and

$$[A_2H] = [A_2H]_{initial} - [A_2^-]$$

which on substitution in the familiar equation

$$H_- = pK_{A_2H} - \log [A_2^-]/[A_2H]$$

gives the required pK_a.

The second-order rate constants have been found to be independent of hydroxide ion concentration in a number of dimethyl sulfoxide–water solutions of varying composition and the acidity constants show no perceptible trend with increasing concentration of any of the A_2H acids so that the two main requirements necessary for the successful operation of the method are well obeyed. The method also depends on having the solutions carefully degassed and being able to perform the detritiations under an inert atmosphere of nitrogen. The acidities can be quoted to within ± 0.1 pK unit, and the general validity of the method has been established by redetermining the pK_a of fluorene, which has been the subject of several studies, and also that of 2-nitro-4-chloroaniline, one of the nitrogen indicators used in setting up the H_- scale.[5] The "standard" acid used was [9-³H]-9-tert-butyl-fluorene. The acidities of two acetophenones and two benzylideneacetones are also given in Table I.

Table I. Acidities in the Dimethyl Sulfoxide–Water Solvent System at 25°

Acid	pK_a	Lit. value
Fluorene	21.0	22.94,[a] 22.83,[a] 20.5,[b] 21.0,[c] 22.1[d]
2-Nitro-4-chloroaniline	16.9	17.1,[b] 17.2[e]
p-Cyanoacetophenone	18.4	
p-Dimethylaminoacetophenone	22.6	
Benzylideneacetone	21.4	
p-Cyanobenzylideneacetone	20.6	

[a] A. Streitwieser, Jr., E. Ciuffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, **89**, 59 (1967). [b] C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967). [c] K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965). [d] K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 173 (1970). [e] R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **42**, 1681 (1964).

The method is well suited for those compounds whose absorption spectra do not undergo significant change on ionization. Furthermore by careful choice of the "standard" acid a wide range of acidities can be covered and the work extended to widely different solvent systems.

(5) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967).

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Conformational Equilibria of Hexahydrotetrazines

Sir:

1,2,4,5-Tetramethylhexahydro-1,2,4,5-tetrazine (1) can exist as five chair conformers 1-V to 1-Z con-

taining up to two axial methyl groups, of which 1-V, with two axial groups on the same side of the ring, can be neglected. Anderson and Roberts[1] interpreted the low-temperature nmr spectrum in terms of a conformer with two axial methyl groups and postulated that the most likely conformer was 1-X. Our group supported[2] 1-W on the basis of dipole moment evidence. Nelsen

1, R = Me
2, R = Et

3, X = H
4, X = D

V   W   X

Y   Z

5   6   7

8   9
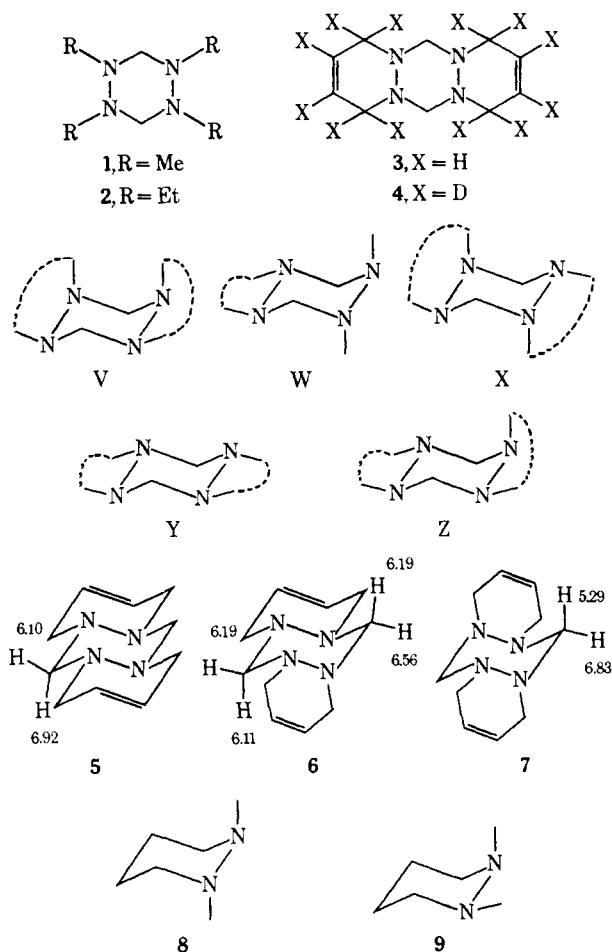
and Hintz[3] claim to have demonstrated, from nmr comparisons with polycyclic compounds, including 3, that 1 exists as conformer 1-X, and ascribe the dipole moment results[2] to impurities. They further claim[3] that the tetraethyl analog (2) exists 85% as the conformer 2-W and 15% as 2-X. Unfortunately their work contains serious errors of assignment and interpretation as well as an unjustified slight on our experimentation and we now show that their conclusions[3] are both quantitatively and qualitatively incorrect, by using 220-MHz spectra of a selectively deuterated compound.

The tricyclic derivative 3 provides the key to the assignment of the nmr spectra of the monocyclic compounds 1 and 2. Nelsen and Hintz[3] interpret the low-temperature nmr spectrum of 3 in terms of a single conformer 3-Z; as will be discussed in the full paper this is easily seen to be incorrect from the spectrum of 3 itself. Further, the low-temperature spectrum (Figure 1) of the selectively deuterated analog 4 clearly demonstrates the presence of the three conformers 3-Z, 3-X,

(1) J. E. Anderson and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 4186 (1968).
(2) R. A. Y. Jones, A. R. Katritzky, and A. C. Richards, *Chem. Commun.*, 708 (1969).
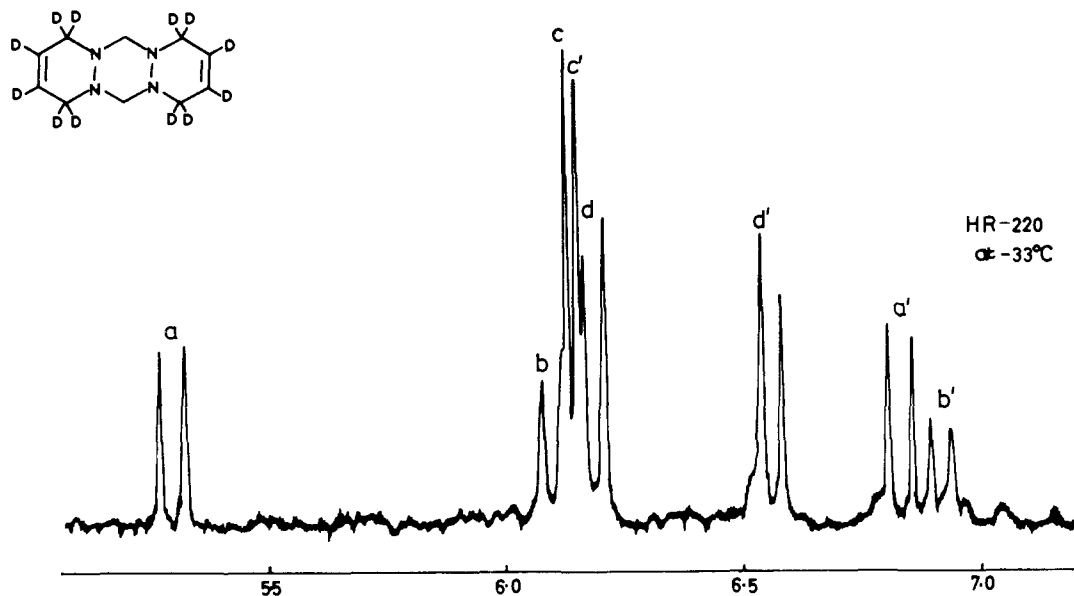(3) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 3138 (1972).

Figure 1. The nmr spectrum (220 MHz) of (4) in $CDCl_3-CFCl_3(80:20)$ at $-33°$.

and 3-Y in the proportions 67:20:13. Our assignment of the individual protons is shown in **5**, **6**, and **7**. Nelsen and Hintz[3] incorrectly assigned the proton at τ 5.29 (which derives from a minor component 3-X) to the conformer 3-Z. The present assignments are based on three criteria: (i) self-consistency in the effects of moving a lone pair from the axial to the equatorial position as the conformation is changed from **5** to **6** and from **6** to **7** (see below); (ii) the assumption that the lone pair orientation will have a greater influence on the shift of the α-equatorial and β-axial protons than on the more remote β-equatorial proton; (iii) the assumption that moving the lone pair from axial to equatorial will deshield rather than shield the α-axial proton.[4] However, the keystone of the arguments below, based on differential shielding, is that the smallest axial–equatorial geminal chemical shift difference of all three conformers is associated with the unsymmetrical conformer Z. This is unambiguous; the relative intensities demand that the four signals in the narrow range from τ 6.11 to 6.56 are associated with this conformer. The reasons which lead us to the particular assignment shown in **5**, **6**, and **7** will be elaborated in the full paper. In this assignment the movement of an axial lone pair to equatorial has the following effects on the various CH proton shifts: α-eq, $+0.46$ to $+0.64$; β-eq, $+0.09$ to $+0.27$; α-ax, -0.73 to -0.82; β-ax, -0.81 to -0.90 ppm. Part of these shifts will be due to the anisotropy of the carbon–carbon double bonds, but the maximum contribution from this source[5] does not exceed 0.1 ppm.

These results may be extended to the monocyclic compounds **1** and **2**, and indicate that the differential chemical shift ($\tau_{eq} - \tau_{ax}$) for the CH_2 groups should be large (*ca.* $+1.5$ ppm) for *both* of the conformers W and X, medium (*ca.* -0.8 ppm) for conformer Y, and small (two different CH_2 groups, *ca.* $+0.4$, $+0.1$ ppm)

(4) P. J. Halls, R. A. Y. Jones, A. R. Katritzky, M. Snarey, and D. L. Trepanier, *J. Chem. Soc. B*, 1320 (1971), and references therein.

(5) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon, Braunschweig, Germany, 1969, pp 85–88.

for conformer Z. In other work[6] we have shown that inversions at nitrogen such as **8** $\rightleftharpoons$ **9**, which do not involve N substituents passing each other, are of low energy. The interconversion of conformers W and Z is of this type. Hence we must consider the low-temperature nmr spectra of **1** and **2** in terms of the *three* possible components: (i) X, (ii) Y, and (iii) W/Z interconverting.

Our nmr results for **1** and **2** are shown in Table I.

Table I. Chemical Shift, Coupling, and Integration Data for the $N-CH_2-N$ Regions of Nmr Spectra Studied[a]

Compound	$N-CH_2-N$ peaks $A(\tau)$	$B(\tau)$	$\Delta\delta$, ppm	J_{gem}, Hz	Relative area	Conformer structure
4	5.29	6.83	1.54	11.5	20	X
	6.10	6.92	0.82	9.5	13	Y
	6.11	6.19	0.08	11.5	33	Z
	6.19	6.56	0.37	9.5	33	Z
1	6.03	6.67	0.64	12.0		W $\rightleftharpoons$ Z
2	5.12	6.8[b]	1.7	14.0	80	X
	6.07	6.38	0.31	12.0	20	W $\rightleftharpoons$ Z

[a] All peaks listed are doublets. [b] Partly obscured by $N-CH_2-C$ peak.

The tetraequatorial conformer Y can be excluded for **1** because of the nonequivalence of the methyl groups. It is clear that the *major* (80%) component of **2** must exist in the conformation 2-X whereas the *minor* (20%) component exists in the interconverting conformations 2-W/Z. Similarly, the tetramethyl derivative exists almost entirely in the interconverting conformations 1-W/Z. It is further apparent that the proportion of the triequatorial form Z is larger for the tetraethyl compound **2** than for the tetramethyl compound **1** in the rapidly interconverting equilibria W/Z.

These conclusions are in good agreement with our previous[2] and more recent dipole moment evidence

(6) R. A. Y. Jones, A. R. Katritzky, D. L. Ostercamp, K. A. F. Record, and A. C. Richards, *Chem. Commun.*, 644 (1971); R. A. Y. Jones, A. R. Katritzky, and R. Scattergood, *ibid.*, 644 (1971); for a full account of this work see R. A. Y. Jones, A. R. Katritzky, K. A. F. Record, and R. Scattergood, submitted for publication to *J. Chem. Soc., Perkin Trans. 2*.

(*pace* Nelson and Hintz[3] the dipole moments are reproducible and are not due to impurities) and also with Raman and infrared evidence as will be discussed in our full paper.
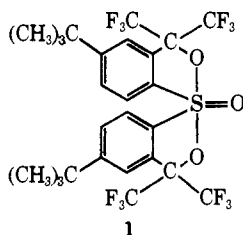
R. A. Y. Jones, A. R. Katritzky,* A. R. Martin[7]
D. L. Ostercamp,[8] A. C. Richards, J. M. Sullivan[9]

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X-Ray Crystal Structure of a Diaryldialkoxysulfurane Oxide[1]

Sir:

We report the results of a single-crystal X-ray structure determination on the recently described[2] sulfurane oxide **1**.[3] This is the first X-ray structural study reported for a pentacoordinate sulfur(VI) compound.

1

The nonequivalence of the trifluoromethyl groups,[2] which is evidenced in the ^{19}F nmr spectrum of **1**, is consistent with most of the structural models which have been considered for such species, including the trigonal bipyramidal model and the tetragonal pyramidal model. The present study establishes an approximate trigonal bipyramidal geometry about sulfur with the electronegative alkoxy groups occupying apical positions and with the two aryl groups and the oxide oxygen occupying equatorial positions.

Sulfurane oxide **1** was recrystallized several times from petroleum ether and a single crystal was selected and mounted in the usual way: $C_{26}H_{24}F_{12}O_3S$, M = 644.5; monoclinic; a = 13.824 (9), b = 12.231 (5), c = 20.846 (11) Å; β = 126°55' (1'); V = 2818 Å^3; Z = 4; ρ_{calcd} = 1.52 g cm^{-3}; $F(000)$ = 1312; space group $P2_1/c$ from systematic absences, $h0l$, when l = $2n$ + 1, $0k0$, when k = $2n$ + 1; nickel filtered Cu Kα X-radiation; λ 1.54178 Å; μ(Cu Kα) = 20.3 cm^{-1}.

A single crystal was used to obtain the intensity data on a Picker FACS-1 diffractometer. A total of 3005 nonzero reflections was obtained using Cu Kα radiation. The structure was solved by the symbolic addition procedure,[4] using the FAME–SYMPL–MAGIC

(1) Paper number XI in a series on sulfuranes. For paper X in this series see J. A. Franz and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 2017 (1973).

(2) E. F. Perozzi and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5519 (1972).

(3) For other examples of pentacoordinate sulfur(VI) species containing halogen ligands, see (a) S. P. von Halasz and O. Glemser, *Chem. Ber.*, **103**, 594 (1970); (b) S. P. von Halasz, O. Glemser, and M. F. Feser, *ibid.*, **104**, 1242 (1971); (c) J. M. Shreeve, *Accounts Chem. Res.*, **6**, 387 (1973).

(4) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

series of programs,[5] and refined initially by Fourier methods. At the present stage of refinement[6] (hydrogen atoms located and anisotropic thermal parameters for the nonhydrogen atoms) the crystallographic R factor on all nonzero reflections is 0.072. Some ambiguity is evident in the location of the hydrogen atoms on the *tert*-butyl groups, indicating the possibility of disorder of these hydrogens due to rotation of 60° about the C–CH$_3$ bonds. A stereoscopic view of the structure is shown in Figure 1.

The only other pentacoordinate sulfur(VI) compound for which structural data are available is sulfur oxytetrafluoride, OSF$_4$. Electron diffraction studies on this compound have resulted in the proposal of various models to account for the data. The models[7–9] are in agreement as to the overall trigonal bipyramidal geometry of the molecule, but there is some uncertainty as to the finer structural details. The internal equatorial F–S–F angle has been reported as 122.8 (1.8)°,[7] 110.01 (74)°,[8] and 110.1 (1.8)°,[9] while the axial F–S–F angle has been reported as 182.8 (7)°,[7] 178.35 (48)°,[8] and 178.8 (4)°.[9] In the first model,[7] the axial F–S–F angle is bent *in* the direction of the equatorial oxygen, *away* from the equatorial fluorines, while in the two more recent models[8,9] the direction of distortion from linearity is *away* from the equatorial oxygen. The structure determination of **1**, showing the O–S–O (axial) angle to be 172.3 (2)° and the distortion from linearity *away* from the equatorial oxygen, supports the more recently proposed structures for OSF$_4$.[8,9]

The C–S–C angle of **1** (117.7 (3)°) is considerably larger than the C–S–C angle of dialkoxydiarylsulfurane, **2** (104.4 (3)°),[10] or of the spirodiaryldiacyloxysulfurane, **3** (107.8 (8)°).[11] The distortion of the trigonal

2

3
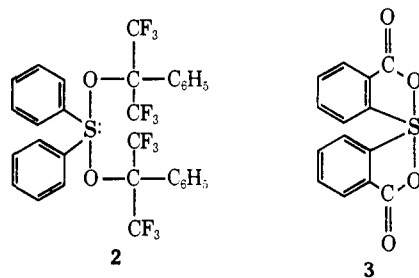
bipyramid which reduces the C–S–C angles of **2** and **3** below 120° has been interpreted[10] as a reflection of the 3s–3p energy level separation, which causes the lone pair of electrons to utilize more of the s character[12] while the S–C bonds tend to acquire more p character. In sulfurane oxide **1** there is no lone pair, hence one would expect the equatorial angles to approach the 120° value appropriate to sp^2 hybridization, as is observed.

(5) (a) E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, Abstracts, American Crystallographic Association, Atlanta, Ga., Jan 1967, Paper A7, p 20; (b) R. B. K. Dewar, Ph.D. Thesis, University of Chicago, 1968.

(6) See paragraph at end of paper regarding supplementary material.

(7) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963).

(8) J. L. Hencher, D. W. J. Cruickshank, and S. H. Bauer, *J. Chem. Phys.*, **48**, 518 (1968).

(9) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969).

(10) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Amer. Chem. Soc.*, **94**, 5010 (1972); **93**, 6674 (1971).

(11) (a) A. Kálmán, K. Sasvári, and I. Kapovits, *Acta Crystallogr.*, *Sect. B*, **29**, 355 (1973); (b) I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).

(12) See, for example, H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).