	9	-1
0	224	7	1	1	131	8	-2	-7	126	8	7	6	20	39	10*	-5	156	6	-4
1	135	6	-1	2	116	6	8	-5	41	23	15*	H,K=	5,	4		-4	0	41	-21*
2	266	8	8	3	133	8	13	-3	161	5	-1	-9	0	40	-39*	-3	165	6	0
3	18	39	-18*	4	37	24	2*	-1	127	6	-4	-8	33	40	-4*	-2	23	45	-11*
4	149	7	11	H,K=	4,	17		1	172	6	-7	-7	41	13	18*	-1	39	17	-17*

STRUCTURE FACTORS CONTINUED FOR $C_{11}H_{19}IO_2S$

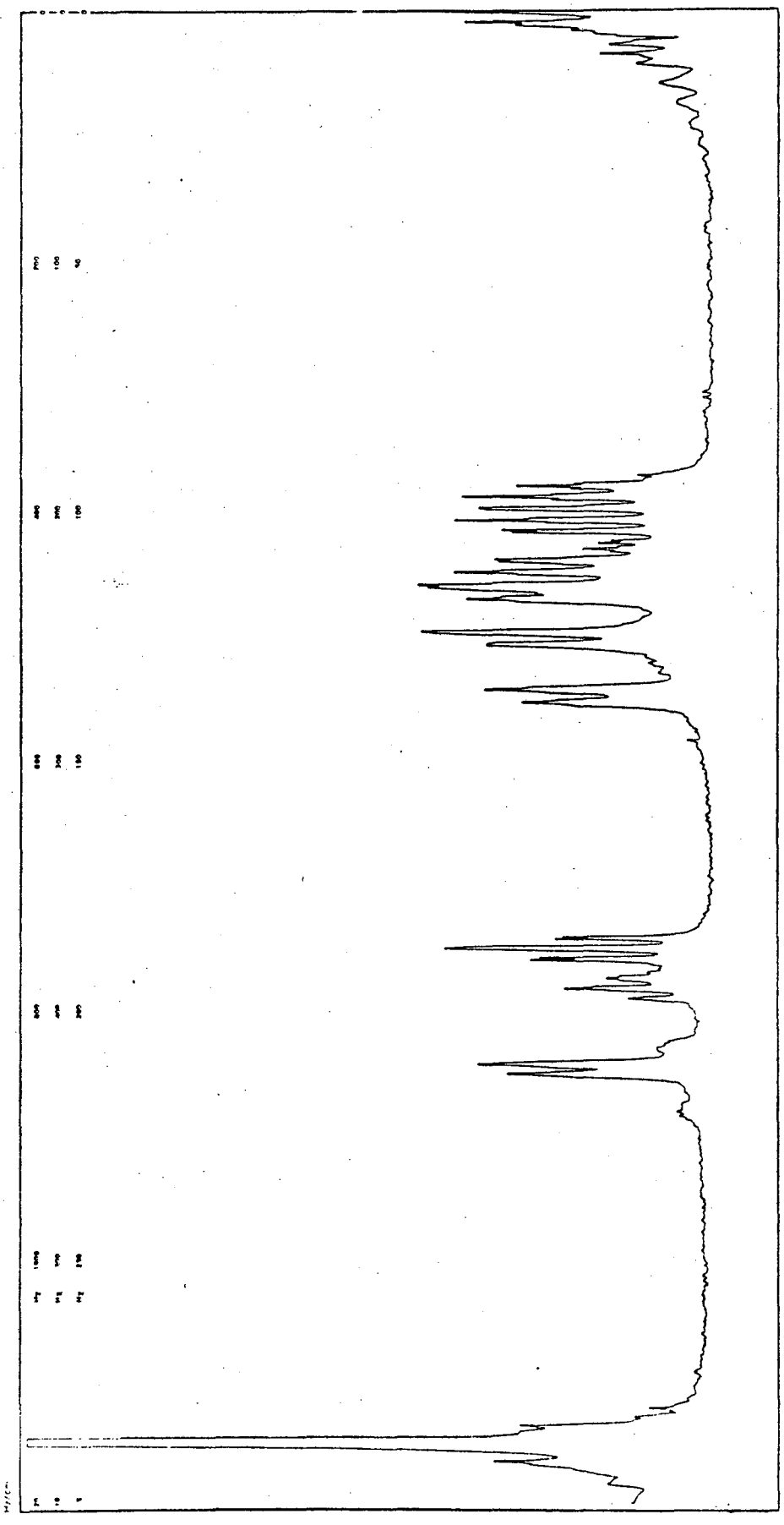
L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
0	94	9	-28	-5	131	6	2	-3	101	6	9	H,K=		6,	0	-9	0	36	-6*
1	120	8	9	-4	42	19	38*	-2	49	53	-10*	-8	32	40	13*	-8	44	12	28
2	102	8	-2	-3	80	8	6	-1	63	13	-13	-6	108	6	-6	-7	37	21	1*
3	174	7	15	-2	52	18	2*	0	60	11	-18	-4	285	8	-8	-6	85	9	-14
4	101	11	7	-1	34	25	16*	1	39	20	-7*	-2	331	9	6	-5	51	16	-12*
5	109	8	6	0	49	14	-15	2	72	13	-16	0	99	11	-11	-4	295	9	-7
6	38	43	9*	1	159	6	3	3	81	8	-7	2	40	16	13*	-3	91	10	-5
H,K=		5,	8	2	57	9	0	4	67	15	14	4	93	11	1	-2	284	6	-8
-9	17	47	6*	3	220	8	12	H,K=		5,	16	H,K=		6,	1	-1	44	28	1*
-8	36	18	35*	4	46	14	-2*	-6	0	48	-17*	-9	53	12	25	0	170	6	-10
-7	41	15	-1*	5	147	8	9	-5	0	31	-4*	-8	95	12	7	1	76	13	2
-6	35	20	-15*	H,K=		5,	12	-4	64	15	2	-7	49	10	11	2	29	33	17*
-5	95	7	-2	-8	0	36	-6*	-3	25	39	-5*	-6	161	8	1	3	40	15	1*
-4	127	6	3	-7	56	10	8	-2	89	7	-8	-5	80	8	3	4	45	12	11
-3	225	8	-1	-6	68	14	9	-1	68	8	4	-4	117	8	6	5	62	30	4*
-2	221	7	-5	-5	51	13	-1	0	143	7	-5	-3	32	42	9*	H,K=		6,	5
-1	299	9	-10	-4	159	8	1	1	63	13	1	-2	68	8	14	-9	81	13	6
0	227	7	3	-3	22	32	-13*	2	82	13	4	-1	64	9	-2	-8	13	51	-0*
1	260	8	-3	-2	251	8	-3	3	20	41	-18*	0	196	6	3	-7	123	7	9
2	143	7	4	-1	39	19	-13*	H,K=		5,	17	1	136	6	-9	-6	52	10	8
3	90	6	2	0	205	7	-13	-6	78	9	5	2	163	7	4	-5	158	7	4
4	34	18	-6*	1	74	7	-1	-5	75	7	22	3	114	6	-6	-4	45	16	-32*
5	42	21	5*	2	158	6	4	-4	85	7	3	4	81	11	-2	-3	27	32	26*
H,K=		5,	9	3	50	19	-2*	-3	59	24	-8*	5	30	36	-13*	-2	14	44	8*
-8	83	11	11	4	59	19	7*	-2	0	31	-11*	H,K=		6,	2	-1	146	7	-4
-7	10	41	6*	5	27	38	8*	-1	79	10	5	-9	26	30	18*	0	68	10	4
-6	151	7	1	H,K=		5,	13	0	63	14	1	-8	25	35	-3*	1	242	8	-0
-5	29	46	-24*	-7	21	32	16*	1	0	31	-25*	-7	39	15	10*	2	65	7	8
-4	221	7	-4	-6	143	7	7	2	91	8	-5	-6	77	12	-1	3	200	7	3
-3	89	11	-17	-5	30	32	27*	3	0	33	-7*	-5	143	6	-3	4	45	15	11*
-2	156	6	-6	-4	154	9	1	H,K=		5,	18	-4	194	7	7	5	123	7	13
-1	189	7	-2	-3	20	29	8*	-5	62	9	16	-3	252	8	-7	H,K=		6,	6
0	21	44	-20*	-2	108	7	3	-4	23	32	-5*	-2	128	7	-6	-9	21	38	6*
1	60	10	-2	-1	43	15	41*	-3	109	7	9	-1	315	10	-1	-8	15	42	-9*
2	84	6	13	0	21	29	11*	-2	36	18	18*	0	120	7	-4	-7	8	31	-19*
3	32	26	-8*	1	49	25	18*	-1	142	8	-1	1	155	6	3	-6	95	9	4
4	79	9	9	2	26	32	-12*	0	0	39	-25*	2	71	7	-1	-5	114	7	-3
5	0	42	-18*	3	17	31	-12*	1	107	9	0	3	34	41	-8*	-4	166	9	9
H,K=		5,	10	4	72	8	12	2	15	36	2*	4	42	28	-9*	-3	192	6	-4
-8	52	11	15	H,K=		5,	14	H,K=		5,	19	5	52	12	20	-2	129	7	3
-7	38	46	-15*	-7	9	44	2*	-5	65	10	-12	H,K=		6,	3	-1	153	6	4
-6	0	32	-6*	-6	38	48	-9*	-4	10	32	8*	-9	0	48	-8*	0	39	41	-18*
-5	24	38	16*	-5	43	19	7*	-3	83	8	6	-8	62	11	2	1	19	33	-30*
-4	151	7	-6	-4	152	6	-5	-2	38	19	37*	-7	28	35	1*	2	41	13	-11*
-3	22	31	10*	-3	90	11	4	-1	52	12	-10	-6	112	7	12	3	21	32	17*
-2	218	8	-12	-2	183	6	-14	0	0	32	-23*	-5	0	40	-14*	4	0	37	-20*
-1	15	32	-24*	-1	103	6	-6	1	29	34	10*	-4	28	32	10*	5	51	14	4
0	273	8	-4	0	173	6	2	H,K=		5,	20	-3	3	32	-32*	H,K=		6,	7
1	50	34	-0*	1	87	10	-5	-4	68	19	6	-2	110	6	-1	-8	54	25	-4*
2	128	6	-2	2	76	9	-18	-3	70	9	1	-1	116	6	-1	-7	113	7	5
3	27	40	-1*	3	47	11	16	-2	82	9	-9	0	205	8	6	-6	115	6	2
4	56	10	12	4	37	18	18*	-1	43	17	-23*	1	126	7	-4	-5	99	7	3
5	0	42	-11*	H,K=		5,	15	0	111	8	7	2	97	6	6	-4	69	9	10
H,K=		5,	11	-7	57	13	-7	1	52	13	5	3	86	8	2	-3	13	47	-1*
-8	34	39	20*	-6	33	34	31*	H,K=		5,	21	4	98	12	14	-2	45	16	21*
-7	100	10	-1	-5	105	7	2	-2	48	23	6*	5	45	23	13*	-1	58	9	4
-6	21	33	13*	-4	36	15	32*	-1	0	32	-13*	H,K=		6,	4	0	83	13	1

L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
1	47	11	-4	1	23	37	-16*	-1	23	31	11*	0	24	33	-13*	1	47	14	23
2	68	10	3	2	138	6	10	0	45	46	17*	1	12	42	12*	2	123	6	10
3	47	17	14*	3	46	12	24	1	39	40	26*	2	73	12	1	3	30	33	3*
4	56	10	10	4	94	8	10	2	36	38	35*	3	22	31	10*	4	113	8	16
5	34	35	-11*	H,K=	6,	12		H,K=	6,	17		4	79	12	11	H,K=	7,	7	
H,K=	6,	8		-7	38	18	14*	-5	57	22	-10*	H,K=	7,	3		-8	37	23	-12*
-8	31	51	22*	-6	29	36	-11*	-4	11	32	6*	-8	27	36	10*	-7	22	31	15*
-7	0	38	-25*	-5	80	9	-2	-3	0	34	-16*	-7	46	17	33*	-6	55	10	12
-6	91	8	-14	-4	49	11	-21	-2	38	21	19*	-6	25	33	-5*	-5	72	9	-10
-5	83	9	-3	-3	142	7	1	-1	91	13	-8	-5	76	8	-9	-4	37	15	31*
-4	211	7	5	-2	101	8	-8	0	36	17	13*	-4	94	7	-15	-3	190	7	-6
-3	159	7	-3	-1	140	7	2	1	105	9	3	-3	149	8	-6	-2	28	30	-2*
-2	270	8	-3	0	62	15	-7	H,K=	6,	18		-2	130	7	-5	-1	243	8	-12
-1	194	7	-8	1	51	10	-2	-4	113	7	3	-1	193	6	-15	0	45	11	1
0	169	6	3	2	25	34	25*	-3	42	17	6*	0	132	7	-5	1	222	7	4
1	97	6	-5	3	0	32	-11*	-2	140	8	-8	1	169	7	-9	2	19	30	12*
2	66	11	-2	4	13	47	-21*	-1	31	36	11*	2	93	9	1	3	100	8	4
3	23	32	-4*	H,K=	6,	13		0	98	8	-2	3	53	13	-5	4	27	39	18*
4	37	17	31*	-7	59	16	25	1	17	33	15*	4	52	25	5*	H,K=	7,	8	
H,K=	6,	9		-6	32	42	18*	H,K=	6,	19		H,K=	7,	4		-8	28	34	22*
-8	52	13	9	-5	39	18	5*	-3	32	33	-2*	-8	37	28	2*	-7	42	16	-5*
-7	69	18	14	-4	35	49	9*	-2	28	33	10*	-7	83	13	-7	-6	26	30	19*
-6	16	32	-19*	-3	49	22	2*	-1	30	37	-2*	-6	20	31	-16*	-5	102	8	-16
-5	23	46	-10*	-2	20	29	17*	0	16	39	-8*	-5	147	6	-9	-4	24	29	11*
-4	19	37	-7*	-1	143	6	4	H,K=	7,	0		-4	43	18	-7*	-3	152	6	3
-3	51	20	-15*	0	8	31	6*	-9	41	17	8*	-3	229	8	-0	-2	39	17	-0*
-2	40	19	-10*	1	158	6	9	-7	110	7	-2	-2	75	9	-5	-1	133	6	-12
-1	221	7	-4	2	29	44	13*	-5	161	7	2	-1	114	11	-12	0	28	31	1*
0	27	47	-6*	3	78	8	4	-3	166	8	1	0	45	15	-1*	1	0	39	-5*
1	221	7	2	H,K=	6,	14		-1	77	12	6	1	26	37	-1*	2	7	34	-11*
2	80	8	15	-7	18	41	8*	1	36	17	2*	2	45	12	4	3	55	10	13
3	164	6	7	-6	75	10	-2	3	98	7	14	3	66	10	-2	H,K=	7,	9	
4	39	15	27*	-5	70	8	-7	H,K=	7,	1		4	46	14	10*	-8	47	13	4
H,K=	6,	10		-4	138	10	-4	-9	60	16	17	H,K=	7,	5		-7	46	17	7*
-8	45	15	29*	-3	155	6	-2	-8	34	35	-1*	-8	80	17	13	-6	39	18	7*
-7	21	41	19*	-2	194	7	0	-7	49	23	-8*	-7	29	31	17*	-5	29	31	24*
-6	0	39	-24*	-1	110	7	-11	-6	22	31	16*	-6	60	15	-5	-4	15	44	-7*
-5	96	8	-1	0	145	6	2	-5	45	13	-1*	-5	28	32	18*	-3	0	29	-8*
-4	68	15	2	1	53	17	-6*	-4	46	13	-1	-4	87	8	6	-2	97	6	9
-3	174	6	-8	2	45	52	-15*	-3	0	40	-23*	-3	25	33	14*	-1	35	22	-7*
-2	34	27	1*	3	25	32	23*	-2	161	7	-2	-2	61	9	9	0	143	6	-6
-1	96	7	-7	H,K=	6,	15		-1	47	14	-13*	-1	81	8	-6	1	40	23	-15*
0	14	33	-4*	-6	20	37	-37*	0	185	7	-0	0	89	9	-10	2	97	10	-0
1	45	12	-5	-5	16	38	-2*	1	67	18	1	1	85	7	-10	3	21	40	-17*
2	31	24	-4*	-4	55	25	-1*	2	147	6	-9	2	89	7	-12	H,K=	7,	10	
3	30	39	12*	-3	28	39	15*	3	32	36	9*	3	53	29	1*	-7	88	14	-5
4	43	16	1*	-2	29	37	11*	4	56	10	1	4	0	51	-3*	-6	77	7	6
H,K=	6,	11		-1	27	39	11*	H,K=	7,	2		H,K=	7,	6		-5	129	7	9
-8	101	8	4	0	69	18	5	-9	38	40	13*	-8	57	22	-11*	-4	97	11	-20
-7	36	38	-20*	1	10	38	6*	-8	52	22	-4*	-7	59	22	4*	-3	108	6	-3
-6	140	6	-4	2	95	8	-5	-7	17	32	12*	-6	97	7	-6	-2	87	11	-4
-5	32	34	-0*	H,K=	6,	16		-6	123	6	0	-5	93	6	7	-1	0	30	-21*
-4	140	6	2	-6	15	48	11*	-5	36	16	23*	-4	97	6	-2	0	0	29	-0*
-3	43	13	7*	-5	24	34	0*	-4	158	7	5	-3	85	8	9	1	23	32	15*
-2	15	45	-9*	-4	42	43	16*	-3	19	33	3*	-2	62	14	-3	2	49	13	10
-1	20	36	14*	-3	49	12	8	-2	119	5	-3	-1	30	36	26*	3	56	10	8
0	81	12	-4	-2	40	33	-13*	-1	10	33	-25*	0	27	34	-10*	H,K=	7,	11	

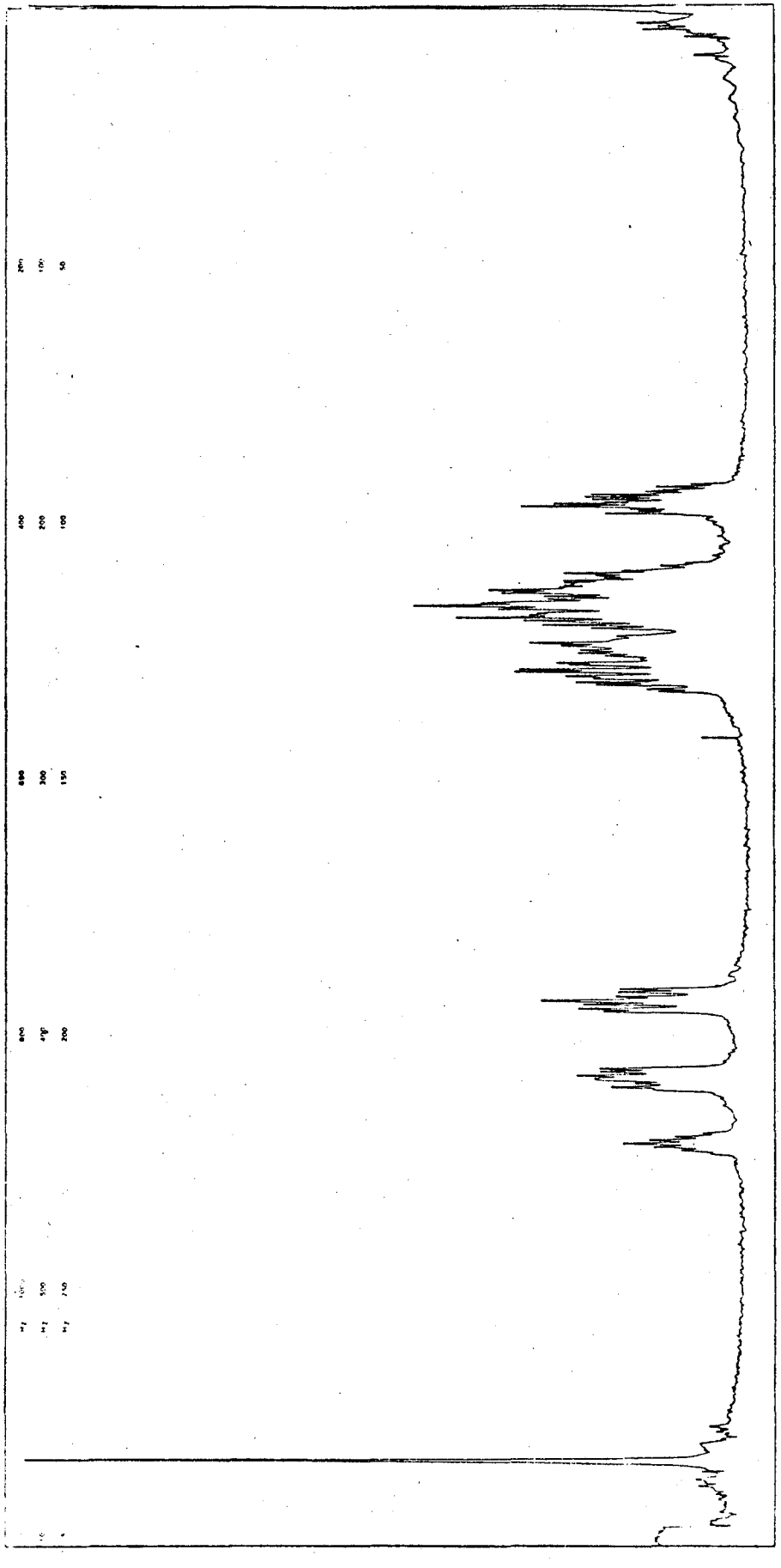
STRUCTURE FACTORS CONTINUED FOR $C_{11}H_{19}IO_2S$

L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
-7	40	44	11*	H,K=	7,	17		-4	34	22	6*	-6	0	31	-21*	H,K=	9,	0	
-6	42	14	18*	-4	0	32	-9*	-3	24	34	0*	-5	82	10	4	-7	0	46	-37*
-5	16	38	8*	-3	52	14	34	-2	35	37	3*	-4	27	37	11*	-5	25	46	24*
-4	42	21	19*	-2	0	43	-11*	-1	35	20	-2*	-3	135	6	4	-3	0	37	-19*
-3	72	9	5	-1	50	15	15	0	105	8	-3	-2	44	14	-15*	-1	39	16	-2*
-2	28	31	18*	0	68	20	3	1	30	47	18*	-1	118	6	2	1	15	34	-17*
-1	115	6	-3	H,K=	8,	0		2	92	8	10	0	44	13	-1	H,K=	9,	1	
0	43	23	-7*	-8	94	8	10	3	0	31	-9*	1	85	8	-3	-7	67	11	8
1	105	7	2	-6	142	6	-2	H,K=	8,	5		2	47	19	-4*	-6	59	10	10
2	0	32	-1*	-4	130	6	-0	-8	32	41	24*	H,K=	8,	10		-5	91	7	1
3	51	14	4	-2	52	29	-8*	-7	0	40	-29*	-7	73	13	2	-4	73	8	-2
H,K=	7,	12		0	25	32	-12*	-6	29	30	8*	-6	44	16	-11*	-3	92	9	5
-7	63	13	16	2	46	15	-16*	-5	83	7	-2	-5	49	49	-8*	-2	65	13	-8
-6	62	11	7	H,K=	8,	1		-4	55	9	0	-4	51	12	2	-1	60	11	1
-5	64	12	-4	-8	26	40	23*	-3	108	6	-2	-3	22	32	-8*	0	39	42	17*
-4	71	8	10	-7	37	25	32*	-2	72	9	-4	-2	0	32	-22*	1	25	33	10*
-3	42	31	-9*	-6	31	33	-12*	-1	105	6	-5	-1	46	13	4	H,K=	9,	2	
-2	43	18	-6*	-5	54	11	-2	0	69	11	0	0	50	17	21*	-7	35	27	31*
-1	53	17	14*	-4	87	7	-8	1	51	29	20*	1	57	19	13*	-6	51	16	19*
0	41	13	31*	-3	89	11	-11	2	12	32	-21*	2	14	38	-6*	-5	14	31	4*
1	41	18	6*	-2	116	7	-9	3	23	39	11*	H,K=	8,	11		-4	34	35	32*
2	0	38	-20*	-1	118	8	4	H,K=	8,	6		-6	42	16	21*	-3	0	37	-29*
H,K=	7,	13		0	86	6	5	-8	21	38	10*	-5	40	23	36*	-2	90	8	-9
-6	39	16	26*	1	46	22	-5*	-7	137	7	8	-4	99	7	15	-1	39	29	-9*
-5	58	10	16	2	0	35	-11*	-6	29	48	-6*	-3	20	33	4*	0	138	7	13
-4	56	21	4*	3	21	41	-4*	-5	164	10	-1	-2	106	8	-8	1	52	14	-11
-3	65	10	7	H,K=	8,	2		-4	31	22	26*	-1	39	16	16*	H,K=	9,	3	
-2	123	9	7	-8	0	37	-2*	-3	101	7	5	0	62	11	-7	-7	22	38	-2*
-1	24	32	-20*	-7	74	11	13	-2	16	43	-17*	1	19	38	15*	-6	24	38	6*
0	132	8	-10	-6	26	29	17*	-1	27	33	6*	H,K=	8,	12		-5	41	26	12*
1	33	42	2*	-5	97	11	0	0	50	12	0	-6	76	13	4	-4	47	25	5*
2	106	7	5	-4	31	21	11*	1	45	17	21*	-5	48	23	8*	-3	83	10	3
H,K=	7,	14		-3	13	33	-1*	2	28	32	5*	-4	83	10	3	-2	50	17	5*
-6	52	11	15	-2	40	20	13*	H,K=	8,	7		-3	0	34	-2*	-1	52	11	13
-5	63	8	12	-1	75	8	2	-7	27	40	11*	-2	34	43	1*	0	33	30	16*
-4	60	10	-4	0	54	13	3	-6	20	37	-10*	-1	42	19	11*	1	28	32	3*
-3	57	11	-1	1	127	8	8	-5	0	41	-24*	0	0	38	-3*	H,K=	9,	4	
-2	52	24	-11*	2	23	35	14*	-4	114	7	-7	1	79	8	20	-7	53	15	13
-1	46	14	-5*	3	93	6	2	-3	43	14	4*	H,K=	8,	13		-6	20	40	18*
0	16	40	-7*	H,K=	8,	3		-2	137	6	-6	-5	72	16	11	-5	39	17	33*
1	28	39	22*	-8	27	40	8*	-1	10	32	7*	-4	35	20	25*	-4	33	41	5*
2	0	39	-2*	-7	23	32	7*	0	102	10	5	-3	109	10	9	-3	33	28	-9*
H,K=	7,	15		-6	0	34	-24*	1	0	31	-23*	-2	50	13	34	-2	32	23	23*
-5	46	32	17*	-5	25	42	-13*	2	56	13	12	-1	100	13	-0	-1	103	7	13
-4	25	34	11*	-4	153	6	-1	H,K=	8,	8		0	24	32	-2*	0	44	16	10*
-3	78	17	2	-3	99	10	0	-7	37	41	15*	H,K=	8,	14		1	104	9	4
-2	30	32	17*	-2	140	8	-6	-6	33	39	5*	-5	20	35	6*	H,K=	9,	5	
-1	120	8	11	-1	97	7	3	-5	0	33	-27*	-4	29	40	6*	-7	35	22	19*
0	24	32	22*	0	117	7	-10	-4	27	31	17*	-3	27	41	18*	-6	99	6	3
1	102	10	10	1	43	15	-18*	-3	0	40	-9*	-2	0	35	-9*	-5	30	45	11*
H,K=	7,	16		2	54	11	-7	-2	73	12	4	-1	60	11	9	-4	114	9	-6
-5	33	21	-10*	3	27	32	6*	-1	12	39	-2*	0	37	38	4*	-3	30	35	8*
-4	92	10	4	H,K=	8,	4		0	79	12	-4	H,K=	8,	15		-2	104	7	-8
-3	41	27	4*	-8	34	36	5*	1	47	14	-4	-4	49	25	-3*	-1	18	32	7*
-2	0	53	-43*	-7	24	33	-2*	2	102	8	10	-3	16	42	8*	0	39	43	-6*
-1	28	31	-2*	-6	54	11	-9	H,K=	8,	9		-2	104	7	13	1	18	39	7*
0	35	41	20*	-5	44	15	-1*	-7	13	33	-9*	-1	0	32	-19*	H,K=	9,	6	

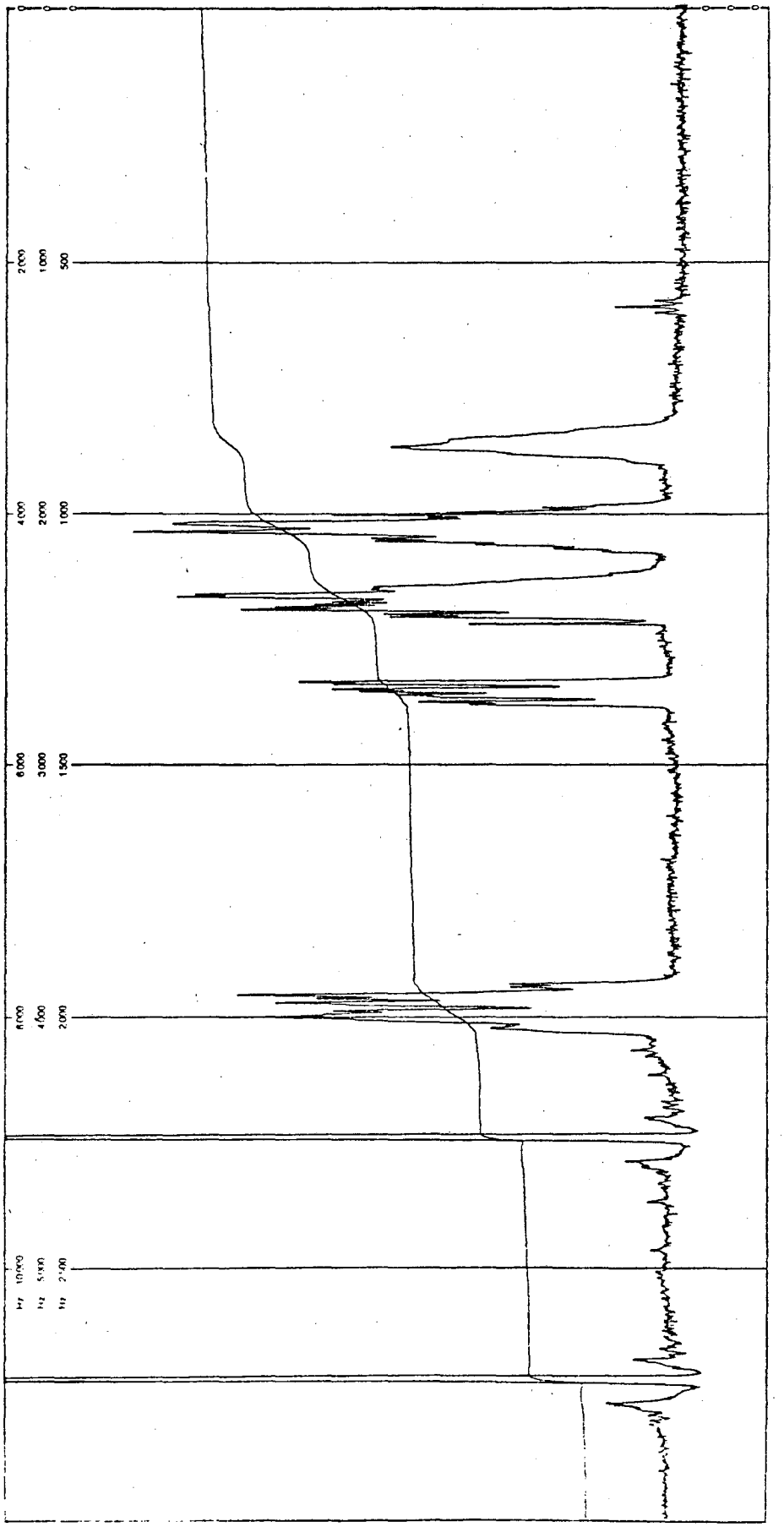
L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL	L	FOB	SG	DEL
-7	42	43	16*	-5	27	36	-24*												
-6	49	11	27	-4	89	9	12												
-5	0	39	-13*	-3	35	30	13*												
-4	32	26	14*	-2	56	12	2												
-3	36	19	26*	-1	10	49	6*												
-2	39	27	10*	H,K= 10, 2															
-1	42	19	-8*	-6	11	36	-7*												
0	31	35	-24*	-5	0	36	-15*												
1	25	39	-27*	-4	26	35	25*												
H,K= 9, 7				-3	53	11	-4												
-6	31	36	-14*	-2	23	33	16*												
-5	46	24	-2*	-1	72	14	-5												
-4	74	11	-8	H,K= 10, 3															
-3	87	7	1	-5	13	33	10*												
-2	77	10	-2	-4	30	38	27*												
-1	68	10	-1	-3	40	16	23*												
0	23	37	-22*	-2	0	33	-13*												
1	25	33	11*	-1	45	27	6*												
H,K= 9, 8				H,K= 10, 4															
-6	0	33	-18*	-5	41	17	5*												
-5	0	34	-18*	-4	35	48	-26*												
-4	43	19	6*	-3	34	25	8*												
-3	21	32	-12*	-2	86	8	10												
-2	76	10	13	-1	22	32	12*												
-1	109	7	10	H,K= 10, 5															
0	79	13	24	-5	103	8	2												
H,K= 9, 9				-4	39	42	1*												
-6	77	17	23	-3	58	12	-8												
-5	27	47	5*	-2	29	38	9*												
-4	65	11	3	-1	44	16	14*												
-3	37	19	2*	H,K= 10, 6															
-2	63	9	12	-5	54	17	4*												
-1	21	44	20*	-4	41	16	18*												
0	34	22	27*	-3	57	14	-3												
H,K= 9, 10				-2	19	39	-1*												
-5	36	30	5*	H,K= 10, 7															
-4	22	32	12*	-4	37	19	14*												
-3	24	35	9*	-3	37	23	1*												
-2	44	14	19*	-2	9	40	3*												
-1	48	27	45*																
0	66	18	-6																
H,K= 9, 11																			
-5	85	9	-4																
-4	0	49	-17*																
-3	128	7	9																
-2	17	33	-7*																
-1	86	8	-4																
H,K= 9, 12																			
-4	23	40	-4*																
-3	0	36	-1*																
-2	58	14	-1																
H,K= 10, 0																			
-6	44	27	10*																
-4	84	8	-2																
-2	83	9	3																
H,K= 10, 1																			
-6	69	17	3																



360-MHz ^{1}H-NMR Spectrum of Salt 1a



360-MHz ^{1}H-NMR Spectrum of Salt 1b



360-MHz ^{1}H-NMR Spectrum of Salt 17

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