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^{1}H NMR Analysis of 1,3,2-Oxadithiolan-2-oxide, 3-Phenyl-1,2,3-oxathiazolidin-2-oxide and 2,5-Dimethyl-1,2,5-thiadiazolidin-1-oxide

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Three analogues of ethylene sulfite, containing oxygen, sulfur or nitrogen as ring heteroatoms in positions 1 and 3 have been prepared, and their NMR data are reported and discussed. The NMR spectra of the compounds have been fully analysed on the basis of ABXY and $[AB]_2$ spin systems. Interpretation of the ^{1}H spectra of the compounds in this series suggests the existence of a single conformation for each of these compounds.

Recently NMR investigations on ethylene sulfite [1] and the various isomers of 4,5-dimethylethylene sulfite [2] have been reported. It is assumed that ethylene sulfites [1,2] exist in a twist-envelope conformation or pseudorotate between twist-envelope conformations with the S=O bond pseudoaxial. Various phosphorus-substituted 1,3,2-dioxaphospholanes [1,3] and 1,3,2-oxathiaphospholanes [4,5] have been carefully studied by NMR. A significant change in the conformation is found upon substitution of a ring oxygen atom in the dioxaphospholanes with a sulfur atom. In order to investigate the effect of ring heteroatoms other than oxygen in ring positions 1 and 3 of ethylene sulfite, the following molecules have been synthesized: 1,3,2-oxadithiolan-2-oxide (I), 3-phenyl-1,2,3-oxathiazolidin-2-oxide (II), and 2,5-dimethyl-1,2,5-thiadiazolidin-1-oxide (III).

EXPERIMENTAL

1,3,2-Oxadithiolan-2-oxide (I) was prepared from thionyl chloride and 2-hydroxy-ethanethiol in diethyl ether using triethylamine as base: b.p.$_{0.1}$ 58 °C; yield 30 %.

3-Phenyl-1,2,3-oxathiazolidin-2-oxide (II) was prepared from 2-phenylaminoethanol according to the method used for compound I; b.p.$_{0.5}$ 122 °C; yellow crystals, m.p. 34–35 °C; yield 45 %.

2,5-Dimethyl-1,2,5-thiadiazolidin-1-oxide (III) was prepared as above from *N,N'*-dimethylethylenediamine; b.p.$_{0.5}$ 52 °C; yield 10 %.

The spectra were recorded on 50 % solutions of compounds I–III in deuterioacetone, deuteriochloroform, or benzene in 5 mm O.D. NMR sample tubes, using a small amount of added TMS as reference and locking substance. The spectra were recorded on a JEOL JNM–C–60H NMR instrument, operating at 60 MHz in internal lock mode with frequency sweep. The spectra for the NMR analysis were obtained with a chart expansion of 1.2 Hz cm^{-1}. The line positions were taken as an average of several spectra, and are assumed to be correct to about 0.05 Hz. The computation was carried out using an UNIVAC 1110 computer and graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

The NMR spectra of compounds I and II consist of two regions with the separation between the two signal groups larger than any of the coupling constants involved.

The signals at the higher frequency (I and II) are assigned to the protons, A and B, at the carbon attached to the ring oxygen atom and the signals at lower frequency to the protons, X and Y, on the carbon adjacent to the sulfur (I) or the nitrogen (II) atom. The higher

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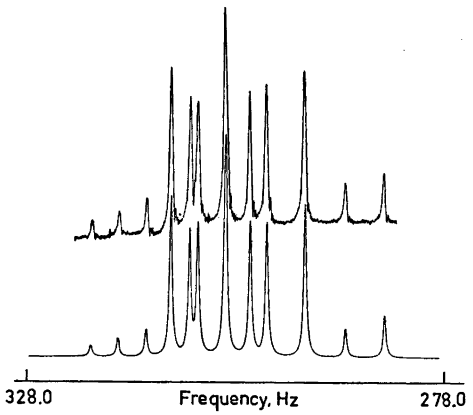


Fig. 1. 60 MHz spectrum of the AB protons in 2-oxo-1,3,2-oxathiasulfolane. Upper: Observed spectrum. Lower: Calculated spectrum.

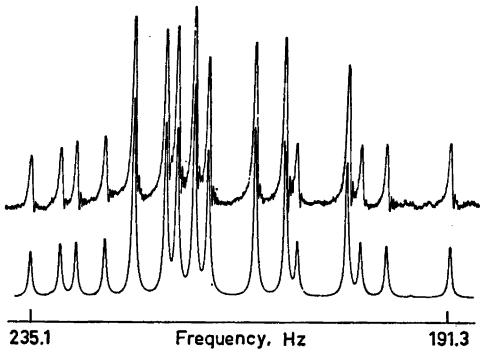


Fig. 2. 60 MHz spectrum of the XY protons in 2-oxo-1,3,2-oxathiasulfolane. Upper: Observed spectrum. Lower: Calculated spectrum.

frequency shift of the AB protons as compared to the XY protons is due to the larger deshielding effect of an adjacent ring oxygen atom as compared to a sulfur or a nitrogen atom.[11] The spectra of compounds I and II were analysed on the basis of an ABXY spin system,[6] and a good correlation between the theoretical and the experimental spectrum was obtained (Figs. 1 and 2). In the analysis of the proton signals in the spectrum of compound II, the protons of the phenyl group have been neglected since coupling to the protons of the parent ring is negligible. The spectrum of III consists of a symmetrical band of signals and can be fully analysed as an $[AB]_2$ spin system. The chemical shift difference between the A and B parts is larger when the compound is dissolved in benzene rather than in deuterioacetone.

The iterative computations for compounds I and II were performed using the computer programme LAOCN3,[7] while compound III was analysed with the aid of the computer programme LACX.[8] The spectral parameters are listed in Table 1. The final RMS values obtained were 0.06 Hz or less when all parameters were allowed to vary. The probable errors in the parameters were less than 0.02 Hz when 32 theoretical transitions were assigned to 29 observed lines for compounds I and II. The probable errors in the parameters of compound III are 0.2 Hz or less when 26 theoretical transitions are assigned.

DISCUSSION

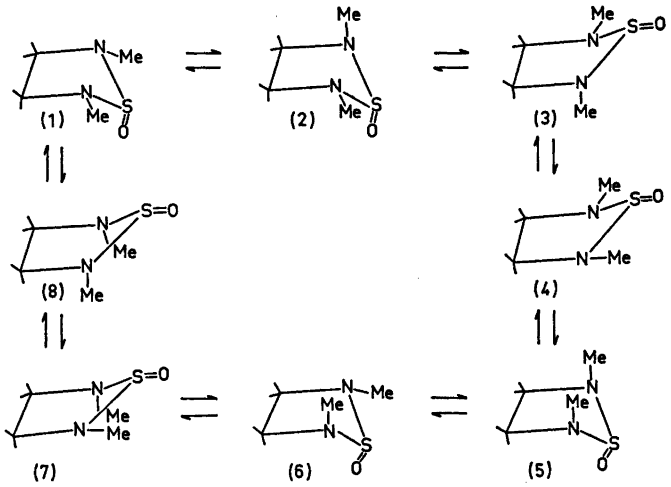
The detailed spectral analysis of compound III was carried out successfully on the basis of an $[AB]_2$ spin system. This implies that this five-membered ring (III) is; (a) planar, or (b) in an envelope form with the sulfur as the "flap" atom, or most likely (c) that intramolecular processes interconvert non-planar forms at a rate that is large on the NMR time scale, but that the inversion at sulfur is either slow on this time scale or does not occur.

The spectral analysis of compounds I and II were carried out on the basis of an ABXY spin system (Figs. 1 and 2). It is, however, not possible to be certain which intramolecular motion, if any, does occur for these compounds, I and II. All the coupling constants obtained are within the expected range for the various coupling paths. The geminal coupling constant of the CH_2-O moiety of compound I is more negative than in compounds II, III, and ethylene sulfite.[1] The values of the geminal coupling constant [9] of the CH_2-X group is sensitive to the electronegativity of X as well as the H–C–H angle. The change in electronegativity of substituents on the methylene group attached to the ring oxygen in compounds I, II, and ethylene sulfite, cannot account for the variation in J_{gem}, −9.71 Hz (I), −8.51 Hz (II), and −8.59 Hz (ethylene sulfite).[1] This change in J_{gem}, as regards I, might be due to different H–C–H angles of I as compared to II and ethylene sulfite. The magnitude of

Table 1. NMR parameters for the compound I, II, and III.[a]

	δ_A	δ_B	δ_X	δ_Y	$^2J_{AB}$	$^2J_{XY}$	$^3J_{AY}$	$^3J_{AX}$	$^3J_{BY}$	$^3J_{BX}$	$^3J_{AA'}$	$^3J_{BB'}$	$J_{AB'}$	Reference
I[h]	5.141	4.970	3.441	3.738	−9.71	−10.85	2.61	5.85	4.71	10.65				This work
II[h]	4.518	4.870	3.709	3.485	−8.51	−8.62	4.28	6.96	6.49	8.38				This work
2-*t*-Butyl-1,3-oxathiolane	4.330	3.643	2.903	2.809	−9.03	−9.76	2.21	5.77	5.02	9.92				Ref. 11
2-*t*-Butyl-2-methyl--1,3-oxathiolane	4.248	3.916	2.925	2.797	−9.06	−9.56	3.21	5.35	4.38	9.63				»
2-Ethyl-2-methyl 1,3-oxathiolane	4.109	4.030	2.969	2.951	−9.40	−9.86	4.08	6.47	6.02	7.18				»
2-Phenyl-1,3-oxathiolane	3.96	3.39	2.56	2.73	−8.59	−9.31	2.79	6.72	6.51	8.39				Ref. 17
III	3.37[b]		3.27[c]			−9.1[d,e]					8.8[e]	8.8[e]	5.9[e,f]	This work
	3.094[b]		2.842[c]			−8.72[d]					6.92	7.23	6.06[g]	

[a] Chemical shifts are ±0.005 p.p.m. Errors in coupling constants are ±0.05 Hz. [b] $\nu_A=\nu_{A'}$. [c] $\nu_B=\nu_{B'}$. [d] $J_{AB}=J_{A'B'}$. [e] Errors in coupling constants are ±0.1 Hz. [f] Deuterioacetone. [g] Benzene. [h] Deuteriochloroform.



Scheme 1.

^2J is, however, within the limits expected in 1,3-oxathiolanes.[10,11] The geminal coupling constants in II and III are better understood when compared with values obtained for 1,3-oxazolidines. The more the nitrogen lone pair bisects the X–C–Y angle, the more negative is the coupling constant.[12]

The inequality of $^3J_{AA'}$ and $^3J_{BB'}$ of compound III is of interest, since it appears to be detectable only when the compound is dissolved in benzene. This may be due to a long range effect of the lone pair of the sulfur atom and the nitrogen atom on ^3J.[12] It is, however, not possible at present to be certain which of these groups gives the major contribution to this inequality in ^3J. Moreover, a similar observation has been made by Haake *et al.*[1] on ethylenesulfite where $^3J_{AA'}$ and $^3J_{BB'}$ are equal when the compound is studied as neat liquid, whereas when it is dissolved in benzene, the two coupling constants are different.

Scheme 1 clearly indicates that in the present case it is not possible to neglect the possibility of nitrogen inversion in compounds II and III.[13,14] Forms with both N–Me groups pseudoaxial may be omitted. Enantiomers with the S=O bond and one N–Me group pseudoaxial and forms with a pseudoequatorial S=O bond may contribute appreciably. Accordingly, it is reasonable to expect that under certain conditions an $[AB]_2$ type spectrum is obtained for III where $^3J_{AA'} \neq {}^3J_{BB'}$.

Inversion at the sulfoxide sulfur atom is shown not to occur in the case of the cyclic trimethylene sulfites.[15,16] Accordingly it is not likely that such an inversion should occur in the compounds I, II, and III. Hence it is reasonable to assume that the S=O bond adopts only one position with respect to the ring. It has been suggested [1,2] for 1,3-dioxa-ring compounds that the high frequency resonance, A, is due to protons *cis* to the substituent at the heteroatom in ring position 2. It is not possible from the available data of compounds I, II, and III, to be certain whether the S=O bond adopts a pseudo axial or equatorial position. The swopping of chemical shifts for the A and B nuclei in compound II, relative to I, is not clearly understood, but it might indicate that the compounds exist in a fixed conformation. It is, however, not possible to arrive at any certain conclusion about the conformation from the available data (Table 1).

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