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The title compounds were prepared and their ^{13}C -nmr spectra were examined. On the basis of the data for the magnitudes of the γ shifts and the δ effects, four isomeric conformations of the compounds were discussed.

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In recent years, a number of conformational analyses of ethylene and trimethylene sulfites have been reported by means of ^{13}C -nmr spectroscopy. For example, Buchanan *et al.* (1) reported upfield shift of 9.1 ppm at C-4 and C-6 of the 4,6-dimethyl-1,3,2-dioxathiane 2-oxides with the axial S=O bond relative to those of the equatorial S=O function. They also pointed out that replacement of a syn-axial hydrogen by a methyl results in the loss of the major part of the γ shift in 4,4-dimethyl-6-methyl-1,3,2-dioxathiane 2-oxides.

With these findings as a background, it is interesting to obtain stereochemical information for the *cis* and *trans* 5-substituted 3-aryl-1,2,3-oxathiazolidine 2-oxides by means of ^{13}C -nmr spectroscopy.

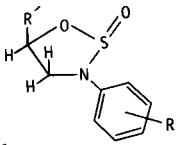
Chemical Shifts of C-4.

The ^{13}C -nmr spectral data for the materials examined as deuteriochloroform solutions are collected in Table 1. We

subdivided the compounds into four types, **a**, **b**, **c**, and **d** as can be seen in Table 1. The *cis* and *trans* isomers without substituents and with *meta* or *para* substituents are designated as the suffix **a** and **b**, respectively, and the isomers with an *ortho*-substituent are the suffix **c** and **d**. For compounds of 3-aryl-5-methyl-1,2,3-oxathiazolidine 2-oxides, the C-4 chemical shifts (mean value) of types **a** and **b** are 50.72 ± 0.05 and 52.82 ± 0.04 ppm, whereas types **c** and **d** are 52.95 ± 0.24 and 54.55 ± 0.24 ppm, respectively.

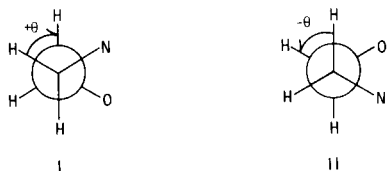
In ^1H -nmr studies at room and low temperatures over a range of 110° on the 3-aryl-1,2,3-oxathiazolidine 2-oxides (2,3), we reported that the oxathiazolidine 2-oxide ring tends to form twist-envelope conformations, that their torsional angles (θ) vary with both the position and the nature of the benzene ring substituent, and that the distortions of the oxathiazolidine ring of the compounds with *meta*- or

Table 1
Carbon-13 Chemical Shifts (δ) of 5-Substituted 3-Aryl-1,2,3-oxathiazolidine 2-Oxides

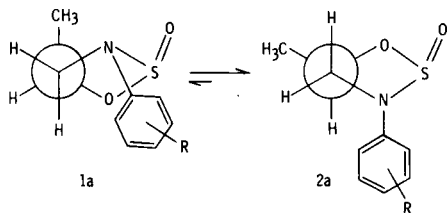


R'	R	Type	Chemical Shifts		R'	Type	Chemical Shifts		R'
			C-4	<i>cis</i> C-5			C-4	<i>trans</i> C-5	
CH ₃	H	a	50.6	83.7	21.0	b	52.7	79.3	18.0
CH ₃	<i>o</i> -CH ₃	c	53.3	82.8	20.2	d	54.9	79.8	19.5
CH ₃	<i>m</i> -CH ₃	a	50.6	83.6	20.9	b	52.7	79.1	18.0
CH ₃	<i>p</i> -CH ₃	a	51.0	83.6	20.9	b	52.9	79.3	18.1
CH ₃	<i>o</i> -Cl	c	52.6	82.8	20.2	d	54.2	80.0	19.3
CH ₃	<i>m</i> -Cl	a	50.6	84.1	21.1	b	52.8	79.5	18.0
CH ₃	<i>p</i> -Cl	a	50.8	83.9	21.0	b	53.0	79.6	18.1
C ₂ H ₅	H	a	48.8	88.9	28.2 9.7	b	50.9	84.3	25.7 9.7
C ₂ H ₅	<i>o</i> -CH ₃	c	51.6	87.9	27.8 9.7	d	53.2	84.8	27.0 9.7
C ₂ H ₅	<i>m</i> -CH ₃	a	48.8	88.7	28.0 9.7	b	50.9	84.1	25.7 9.7
C ₂ H ₅	<i>p</i> -CH ₃	a	49.2	88.7	28.2 9.8	b	51.2	84.2	26.0 9.8
C ₂ H ₅	<i>o</i> -Cl	c	50.8	87.8	27.6 9.7	d	52.4	84.8	26.7 9.7
C ₂ H ₅	<i>m</i> -Cl	a	48.8	89.2	28.3 9.8	b	51.0	84.5	25.8 9.8
C ₂ H ₅	<i>p</i> -Cl	a	49.0	89.1	28.2 9.8	b	51.1	84.5	25.8 9.8

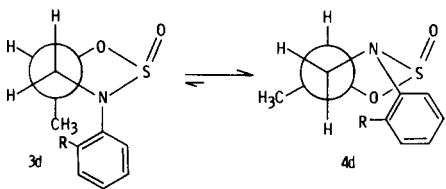
para-substituents and without a substituent are in the direction of the I projection, while those with an *ortho*-substituent cause a distortion toward the II projection, as can be seen in the following diagram.



If these conformations can be applied to the present compounds, the following considerations are possible. For the *cis* **a**, with a *meta*- or *para*-substituent and without a substituent, there will be repulsive van der Waals interaction about 4.6 KJ/mole between the syn-axial methyl group and the S=O function (4) in **1a** which will force the conformational equilibrium toward **2a**. Also gauche methyl and N interaction will destabilize **1a** (5). In the *trans* **d** which has an *ortho*-substituent, there is steric

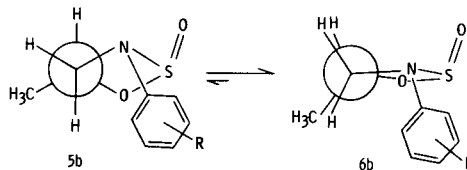


repulsion between the methyl group and the *ortho*-substituent in **3d**. Consequently, the preferred conformation of **d** should be **4d** in which the methyl is essentially equatorial and the hydrogen atom on C-5 is axial. The shift differences of C-4 for **a** and **d** are consistent with these conformational arguments. The relationship between the C-4 and the sulfoxide oxygen in **2a** is gauche, whereas the same relationship in **4d** is not gauche. That is, the upfield shift of 3.9 ppm at C-4 in **2a** relative to **4d** is due to the gauche γ relationship between the axial sulfoxide oxygen and the C-4 ring carbon in **2a**. Such effects are well documented in chair conformers of thiane oxides (6) and methylated sulfites (1).

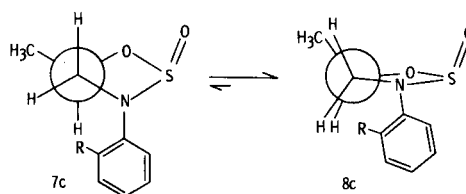


In the case of *trans* **b**, there is no apparent reason to disfavor the gauche conformer. But, the chemical shift of C-4 appeared at an intermediate value between **a** and **d**. From the result of the ^{13}C -nmr data, it can be considered that geometry of **b** between the C-4 carbon and the sulfoxide

oxygen may assume intermediate geometry between **2a** and **4d**, namely, an eclipsed conformation **6b**.



For the *cis* **c** which has an *ortho*-substituent, there is minor steric repulsion between the axial hydrogen on C-5 and the *ortho*-substituent compared with the compound **d**. The chemical shift of C-4 appeared at an intermediate value between **a** and **d**. Therefore, it can be considered that the geometry of **c** between the C-4 carbon and the sulfoxide oxygen may assume intermediate geometry between **2a** and **4d**. From these arguments, the preferred conformation is assumed to approach the eclipsed conformation **8c**.



Chemical Shifts of C-5.

For 3-aryl-5-methyl-1,2,3-oxathiazolidine 2-oxides, the C-5 chemical shifts (mean value) of types **a** and **c** appeared at around 83.5 ppm, whereas those of types **b** and **d** at 79.5 ppm. The upfield shift of 4 ppm at C-5 of types **b** and **d** relative to those of types **a** and **c** is due to the gauche γ relationship between the sulfoxide oxygen and the C-5 ring carbon in **b** and **d**.

Chemical Shifts of the Methyl Carbon on C-5.

The conformational argument between types **a**, **b**, **c**, and **d** is also demonstrated by the shielding shift data due to the δ effect. The chemical shifts (mean value) of types **a** and **c** of 3-aryl-5-methyl-1,2,3-oxathiazolidine 2-oxides are 20.7 ppm, whereas the chemical shifts of types **b** and **d** are 18.4 ppm.

For a sterically interacting δ -methyl group, it has recently been found that appreciable deshielding effects are operative (7). For example, Buchanan *et al.* (1,8) reported the δ effect in 4,6-dimethyl-1,3,2-dioxathiane 2-oxide with an axial S=O bond. The 21.0 ppm shielding for methyl on C-4 indicates an equatorial orientation but the axial methyl on C-6 appears at lower field at 22.4 ppm.

For this reason, the *cis* methyl for **2a** and **8c** appeared at lower field (about 2.3 ppm) than those for *trans* methyl **4d** and **6b**.

The similar γ and δ effects were also observed for 5-ethyl-substituted compounds as can be seen in Table 1.

EXPERIMENTAL

The ^{13}C -nmr chemical shifts were determined in a similar manner to that reported previously (9). The preparations and the physical properties of 3-aryl-5-methyl-1,2,3-oxathiazolidine 2-oxides have been reported in an earlier paper (10). 3-Aryl-5-ethyl-1,2,3-oxathiazolidine 2-oxides were obtained in a similar manner to that of 5-methyl substituted compounds and the structure is supported by analytical and spectral data.

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