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PROTON NMR CRITERIA FOR CONFIGURATIONAL ASSIGNMENT OF S-METHYLTHIANIUM CATIONS

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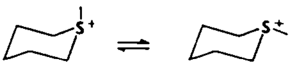
Abstract—Certain ^{1}H NMR features are reported for several conformationally biased diastereomeric pairs of 6-membered methylsulphonium cations (**4**–**7**) the members of each pair differing for the axial or equatorial orientation of the S^+–CH_3 group. The configurational assignment being secured by ^{13}C NMR, the scope of a number of ^{1}H NMR parameters is discussed as criteria for configurational and conformational analysis. Two mobile systems have also been considered, **2** and **9**, whose ^{1}H NMR is consistent with their (independently determined) conformer distribution.

Recently Eliel *et al.*[1] have shown that the equilibrium position between diastereomeric *cis*- and *trans*-4-t-butyl-1-methylthianium cations (**1a** and **1b**) is: *trans*/*cis* = 60/40 (i.e. the equatorial isomer is slightly favored) and that the same conformational preference holds for the unbiased thianium cation (**2**):

1a 40 **1e** 60



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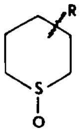
These contentions are based on clear-cut ^{13}C NMR evidence, confirmed by X-ray structural analysis (of the 4-t-butyl derivatives).[1]

These findings, while in agreement with the known behaviour of second-row heterocycles† are at variance with a previous assignment by Lambert *et al.*, according to whom only the equatorial conformation of 1-methylthianium would be populated (>90%).[7] This latter assignment was based on the value of the geminal coupling constant of the α-methylene protons, Jae(α) = 12·3 Hz, suggestive of an essentially equatorial Me substituent.[7] For the corresponding sulphoxide systems (**3**), Jae(α) is known to be a sensitive probe for the axial or



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equatorial orientation of the 1-oxide substituent[3c,4]‡ and is considered to be a generally valid configurational criterion for compounds of this type.[4,8] Since the dependence of Jae(α) on the orientation of the substituent on the heteroatom is actually related to orientation of the alpha H–C–H bisector relative to the lone pair on the adjacent hereroatom,[9] it is intriguing that this otherwise sound criterion should fail for the Me substituent.

In the course of an extensive investigation, by ^{13}C NMR and high-field ^{1}H NMR, of the conformational and configurational properties of sulphur heterocycles, we have collected several pieces of evidence which, while allowing us to shed light on the above anomaly, also establish the scope of a number of ^{1}H NMR criteria useful for configurational assignment. In this brief account, which may be considered the sulphonium analog of the paper on cyclic sulphoxides recently published by Lett and Marquet,[8] we limit ourselves to discussing these criteria.§ To this end, a selection of NMR parameters are reported of a number of conformationally biased diastereomeric pairs of S-methylthianium cations (**4**–**7**), the members of each pair differing for the axial or equatorial orientation of the S–CH_3 group. In addition we report on another conformationally biased system (**8**) the structure

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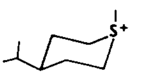
†Heterocycles containing one second-row atom normally do not display a strong conformational preference for the 1 substitutuent (unlike cyclohexane or piperidine[2]), and the axial orientation may actually be preferred, albeit slightly. Thus in thiane 1-oxide[3] and in thiane 1-(N-tosyl)imide[4] the axial conformer predominates somewhat (~60%); similarly, for phosphorous heterocycles, the equilibrium slightly favors the equatorial conformer of 1-methylphosphorinane at low temperature, while the axial one becomes favored at room temperature;[5] for silicon, reliable estimates indicate that the two conformers of 1-methylsilacyclohexane should be about equally populated.[6]

‡The Jae(α) values differ by as much as 2·0–2·5 Hz, the axial conformer having the higher (absolute) value, Jae(α) = 14·0–15·0 Hz.

§More comprehensive accounts of the ^{1}H and ^{13}C NMR behaviour of sulphur heterocycles will appear elsewhere. A first partial account, concerning the ^{13}C spectra of only a few such heterocycles, is given in Ref. 10.

of which allows the existence of one diastereomer only, and this is equatorial. For all these systems independent configurational assignments were obtained by ^{13}C NMR analysis.

Finally, we have re-examined S-methylthianium, and analyzed a similarly mobile system, 1,4,4-trimethylthianium (**9**), the conformational equilibrium of which was estimated by ^{13}C NMR.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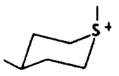
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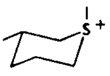
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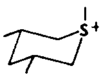
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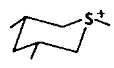
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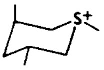
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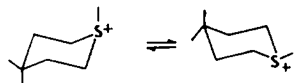
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RESULTS

As it is now well established[1,10] the conformational setting of S–Me in thianium cations can be unambiguously assigned by ^{13}C NMR.[1,10] Various ^{13}C NMR criteria are available,[10] but for the sake of the present discussion it is sufficient to consider the resonance of the S–$\underset{\cdot}{C}H_3$ carbon, which occurs in the equatorial isomer some 8 ppm downfield with respect to the corresponding resonance of the axial isomer.[1,10] The pertinent data are collected in Table 1 (II column) and leave little doubt as to the configurational assignment. Table 1 also reports the values of the ^1H NMR parameters which are considered to be useful probes of the orientation of the 1 substituent.[7,11,12] These are: (i) the geminal coupling of the α protons; (ii) the chemical shift difference of the α protons, $\delta_{ea}(\alpha) = \delta_{He}-\delta_{Ha}$;† (iii) the field at the AB quartet midpoint, $\delta_{mdp}(\alpha)$; (iv) the chemical shift of the β protons.[12]

Table 1. ^{13}C and ^1H NMR parameters for ring-substituted conformationally biased S-methylthianium cations

Compound	δ_{SCH_3}[a] (ppm)		Jae(α)[b] (Hz)	δae(α)[c] (ppm)	δax(β)[d] (ppm)	δmdp(α)[e] (ppm)
4e	27·5		12·0	0·50	1·5–1·7	3·42
4a	19·0		15·5	0·10	1·82	3·38
5e	27·5		12·0	0·49		3·38
5a	19·5		15·0	0·12		3·32
6e	27·8	C_2	13·0	0·69		3·15
		C_6	12·0	0·61		3·28
6a[f]	20·4	C_6	15·0	0·10		3·22
7e	28·1		12·0	0·78	2·00	3·11
7a	20·4		14·0	0·30	2·22	3·03
8	27·2	C_2	12·0	0·31		3·34
		C_6	12·0	0·71		3·14

[a] ^{13}C chemical shift; ppm downfield from $(\underset{\cdot}{C}H_3)_3SiCD_2CD_2COOH$. Conversion to TMS requires subtraction of 1·8 from the reported value.[10]

[b] Geminal coupling constant of the α-protons.

[c] Chemical shift difference ($H_{eq} - H_{ax}$) of the α-protons.

[d] Chemical shift of the axial β-proton.

[e] Field at the AB quartet midpoint (α protons).

[f] The 250 MHz of this compound is very complicated. Double irradiation of the protons resolves only one of the two AB quartets. On the basis of the δmdp(α) value this quartet seems likely to pertain to the protons at C_6.

It appears from Table 1 that the Jae(α) criterion is a reliable one for gauging the orientation of the S–Me substituent: Indeed the (absolute) values of Jae(α) are invariably higher for the axial than for the equatorial isomers, typical figures being 15·0 and 12·0 Hz, respectively. When there are no ring substituents, or when ring substituents are removed from the α-pair, the above limits (15·0 and 12·0 Hz) can be utilized to obtain a rough estimate of the conformers population in mobile systems; conversely, for mobile systems of known conformer distribution, Jae(α) can be estimated and compared with the experimental value. Deviations from the above limiting values may be observed in the presence of ring-substituents adjacent to the geminal pair (i.e. β to the heteroatom). Such deviations do not exceed 1 Hz, however (*cis*-**6** and *trans,trans*-**7**) and, even in the presence of adjacent substituents, Jae(α) can be used to assign the configuration *if both isomers (or conformers) can be observed separately.*

If, as we have confirmed, the Jae(α) criterion is a valid one, there appears to be no way of reconciling the conformer distribution of 1-methylthianium as obtained from ^{13}C analysis[1] with the value of Jae(α) reported by Lambert.[7] We have therefore re-examined the PMR spectrum of this compound and found Jae(α) = 13·5 Hz, significantly higher than the previously reported value, and in reasonably good agreement with that (13·2 Hz) computed from the conformer distribution[1] (Table 2).

Table 2 also reports the NMR data for another conformationally mobile system, 1,4,4-trimethylthianium. From the observed ^{13}C chemical shift of S–$\underset{\cdot}{C}H_3$, 22·6 ppm, the approximate conformer distribution can be estimated to be 60% axial, 40% equatorial[1,10] (see also footnote *b*, Table 2). The observed geminal coupling, Jae(α) = 13·8 Hz, actually coincides with that calculated from the above conformational equilibrium population and the limiting Jae(α) values for axial and equatorial conformers (15·0 and 12·0 Hz, respectively). The Jae(α) value is hereby confirmed to be a sound configurational criterion.

Before proceeding further in our analysis of configurational criteria, it is interesting to remark how the proportion of axial conformer increases (from 40 to 60%)

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†For all conformationally biased systems herein reported, the equatorial α proton appears to be upfield, so that $\delta_{ea}(\alpha) > 0$ throughout. For the conformationally mobile systems, **2** and **9**, the α-proton cis to S–CH_3 appears to resonate upfield.

Table 2. ^{13}C and ^{1}H NMR parameters for conformationally mobile S-methylthianium cations (D_2O solvent)

Compound	δ_{SCH_3}[a] (ppm)	% axial[b] conformer	Jae(α)[c] obs (Hz)	Jae(α)[d] calcd. (Hz)	δea(α)[e] (ppm)	δmdp(α)[f] (ppm)
2	24·0	40	13·5	13·2	0·36	3·40
9	22·6	60	13·8	13·8	0·27	3·35

[a] See footnote *a*, Table 1.

[b] Computed from the observed ^{13}C chemical shift of S–$\underset{\cdot}{C}H_3$ and assuming δ_{SCH_3} = 19·0 and 27·5 ppm for the axial and equatorial conformer respectively. The latter are the shifts observed for *cis*- and *trans*-4-isopropylthianium, respectively.[10]

[c] See footnote *b*, Table 1.

[d] Computed from Jae(α) = 15·0 and 12·0 Hz for axial and equatorial conformer, respectively, and the estimated conformer distribution.

[e] Chemical shift difference between α protons.

[f] See footnote *e*, Table 1.

in the 4,4-dimethyl compound. Similar changes had been observed[4] for the corresponding S-oxides and S-tosylimides, though of lesser proportion (62–70% axial for the oxide,[3,4] and 60–73% axial for the imide[11,4]). These changes have been accounted for by Lambert in terms of reduction of the $C_3C_4C_5$ angle in the 4,4-dimethyl systems causing the axial protons at C_3C_5 to bend away from the 1-position,[4] thereby reducing the non-bonding interactions (or perhaps increasing the attractive interactions which are supposed[7] to be responsible for the axial preference in these systems). The greater magnitude of the effect for the Me substituent may be related to its greater steric requirements relative to O or NTs. In any case, our findings confirm the suggestion that the increase of axial conformer population is a general phenomenon for 6-membered rings having a *gem*-Me_2 grouping at C_4.[4,13]

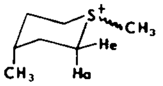
As to the second configurational criterion, $\delta_{ea}(\alpha)$, the data of Table 1 indicate it also can be applied, with certain provisions, for structural assignment of sulphonium cations.

In the absence of *axial* ring-substituents, the equatorial isomer has the larger $\delta_{ea}(\alpha)$, in the 0·5 – 0·7 ppm range, while the axial isomer has the smaller $\delta_{ea}(\alpha)$, in the 0·1 – 0·3 ppm range. A closer examination of the chemical shift of the individual protons reveals that the decrease of $\delta_{ea}(\alpha)$ in going from S–Me equatorial to S–Me axial, is the result of a simultaneous shielding of the equatorial proton (by ~0·3 ppm) and deshielding of the axial one (by ~0·1 ppm).[†]

The data of Table 1 allow some further remarks about the $\delta_{ea}(\alpha)$ values. It may be noticed that **6e**(C_2), **7e**, and **8**(C_6) have the highest $\delta_{ea}(\alpha)$ values: 0·69, 0·72 and 0·71, respectively, that is about 0·2 ppm greater than "normal".[‡] These systems are all characterised by the presence of an equatorial Me substituent at the adjacent carbon (β to the heteroatom), and this accounts for the increase of $\delta_{ea}(\alpha)$. In cyclohexane, an equatorial Me is known to shield both adjacent protons, though the axial one more,[14] and this effect appears to be present in thiane as well. Since, the axial alpha proton is the more shielded, the presence of the equatorial Me at beta increases $\delta_{ea}(\alpha)$. Naturally this increase should carry over to the corresponding $^+$S–CH_3 axial isomers: indeed the only pertinent datum available agrees with this notion; in fact for **7a** $\delta_{ea}(\alpha)$ = 0·3 ppm, against a "normal" value of 0·1 ppm. Thus the difference [$\delta_{ea}(\alpha)$]eq-[$\delta_{ea}(\alpha)$]ax is about constant at 0·4 ppm, independent of whether there are equatorial substituents at the β-position.

It is now interesting to consider briefly the case of axial ring-substituents, of which we have one example, **8**. Although for systems such as this there can be no comparison with the S-CH_3 axial isomer (because of the *syn*-axial interaction between Me groups) it is interesting to observe that, at the alpha position adjacent to the axial Me, C_2, the value of $\delta_{ae}(\alpha)$ is considerably reduced (0·31 ppm, Table 1). Consideration of the individual proton resonances reveals that this results from shielding of the *cis* equatorial proton and deshielding of the *trans* axial proton (the latter still remains the more shielded, however). This is precisely what would be expected for an axial Me group in cyclohexane;[14] again, the parallelism is only qualitative.

Although our data do not include any conformationally biased systems having an axial Me at C_4, it is foreseeable that the presence of such a group would have a perturbing influence on $\delta_{ea}(\alpha)$. The *direction* of this perturbance, however, can be predicted by analogy with cyclohexane, where an axial Me has a small deshielding effect on both protons situated on the β carbon, though somewhat greater on the *syn*-diaxial proton.[14]



Thus in a situation such as that depicted here, $\delta_{ea}(\alpha)$ will become *less positive.* The effect will be approximately independent of the orientation of the S–Me group, so that the difference $[\delta_{ea}(\alpha)]_{eq} - [\delta_{ea}(\alpha)]_{ax}$ should still not differ much with respect to unperturbed systems, i.e. about 0·4 ppm.[§] The last column of Table 1 reports the field at the AB quartet midpoint, $\delta_{mdp}(\alpha)$. Although the differences within each isomeric pair amount to only a few hundredth of ppm (0·04 to 0·08 ppm, i.e. 10–20 Hz at 250 MHz), in each pair the axial isomer has the higher field midpoint independent of substituents elsewhere in the ring. Thus the value of $\delta_{mdp}(\alpha)$ appears to be a reliable configurational criterion *when both isomers can be separately observed.*

[†] *Qualitatively*, but not quantitatively, this effect is similar to that observed in methylcyclohexanes, where the change from $Me_{(eq)}$ to $Me_{(ax)}$ brings about shielding (by ~0·1 ppm) of the adjacent equatorial protons, and deshielding (by ~0·5 ppm) of the axial ones.[14]

[‡] By "normal" it is meant what is observed in the absence of perturbing influences, i.e. when the biasing group is equatorial *and* removed from the geminal pair under consideration (e.g. systems **4** and **5**).

[§] Lambert[4] has studied the PMR spectra of 4,4-dimethylthiane 1-oxide and 1-(N-tosyl)imide at sufficiently low temperature to observe the separate conformers. All $\delta_{ea}(\alpha)$ values are considerably smaller than for the corresponding unmethylated thiane derivatives, probably due to a deshielding effect on the axial α-proton by the *syn*-axial Me at C_4. What appears to be most interesting, however, is the observation that $\delta_{ea}(\alpha)$ for the axial isomer of the imide (0·17 ppm) is actually *greater* than $\delta_{ea}(\alpha)$ for the equatorial isomer (0·07 ppm).[4] Unfortunately Lambert could not provide the sign of $\delta_{ea}(\alpha)$; it seems likely, however, that there may be a sign inversion, i.e. for the axial isomer, the axial proton is downfield and $\delta_{ea}(\alpha) < 0$. If this is so, for 4,4-dimethylthiane (N-tosyl)imide, $[\delta_{ea}(\alpha)]_{eq} - [\delta_{ea}(\alpha)]_{ax}$ = 0·24 ppm, not much different from the value relative to the unmethylated derivative (0·34 ppm).[4]

A further and well known ^{1}H NMR criterion for configurational assignment of cyclic sulphoxides is the so-called "*syn*-axial" effect. What it amounts to is a dramatic deshielding (0·5–1·0 ppm) of the β-protons which are in a *syn* diaxial situation with respect to the S–O bond.[12] Although the nature of this effect, and more generally of the shielding effects of the sulphinyl group, is controversial[8,15–17] there is no question about its being a useful configurational probe.[8,12] It was therefore interesting on more than one count to investigate the shielding effect of axial S$^-$–Me on the axial β-protons. Pertinent data are available for two isomeric pairs, **4a**, **4e** and **7a**, **7e**, which are reported in Table 1 (sixth column). As shown, the axial β-proton appears to be deshielded in the S$^-$–Me axial isomers (**4a** and **7a**) with respect to the corresponding equatorial isomers (**4e** and **7e**). The direction of the effect is then the same for S$^+$–Me and S–O, although its magnitude appears to be smaller for the former (0·2 ppm),† large enough, however, to be useful for configurational assignment.

Aside from this useful application, however, this deshielding effect is interesting as it completes the picture of the similarity of shielding effects of S–O and S$^+$–Me groups. For α-protons the parallelism of shielding effects has already been observed by Fraser and Schuber[17] who suggested that the dominant influence is the lone pair, rather than that the S–O or S$^+$–Me bond. This view has recently been criticised by Lett and Marquet[8] who proposed that the effect of the sulphinyl group should be considered as the resultant of several factors, such as the lone pair effect, the polarity of the S–O bond, and the Van der Waals interaction between the negatively charged O atom and the *syn* β-H's. The latter was suggested as the most important factor in the *syn*-axial effect.[8] Our results, which extend to the β-H's the parallelism of shielding effects of S–O and S$^+$–Me groups, seem to support Fraser's view.[17] However, we believe the interplay of the various factors is too complicated to permit consideration of the individual contributions and any reliable estimate of their relative importance. At the present stage, the above parallelism of shielding effects can best be applied as an empirical generalisation, useful for configurational correlation.

EXPERIMENTAL

NMR spectra. Proton noise-decoupled ^{13}C NMR spectra were recorded at 25·2 MHz on a Varian XL-100-15 spectrometer by Fourier transform technique. The measurements were carried out on nearly saturated soln (~0·3 to 1·0 M) in D_2O using $Me_3SiCD_2CD_2COONa$ as internal standard.[10] The chemical shifts reported are within 0·2 ppm.

Proton NMR spectra were recorded at 250 MHz on a CAMECA instrument. The spectra of the equatorial sulphonium cations, **4e**, **5e**, **6e** and **7e**, were obtained either from the pure isomer or, when the isomer separation could not be achieved, from isomeric mixtures containing 80–90% of the equatorial isomer (i.e. the kinetically controlled distribution; see below). These spectra were all first order. The spectra of the axial isomers, **4a**, **5a**, **6a** and **7a**, were obtained from equilibrated isomeric mixtures which contained (see below) 40–45% axial isomer. As can be seen from Table 1, the circumstance that $\delta_{\mathrm{mdp}}(\alpha)$ for axial and equatorial isomers nearly coincide, while $\delta_{\mathrm{ea}}(\alpha)$ is considerably larger for the latter, allows the observation of the α protons of the axial isomers. Their spectra, however, are second order and the parameters of the α protons were derived from the analysis of the AB spectrum obtained by double irradiation of the β protons.

Materials. All the sulphonium cations used were in the form of fluoborate salts, obtained by methylation of the corresponding sulphides with trimethyloxonium fluoborate in dichloromethane at 0°. By this procedure the mixture normally contains from 80–90% of the equatorial isomer. Separation of the major isomer could be achieved by fractional crystallisation for **5e** and **7e**. None of the axial isomers could be obtained in the pure form. Equilibration of the equatorial and axial isomers was achieved via thermal pyramidal inversion of the S atom[19] (60 hr at 100°).

With the exception of *cis*- and *trans*-3,5-dimethylthiane, all sulphides are known compounds.[10,20,21] We obtained them via the following reaction sequence: (1) Reduction of the suitably substituted glutaric acid derivative with LAH in ether to the corresponding 1,5-pentanediols (~80% yield). (2) Conversion of the diols to the dimesylates ($MeSO_2Cl$, pyridine; ~95%). (3) Cyclisation of the dimesylates to thianes with Na_2S in 95% ethanol under reflux (~60%).

cis- *and* trans-3,5-*Dimethylthiane.* A mixture of these sulphides was obtained using as starting material a commercial mixture (Fluka) of *meso*- and (*dl*)-2,4-dimethylglutaric acid. Separation of the sulphides was achieved by fractional distillation (spinning band column, Perkin Elmer M251). Isomer identification was readily secured by ^{13}C NMR analysis.[18]

cis-3,5-*Dimethylthiane*, b.p. 156–157°, 760 mm. Trans-3,5-*dimethylthiane*, b.p. 160–161°, 760 mm.

cis- *and* trans-4-*Isopropyl*-1-*methylthianium fluoborates*, **4a** and **4e**, have been previously described.[10]

cis- *and* trans-1,4-*Dimethylthianium fluoborates*, **5a** and **5e**. Methylation of 4-methylthiane yielded a crude mixture containing about 80% of the *trans* isomer. Fractional crystallisation from H_2O yielded the *trans* isomer in pure form, m.p. 130–131°. (Found: C, 38·47, H, 7·01; S, 14·70. Calcd. for $C_7H_{15}SBF_4$: C, 38·55; H, 6·93; S, 14·70). Thermal equilibration gave an isomeric mixture containing 41% axial isomer ($K = eq/ax = 1{\cdot}4_2$).

cis- *and* trans-1,3-*Dimethylthianium fluoborates.* The crude product was a low melting solid which appeared to contain about 85% of the *cis* isomer. No significant separation could be achieved by fractional crystallisation from MeOH. (Found: C, 38·63; H, 6·86; S, 14·58. Calcd. for $C_7H_{15}SBF_4$ C, 38·55; H, 6·93; S, 14·70%).

Thermal equilibrium yielded an isomeric mixture containing 43% axial isomer ($K = 1{\cdot}3_3$).

cis,cis- *and* trans,trans-1,3,5-*Trimethylthianium fluoborates*, **7e** and **7a**. The crude mixture contained about 90% of the *cis*, *cis* isomer. Fractional crystallization from Me_3OH yielded the pure *cis,cis* isomer, m.p. 75·0–75·5° (Found: C, 41·53; H, 7·34; S, 13·89. Calcd. for $C_8H_{17}SBF_4$: C, 41·40; H, 7·38; S, 13·81%). Thermal equilibration gave an isomeric mixture containing 45% of the *trans,trans* isomer ($K = 1{\cdot}2_5$).

trans,cis-1,3,5-*Trimethylthianium fluoborate*, **8**. Alkylation of *trans*-3,5-dimethylthiane gave only one product, the title compound, m.p. 96–97°, recrystallized from EtOH. (Found: C, 41·33; H, 7·40; S, 13·77. Calcd. for $C_8H_{17}SBF_4$: C, 41·40; H, 7·38; S, 13·81%).

1,4,4-*Trimethylthianium fluoborate*, **9**. m.p. 273–275°, recrystallized from EtOH/Et_2O. (Found: C, 40·95; H, 7·44; S, 13·96. Calcd. for $C_8H_{17}SBF_4$: C, 41·40; H, 7·38; S, 13·81%).

REFERENCES

[1] E. L. Eliel, R. L. Willer, A. T. McPhail and K. D. Onan, *J. Am. Chem. Soc.* **96**, 3022 (1974).

[2] J. B. Lambert, W. L. Oliver, Jr. and B. S. Packard, *Ibid.* **93**, 933 (1971).

[3a] C. R. Johnson and D. McCants, *Ibid.* **86**, 2935 (1964); [b] J. C. Martin and J. J. Uebel, *Ibid.* **86**, 2936 (1964); [c] J. B. Lambert and R. G. Keske, *J. Org. Chem.* **31**, 3429 (1966).

[4] J. B. Lambert, D. S. Bailey and C. E. Mixan, *Ibid.* **37**, 377 (1972).

[5] S. I. Featherman and L. D. Quin, *J. Am. Chem. Soc.* **95**, 1699 (1973).

[6a] M. T. Tribble and N. L. Allinger, *Tetrahedron* **28**, 2147 (1972); [b] R. J. Ouelette, D. Baron, J. Stolfo, A. Rosenblum and B. Weber, *Ibid.* **28**, 2163 (1972).

[7] J. B. Lambert, C. E. Mixan and D. H. Johnson, *J. Am. Chem. Soc.* **95**, 4634 (1973).

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†For the corresponding sulphoxides the syn-axial effect amounts to about 0·5 ppm.[18]

[8] For a recent review of PMR criteria for configurational assignment of cyclic sulfoxides, see R. Lett and A. Marquet, *Tetrahedron* **30**, 3379 (1974).

[9] R. Cahill, R. C. Cookson and T. A. Crabb, *Ibid.* **25**, 4681 (1969).

[10] G. Barbarella, P. Dembech, A. Garbesi and A. Fava, *Org. Mag. Resonance* **7**, 000 (1976).

[11] J. B. Lambert, C. E. Mixan and D. S. Bailey, *J. Am. Chem. Soc.* **94**, 208 (1972).

[12] K. W. Buck, A. B. Foster, W. W. Pardoe, M. H. Qadir and J. M. Webber, *Chem. Comm.* 759 (1966). See also Ref. 8.

[13] D. S. Bailey, J. A. Walder and J. B. Lambert, *Ibid.* **94**, 177 (1972).

[14] H. Booth, *Tetrahedron* **22**, 615 (1966).

[15] A. B. Foster, R. D. Inch, M. H. Qadir and J. M. Webber, *Chem. Comm.* 1086 (1967).

[16] R. D. G. Cooper, P. V. DeMarco, J. C. Cheng and N. D. Jones, *J. Am. Chem. Soc.* **91**, 1408 (1969).

[17] R. R. Fraser and F. J. Schuber, *Can. J. Chem.* **48**, 633 (1970).

[18] G. Barbarella, unpublished.

[19] A. Garbesi, N. Corsi and A. Fava, *Helv. Chim. Acta* **53**, 1499 (1970).

[20] E. V. Whitehead, R. A. Dean and F. A. Fidler, *J. Am. Chem. Soc.* **73**, 3632 (1951).

[21] L. Schmerling and J. P. West, *Ibid.* **74**, 2885 (1952).