

e.g., Ib and c, $\bar{\nu}$ about 3625 cm.^{-1}) and III (hydroxyl hydrogen staggered between two adjacent carbon atoms, *e.g.*, Ia, $\bar{\nu}$ about 3617 cm.^{-1}) for secondary alcohols. Based on these observations, the increase in the frequency of the absorption maximum in going from an equatorial to an axial hydroxyl epimer may be explained by the absence of the contribution of the type III conformation (*e.g.*, Ia), the population of which would be negligible due to diaxial steric interactions. This situation does not exist for the equatorial epimers. If this theory is correct, *direct conformational assignment of the hydroxyl group may be made on the basis of its band shape: a symmetrical band for an axial, an unsymmetrical band for an equatorial hydroxyl group.*

We have examined a series of epimeric alcohols of simple carbocyclic, azabicyclic, and steroid systems in dilute carbon tetrachloride solution ($<0.02 M$) using a high resolution grating spectrophotometer. The free O-H stretching band was very slowly scanned on an expanded abscissa (5 $\text{cm.}^{-1}/\text{cm.}$). Absorbancy correction factors⁸ due to the spectral slit width used (less than 2 cm.^{-1}) were considered to be negligible and were not applied. The absorption bands thus obtained may be characterized as being either symmetrical or unsymmetrical merely by inspection, although even the symmetrical bands tend to possess certain minor features of asymmetry. For quantitative characterization the symmetry of the band may be expressed as the α/β ratio which results from measurements of the segments of the half band width⁹ ($\Delta\nu_{1/2}$) on the high (α) and low (β) frequency sides of $\bar{\nu}_{\text{max}}$. Thus, the band symmetry should decrease as α/β departs from unity. The results summarized in Table I reveal that an α/β ratio which deviates from unity by less than 10% would appear to be a firm indication of an axial hydroxyl conformation.

TABLE I
FREE O-H STRETCHING INFRARED ABSORPTION DATA^a FOR
CYCLIC ALCOHOLS

Equatorial alcohols	$\bar{\nu}_{\text{max}}$, cm.^{-1}	α/β
Pseudotropine	3623	0.38
<i>cis</i> -2,10-H-2-Hydroxyquinolizidine ^b	3624	.43
<i>trans</i> -1,10-H-1-Hydroxyquinolizidine ^b	3636	.57
<i>trans</i> -3,10-H-3-Hydroxyquinolizidine ^b	3628	.63
3 β -Cholestanol	3624	.57
Epiandrosterone	3623	.70
Cholesterol	3624	.64
<i>trans</i> -4- <i>t</i> -Butylcyclohexyl alcohol	3624	.64
Menthol	3628	.55
Axial alcohols		
Tropine	3626	1.08
<i>trans</i> -2,10-H-2-Hydroxyquinolizidine ^b	3627	0.90
3 α -Cholestanol	3627.5	.94
Androsterone	3627.5	.92
<i>cis</i> -4- <i>t</i> -Butylcyclohexyl alcohol	3628	.98

^a Perkin-Elmer Model 421 spectrophotometer, slit program 1000 \times 1. ^b For conformational assignments of the hydroxyquinolizidines, see C. P. Rader, G. E. Wicks, Jr., and H. S. Aaron, Abstracts of the 144th National Meeting of the American Chemical Society, March 31-April 5, 1963, Los Angeles, Calif., p. 40M; F. Bohlmann, E. Winterfeldt, O. Schmidt, and W. Reusche, *Chem. Ber.*, **94**, 1767 (1961).

This simple correlation may not hold in the case of a vicinally substituted axial alcohol. The spatial environment of each of the type II conformers (*e.g.*, Ib or c) will no longer be identical upon unsymmetrical vicinal substitution. Neomenthol, for example, gives an over-all symmetrical band, but with a doublet

($\bar{\nu}_{\text{max}}$ values of 3628 and 3632 cm.^{-1}) of near equal intensities. A strict application of the method used for the quantitative characterization of band symmetry would result in an equatorial assignment (α/β , 0.60) to a known axial hydroxyl group. When an instrument of lower resolving power is used, neomenthol gives a symmetrical free O-H stretching band which corresponds to an axial alcohol.

Piccolini and Winstein¹⁰ examined the first overtone of the hydroxyl stretching frequency for a series of compounds, discussed their results from the standpoint of singlet *vs.* doublet character of the bands, and attempted to establish the structural variations which lead to doublet (*i.e.*, unsymmetrical) band character due to steric interactions. They have observed neomenthol to give a symmetrical band in the first overtone, a result confirmed by the present authors. The scope of the steric effect in this phenomenon, however, has not been delineated. Effects of vicinal substitution upon shifts in the frequency of type II and type III conformations have been noted in non-cyclic systems.^{7,11} The presence of functional moieties which can lead to intramolecular hydrogen bonding¹² may also result in an unsymmetrical band for an axial hydroxyl epimer (*e.g.*, epicholesterol¹³).

The noted exceptions notwithstanding, the analysis of the shape of the O-H stretching band constitutes a powerful tool for direct conformational assignment in a rigid six-membered ring system. More subtle applications of the phenomenon are foreseen in the projected areas of conformational analysis and stereochemical assignments in other ring systems.¹⁴ For these purposes both the fundamental and first overtone spectral bands appear to be useful. A recent study of the shape of hydroxyl absorption bands has yielded results from the first overtone which are similar to those from the fundamental.¹⁵ Further comparisons of these two spectral bands are desirable.

Additional and more detailed reports on the applications of this phenomenon will be made at a later date.

Acknowledgments.—We are grateful to Dr. A. Siakotos for furnishing samples of the steroid alcohols and to the Glidden Co. of Jacksonville, Florida, for providing a generous supply of *d,l*-neomenthol.

(10) R. Piccolini and S. Winstein, *Tetrahedron Letters*, No. 13, 4 (1959).

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(12) *E.g.*, H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **85**, 784 (1963).

(13) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 306 (1959).

(14) *E.g.*, P. Hirsjärvi and K. Salo, *Suomen Kemistilehti*, **32**, 280 (1959). These workers have correlated the configurations of *endo* and *exo* bicyclo-[2,2,1]heptanols with the band widths and positions of the maxima of the fundamental free O-H stretching absorption.

(15) F. Dalton, G. D. Meakins, J. H. Robinson, and W. Zaharia, *J. Chem. Soc.*, 1566 (1962). These investigators report a symmetrical band to result from 3 β -cholestanol, an equatorial alcohol which has clearly given an unsymmetrical band in the present study.

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Sulfur Monofluoride: The Microwave Spectrum of a Second Isomer¹

Sir:

Three recent communications have been published concerning sulfur monofluoride. Kuczukowski and Wilson² using mass and microwave spectroscopy showed

(1) This work was supported by a grant extended Harvard University by the Office of Naval Research.

(2) R. Kuczukowski and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **85**, 2028 (1963).

(8) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

(9) R. N. Jones and C. Sandorfy in W. West, "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 272.

that one of the reaction products obtained by heating argentous fluoride and sulfur is the pyramidal $S=SF_2$ form. Seel and Göllitz,³ using a different synthesis, were also able to establish the existence of the pyramidal $S=SF_2$ form on the basis of its infrared spectrum. Glemser, Heussner, and Haas⁴ have also reported a preparation of S_2F_2 but have not drawn any conclusions as to the structure. We are now able to demonstrate that a second isomer of S_2F_2 exists with a nonplanar chain FSSF structure analogous to S_2Cl_2 .⁵

The first indication that two isomeric forms of S_2F_2 existed⁶ was obtained during the earlier investigation of the $S=SF_2$ form.² When the crude products of the reaction between AgF and S were volatilized at different rates into the mass spectrometer, a varied cracking pattern was obtained for mass peaks attributable to S_2F_2 . In addition, with a sample in the microwave cell at Dry Ice temperature, a set of absorptions was noted whose intensity steadily decreased with a first-order half-life of approximately 15 min. These microwave lines could not be explained by the $S=SF_2$ form or known impurities. Both of these properties disappeared when the reaction products were fractionally distilled in order to obtain pure $S=SF_2$, presumably due to decomposition of the reactive FSSF species with the distillation apparatus.

In the investigation of the microwave lines from FSSF, it was found possible to enhance their initial intensity by dosing of the bulk reaction product into the absorption cell from slush baths below -100° . A complete separation was unnecessary since the characteristic decay rate identified the transitions arising from the FSSF species.

The observed and calculated microwave spectra for this species are listed in Table I. The transitions were assigned on the basis of their Stark effects and agreement obtained with the calculated rigid rotor spectrum. The rotational constants used in the calculations and the derived moments of inertia are listed in Table II

TABLE I
MICROWAVE SPECTRUM OF FSSF^a (MC./SEC.)

Transition	Observed	Calculated
$0_{00} \rightarrow 1_{11}$	13843.46	13843.47
$1_{01} \rightarrow 2_{12}$	18983.41	(18983.41) ^b
$7_{16} \rightarrow 7_{25}$	23368.35	23366.31
$6_{15} \rightarrow 6_{24}$	23871.05	23869.35
$2_{02} \rightarrow 3_{13}$	24018.83	(24018.83)
$5_{14} \rightarrow 5_{23}$	24355.65	24354.79
$4_{13} \rightarrow 4_{22}$	24798.45	24798.05
$3_{12} \rightarrow 3_{21}$	24178.50	24178.18
$7_{15} \rightarrow 7_{26}$	28806.32	28807.72
$3_{03} \rightarrow 4_{14}$	28954.70	(28954.70)
$8_{18} \rightarrow 8_{27}$	29679.35	29681.16
$1_{10} \rightarrow 2_{21}$	36390.08	36390.47
$1_{11} \rightarrow 2_{20}$	36605.47	36606.50

^a A conventional Stark modulated spectrometer was employed. Frequencies were reproducible to ± 0.1 Mc. ^b Transitions in parentheses used to calculate the rotational constants.

TABLE II
ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR $F^{32}S^{32}SF$

A	B	C
11273.50 Mc./sec.	2782.08 Mc./sec.	2569.97 Mc./sec.
I_a	I_b	I_c
44.8424 Amu. \AA^2	181.7097 Amu. \AA^2	196.7069 Amu. \AA^2

(3) F. Seel and D. Göllitz, *Chimia*, **17**, 207 (1963).

(4) Von O. Glemser, W.-D. Heussner, and A. Haas, *Naturwissenschaften*, **50**, 402 (1963).

(5) E. Hirota, *Bull. Chem. Soc. Japan*, **31**, 130 (1958).

(6) R. Kuczkowski, Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June, 1963.

An alternation in intensity due to nuclear spin statistical weights was observed for transitions of different symmetry. Rough intensities for the $3_{12} \rightarrow 3_{21}$, and $5_{14} \rightarrow 5_{23}$ transitions compared to the $4_{13} \rightarrow 4_{22}$ transition indicated a nuclear statistical weight factor of 3 to 1, respectively. This establishes that the molecule has a C_2 symmetry axis which can exchange a pair of equivalent fluorine atoms with nuclear spin of $1/2$. Quantitative measurements of the frequency shifts *vs.* voltage squared for the three Stark lobes of the $2_{02} \rightarrow 3_{13}$ transition indicated that only "b" type selection rules were operating, which further confirms the C_2 axis.

It proved possible to correlate the intensity of the microwave lines with mass spectral peaks. Whenever the microwave lines reported here were absent from a sample, the mass spectrum could be explained in terms of the $S=SF_2$ isomer and/or known impurities. However, when these transitions were intense, then the $51(SF^+)$, $64(S_2^+)$, and $83(S_2F^+)$ *m/e* peaks increased while the $70(SF_2^+)$ *m/e* peak decreased relative to the $102(S_2F_2^+)$ *m/e* peak when compared to the cracking pattern of pure $S=SF_2$. No unexplained peaks were detected to *m/e* units greater than 102.

The mass spectral data demonstrate that sulfur and fluorine are elements in the molecules giving rise to the microwave spectrum and indicate that it almost certainly has the molecular formula S_2F_2 . The nuclear spin statistics and absence of an unpaired electron also permit only two fluorine atoms in the molecule. The moments of inertia alone can eliminate SF_2 and pyramidal or chain S_3F_2 as possibilities. The only possible species remaining which gives reasonable structural parameters is a nonplanar, chain-type FSSF molecule. The moments of inertia are insufficient to calculate a unique structure for this species without assuming one parameter. Hence, they fit a range of structures with $d(SS)$ between 1.85 and 2.05 \AA ., $d(SF)$ between 1.55 and 1.65 \AA ., and $\angle SSF$ and dihedral angles in the vicinity of 109 and 90° , respectively. This type of structure is similar to that reported for S_2Cl_2 and S_2Br_2 .⁵ For example, S_2Cl_2 has $d(SS) = 1.97 \pm 0.03$ \AA ., $\angle SSCl = 107 \pm 2.5^\circ$, and a dihedral angle of $82.5 \pm 12^\circ$.⁵ The range of sulfur-fluorine bond lengths is also reasonable compared to other molecules.^{7,8}

Therefore, on the basis of the correlation of the microwave spectrum with mass spectral peaks, the alternating intensities due to fluorine nuclear spin statistical weights, and the reasonable structure which will fit the moments of inertia, we conclude that the reported microwave spectrum is due to the nonplanar chain FSSF form of sulfur monofluoride and consequently that S_2F_2 exists in two isomeric forms.

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(7) W. Kirchhoff and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **84**, 334 (1962). See Table III in paper.

(8) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

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Use of a π -Complex of an Olefin as a Photochemical Catalyst

Sir:

We wish to report an unusual catalytic effect due to a π -complex on the photochemistry of 1,5-cyclooctadiene in solution. The π -complex was that of cuprous