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A REMARKABLE DIFFERENCE IN THE CONFORMATIONAL PREFERENCE OF THE SO-BOND IN 1,3-DITHIANE-1-OXIDES AND 1,3-OXATHIANE-3-OXIDES.

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The sulfoxide group shows a lot of interesting stereochemical features (1). In thiane-1-oxide the axial conformation (62% of the mixture at -90°C) is favored by 175 cal/mole (2). Introduction of a 3,3-dimethyl grouping reverses this axial preference into a pronounced equatorial one (3). This seems to indicate that an attractive interaction between the SO-bond and the synaxial protons is at the basis of this unusual conformational behaviour (3). Further evidence is provided by the fact that lengthening the bonds of the system by going to selenane-1-oxide increases the proportion of the axial conformer (84% at -102°C) (4).

Systems containing adjacent polar bonds e.g. 1,2-oxathiane-2-oxide; 1,2-dithiane-1-oxide (5), 1,3-dioxa-2-thia(selena)-cyclo-hexane-2-oxide (6) and even 4, 4,6, 6-tetramethyl-1,3-dioxa-2-thiacyclo-hexane-2-oxide (7) exist in chair conformations with axial SO-bonds. This may, at least in part, be attributed to dipolar effects (5, 7).

Recently it was shown that on treatment of either cis- or trans-2-t-butyl-1,3-dithiane-1-oxide with NaOD in DMSO, the equilibrium mixture formed favours the trans-isomer (69% at 84° $-\Delta G = 500$ cal. mole^{-1}) which has the lower dipole moment (3.56D versus 4.39D for cis-isomer) and in which the S-O bond occupies the equatorial position.

We have investigated the conformational behaviour of the SO-bond in 1,3-oxathiane-3-oxide (bp. 90°C/0.14 mm) (I); 5,5-dimethyl-1,3-oxathiane-3-oxide (mp. 87,5-88 °C) (II); 1,3-dithiane-1-oxide (mp. 87-88°C) (III) and 5,5-dimethyl-1,3-dithiane-1-oxide (mp. 84-84.5°C) (IV) by LT (low temperature)-NMR experiments in freon 21 on a 100 MHz apparatus.

The results (Table 1) show a pronounced difference between the oxathiane and the dithiane series : the 1,3-oxathiane-3-oxide (I) possesses an axial SO preference (84% at -98°C, $-\Delta G = 570$ cal/mole) whereas the 1,3-dithiane-1-oxide (III) contains only 15% of the axial form. The effect of the 5,5-dimethylgrouping in decreasing the proportion of the 1-axial isomer (10% at -102°C, $-\Delta G = 730$ cal/mole) for (II) is quite normal (3). IV becomes ananchomer, *e.g.* exclusively equatorial, significantly more than the 80% for 2,2-dimethyl-1,3-dithiane-1-oxide as was deduced recently (8) from its dipole moment of 3.74 D.

The two oxathianesulfoxides (I and II) offer the first example in the six-ring sulfoxides for which it is possible to evaluate quantitatively the axial-SO-disfavouring effect of a syn-axial methyl group : this amounts 1.3 kcal/mole.

The preference for the axial position in I, which is even more pronounced than in thiane-1-oxide, is remarkable. If the axial isomer had the larger dipole moment (which can be predicted by comparison with the two *t*.butyldithiane-sulfoxides, vide supra), one would have expected an opposite order of axial preference on the basis of presumbly increased unfavourable dipolar effects in the axial form of I.

Rationalization of the above observations may probably be found in terms of "a balance between attractive and repulsive interactions" with a dynamic concept of the SO-bond as basis (1, 10); that means that it is able to adapt its stereoëlectronic features to those of the very molecule.

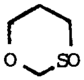
The conformations were distinguished, applying following criteria (1, 3, 9) (Table 1): the AB-quartet of the isomer with the oxide-group equatorial (lone pair axial) is characterized by (a) the smaller coupling constant (2J2), (b) the largest chemical-shift difference ($\Delta\nu 2$) and (c) the lowest field centerpoint ($\bar{\delta}_2$).

In order to obtain an independent confirmation of our assignments, we measured the benzene (ΔC_6H_6) and trifluoro-acetic acid (ΔTFA) solvent shifts versus chloroform at room temperature (RT) (1, 9). In table 2 the procedure is illustrated for the 1,3-dithiane-1-oxide case : C_6H_6 associates preferentially at the positively charged SO-sulfur, shielding the protons more remote from the oxygen atom (ΔC_6H_6 H2e = 0.725 > ΔC_6H_6 H2a = 0.58); TFA associates with the SO-oxygen by a hydrogen bond, deshielding the syn oxygen protons (/ΔTFA H2a / = 0.57 > / ΔTFA H2e / =

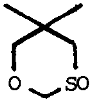
0.38). All results are in agreement with the above configurational conclusions, except in the case of 1 for which the equilibrium is very sensitive to temperature changes and shows a 1/1 distribution at RT.

Table I.

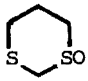
LT-analysis of the four sulfoxides.



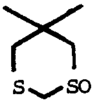
I



II



III



IV

	I SO_e		I SO_a	II SO_e		II SO_a
isomers %	16.5		83.5	89.5		10.5
T, $K^{(\bullet\bullet)}$, $-\Delta G$	-98°C, 5.17,		570 cal/mole	-102°C, 8.55,		730 cal/mole
δ H2e(ppm)	5.19		4.88	5.26		5.04
δ H2a(")	4.09		4.50	3.96		4.43
$\bar{\delta}_2$ (")	4.64	$<$	4.69	4.61	$<$	4.74
$\Delta\nu_2$(")	1.10	$>$	0.38	1.30	$>$	0.60
$[^2J_2]$(Hz)	9.5	$<$	12.2	9.5	$<$	12.8

	III SO_e		III SO_a	IV SO_e		IV SO_a
isomers %	84.6		15.4	> 95		
T,$K^{(\bullet\bullet)}$ $-\Delta G$	-92°C, 5.66,		630 cal/mole	-96°C		
δH2e (ppm)	4.08		3.91	4.07		
δH2a (")	3.70		3.73	3.49		
$\bar{\delta}_2$ (")	3.89	$>$	3.82	3.78		
$\Delta\nu_2$(")	0.38	$>$	0.18	0.58		
$[^2J_2]$(Hz)	12.4	$<$	15.5	$12.3^{(\bullet)}$		

$\bar{\delta}_2 = (\delta H2e + \delta H2a)/2$

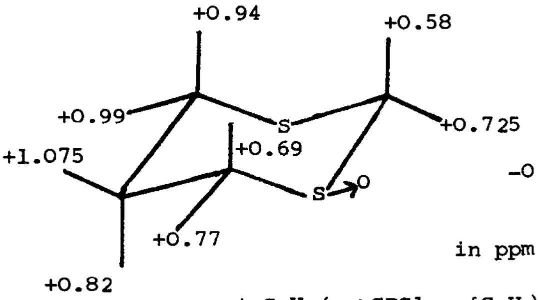
$\Delta\nu_2 = [\delta H2e - \delta H2a]$

(•) constant from -8°C → -96°C

(••) K taken always > 1

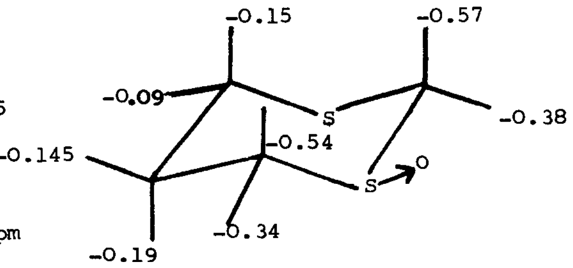
Table II.

ΔC_6H_6 and ΔTFA, RT-values of III. (abstracted from 300 MHz ^{1}H-NMR spectra)



in ppm

$\Delta\ C_6H_6 (= \delta CDCl_3 - \delta C_6H_6)$



Δ TFA(= $\delta CDCl_3 - \delta$ TFA)

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