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Steric Effects on Carbon-13 Chemical Shifts in 3-Aryl-1,2,3-oxathiazolidine 2-Oxides

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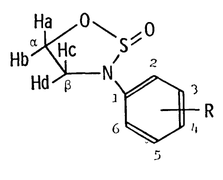
Synopsis. The carbon-13 NMR spectra of 3-aryl-1,2,3-oxathiazolidine 2-oxides were obtained and discussed. Some of the carbon shifts are greatly influenced by the conformation of the oxathiazolidine ring.

In a previous paper,[1] we reported the conformations of a series of 3-aryl-1,2,3-oxathiazolidine 2-oxides (**1**) as determined by means of their ^{1}H-NMR spectra. In continuation of our studies concerning the steric structure of **1**, this paper will describe the relationships between their carbon-13 NMR spectra and the conformational structures of the oxathiazolidines.[1]



1

I, R=H
IIa, R=*o*-CH_3
IIb, R=*m*-CH_3
IIc, R=*p*-CH_3
IIIa, R=*o*-OCH_3
IIIc, R=*p*-OCH_3
IV, R=*p*-Br
Va, R=*o*-Cl
Vb, R=*m*-Cl
Vc, R=*p*-Cl

Experimental

Measurements. The ^{13}C-NMR spectra were obtained using a JNM-PS-100/EC-100 spectrometer equipped with a Fourier transform recorder at 25.15 MHz under a complete proton decoupling. The pulse width and repetition time were 10.2 μs and 6 s respectively. The spectral width and data points were 6250 Hz and 8191 respectively. The chemical shifts were reported in ppm downfield from the internal TMS, using deuteriochloroform.

Compounds. The preparations and the physical properties of **1** were reported in a previous paper by the present authors.[2,3]

Results and Discussion

Carbon-13 NMR measurements were made on the above 10 compounds. The carbons in the oxathiazolidine ring are represented by the notations of C-α and C-β respectively, and those in the benzene ring, by C-1—C-6, as is shown in the above diagram. The assignments of the carbons were made on the basis of (1) the relative signal intensity, (2) the off-resonance decoupling technique, and (3) the predicted chemical shifts obtained by the aid of the additivity rule.[4]

As can be seen in Table 1, the C-α signals appeared at around 70 ppm, whereas the C-β appeared at 46—49 ppm. The observed shifts from C-1 to C-6 were in close agreement with the predicted values for the compounds with an *m*- or *p*-substituent except for the case of IIIc. On the other hand, the shifts of C-1, C-2, and C-6 for the compounds with an *o*-substituent deviated from the predicted ones. In IIIa, the C-3 signal is shifted upfield compared with the predicted one (−3.1 ppm). This fact is considered to be a steric shift caused by the preferred conformation of the terminal CH_3 of the OCH_3 group being turned away from the C-1 and being now close to C-3.[5]

Table 2 shows the values obtained by subtracting the substituent parameters (S.P.) from the observed

TABLE 1. ^{13}C CHEMICAL SHIFTS (ppm) OF 3-ARYL-1,2,3-OXATHIAZOLIDINE 2-OXIDES

Compd No.	C-α	C-β	C-1	C-2	C-3	C-4	C-5	C-6	CH_3 or OCH_3
I	70.9	45.9	140.7	116.5	129.8	122.7	129.8	116.5	—
IIa	70.9	48.2	137.2 (141.4)	135.3 (125.4)	131.0 (130.5)	126.7 (122.6)	126.7 (126.9)	125.0 (116.4)[a]	18.2
IIb	70.6	46.1	140.2 (140.6)	117.5 (117.2)	139.7 (138.7)	123.8 (123.4)	129.5 (129.7)	113.9 (113.6)	21.5
IIc	70.4	46.1	137.7 (137.8)	117.2 (116.4)	129.9 (130.5)	132.3 (131.6)	129.9 (130.5)	117.2 (116.4)	20.4
IIIa	69.5	45.8	130.0 (126.1)	150.4 (147.7)	112.0 (115.1)	124.3 (123.4)	121.4 (121.8)	119.6 (117.3)	55.7
IIIc	71.0	46.9	132.9 (133.0)	120.4 (117.5)	114.9 (115.4)	156.4 (154.1)	114.9 (115.4)	120.4 (117.5)	55.5
IV	71.1	46.4	140.0 (139.1)	118.3 (118.2)	132.7 (133.2)	115.3 (117.2)	132.7 (133.2)	118.3 (118.2)	—
Va	71.4	47.4	143.5 (141.2)	136.7 (122.7)	130.6 (130.2)	127.5 (124.0)	128.0 (127.9)	125.8 (117.7)	—
Vb	70.9	46.1	141.9 (142.0)	116.1 (116.9)	135.2 (136.0)	122.4 (123.2)	130.8 (131.2)	114.5 (114.6)	—
Vc	71.1	46.4	139.5 (138.8)	118.0 (117.8)	129.7 (130.2)	127.9 (128.9)	129.7 (130.2)	118.0 (117.8)	—

a) Calcd value.

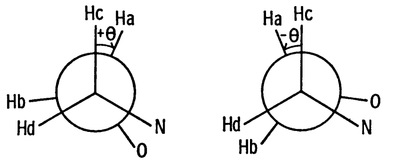
Table 2. Chemical shifts differences $\Delta = \delta_{obsd} - S.P.$

Compd No.	C-1	C-2	C-3	C-4	C-5	C-6	Torsion[a] angle θ
I	140.7	116.5	129.8	122.7	129.8	116.5	15
IIa	136.5	126.4	130.3	126.8	129.6	125.1	−11
IIb	140.3	116.8	130.8	123.1	129.6	116.8	12
IIc	140.6	117.3	129.2	123.4	129.2	117.3	11
IIIa	144.4	119.0	126.4	123.3	129.1	118.6	−5
IIIc	140.6	119.4	129.3	125.0	129.3	119.4	4
IV	141.6	116.6	129.3	120.8	129.3	116.6	14
Va	143.1	130.5	130.2	126.2	129.9	124.5	−11
Vb	140.6	115.7	129.0	122.0	129.5	116.4	15
Vc	141.4	116.7	129.3	121.7	129.3	116.7	12

a) These values are taken from Ref. 1.

values. Consequently, these values show mainly the effects of the oxathiazolidine ring on the shifts of the benzene-ring carbons. From the data of I, the substituent parameters of the oxathiazolidine ring can be obtained as follows: +12.2 for C-1, −12.0 for *ortho*, +1.3 for *meta*, and −4.8 for *para* carbons. In the compounds with an *m*- or *p*-substituent, the individual carbon shifts come close to those of I, and the electronic effects of the substituent may contribute greatly to the shifts of benzene carbons. In these cases, there is no steric hindrance between either benzene or oxathiazolidine rings. In IIa, IIIa, and Va, the shifts of C-1, C-2, and C-6 deviate greatly from those of I.

In a previous paper,[1] we reported that the oxathiazolidine rings tend to form twist-envelope conformations, that their torsion angles with both the position and the nature of the ring substituent, and that the distortions of the oxathiazolidine ring of the compounds with *m*- and *p*-substituents are in the direction of the **2** projection, while those with an *o*-substituent cause a distortion toward the **3** projection, as can be seen in the following diagram. The values of the torsion angles are listed in Table 2.



2 **3**

θ: Torsion angle

In order to obtain further information about the conformational influence of the oxathiazolidine ring on the shifts of benzene-ring carbons, an attempt was made to plot the shifts of the ring carbons against their torsion angles.

As can be seen in Fig. 1, all the shifts of C-1 in the cases of the *m*- and *p*-substituents appeared at about 141 ppm, regardless of the torsion angle, while that of IIa appeared upfield about 4.5 ppm, and those of IIIa and Va shifted downfield about 3.4 and 2.1 ppm respectively. In IIa, the preferred comformation of the oxathiazolidine ring may be considered, from the evidence of the upfield shifts for both C-1 and methyl carbon (Table 1), that in which the lone pair of electrons on nitrogen is located close to the *o*-substituted methyl group. In the case of IIIa or Va, the lone pair of nitrogen was turned away from the *o*-substituent. On the other hand, two kinds of good linear correlations are obtained in the cases of C-2 and C-6. The left line is due to the data of the compounds bearing an *o*-substituent (Projection **3**), while the right line is due to those bearing an *m*- or *p*-substituent (Projection **2**). From the slopes of these lines, the effects on the chemical shifts of the *o*-substituent are larger than those of the other conformation.

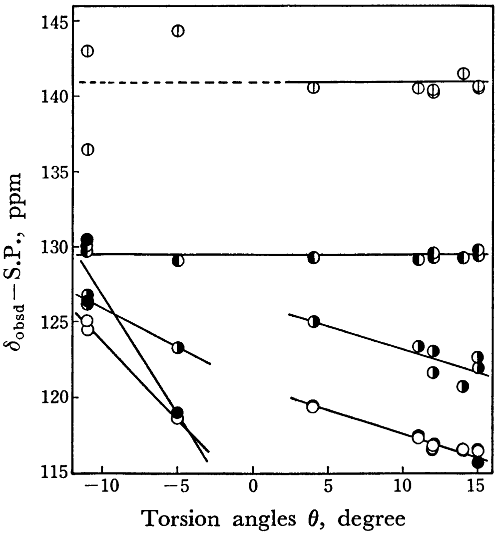


Fig. 1. Plots of the chemical shifts of benzene ring carbons *vs*. torsion angles.

⦶: C-1, ●: C-2, ◐: C-3, C-5, ◑: C-4, ○: C-6.

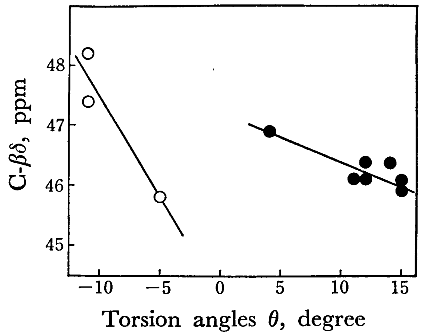


Fig. 2. Plots of the chemical shifts of C-*β* *vs*. torsion angles.

○: The compound bearing an *o*-substituent,

●: *m*-, or *p*-substituent.

The correlation of the chemical shifts of C-*β* *versus* their torsion angles is shown in Fig. 2. The effects on the chemical shifts of the *o*-substituent are shown to be larger than that of the *m*- or *p*-substituent, just as in Fig. 1.

References

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