Low-temperature NMR Studies of the Conformations of 3-Aryl-1,2,3-oxathiazolidine 2-Oxides

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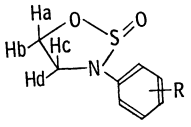
A complete iterative NMR spectral analysis has been carried out for twelve 3-aryl-1,2,3-oxathiazolidine 2-oxides at several low temperatures over a range of 111 °C. The magnitudes of the two vicinal coupling constants either increased or decreased markedly with a decrease in the temperature. On the basis of the resulting vicinal coupling constants, the correlations between the ratios of the vicinal coupling constants and the corresponding torsion angles were obtained and made it possible to assign their twist-envelope conformations. From the experimental data, the parameters of the Karplus equation could be given:

$$J\,\mathrm{vic} = 5.3 - \cos(135\pm\theta) + 4.3\cos 2(135\pm\theta)$$
$$+45° \geq \theta \geq -45°$$

In a previous paper of this series, the twist-envelope conformations have been assigned to the oxathiazolidine ring of 3-aryl-1,2,3-oxathiazolidine 2-oxides (**1**) on the basis of the vicinal coupling constants at room temperature.[1] These assignments are consistent with the results of the solvent-shift determinations.

The present study was initiated in order to examine the NMR spectral data at several low temperatures for the following compounds:



1

I, R=H	IIIc, R=*p*-OCH_3
IIa, R=*o*-CH_3	IV, R=*p*-Br
IIb, R=*m*-CH_3	Va, R=*o*-Cl
IIc, R=*p*-CH_3	Vb, R=*m*-Cl
IIIa, R=*o*-OCH_3	Vc, R=*p*-Cl
IIIb, R=*m*-OCH_3	VI, R=2,4,6-tri-Cl

Experimental

Compounds. A series of **1** compounds was prepared and was then purified by a previously reported method.[2,3] The reaction conditions and the physical properties of **1** were reported in our previous paper.[1]

NMR Spectral Determination. All the NMR spectra were recorded at 100 MHz on a Japan Electron Optics Model JNM-PS-100 spectrometer equipped with a Japan Electron Optics Model JNM-VT-3C variable-temperature controller, using acetone-d_6 as the solvent (0.5 mmol/ml). The probe temperature was measured both with a thermocouple and by the peak separation of a calibrated methyl alcohol sample; it is considered accurate to ±2 °C. The chemical shifts were reported in ppm downfield from the internal TMS. The details of the analyses and the stereochemical assignments were also provided in the previous paper.[1]

Results and Discussion

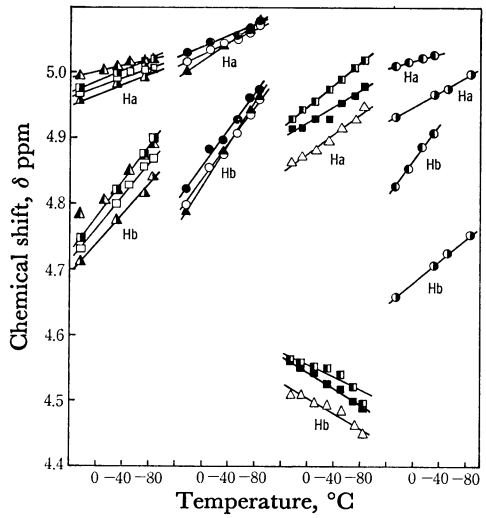
Spectra at Low Temperatures in an Acetone-d_6 *Solution.* Table 1 shows the NMR spectral data for the methylene protons of the **1** compounds at room temperature. Insignificant variations are observed in the NMR parameters in acetone-d_6 solutions relative to those in CCl_4 or $CDCl_3$–CCl_4 solutions at room temperature.[1] In this study, the shapes of all the NMR signals at several low temperatures over a range of 111 °C are quite similar. That is, cooling a sealed NMR tube containing one of the **1** compounds in acetone-d_6 at temperatures down to −85 °C (with the exception of the VI compound) produced no major change in the signals.

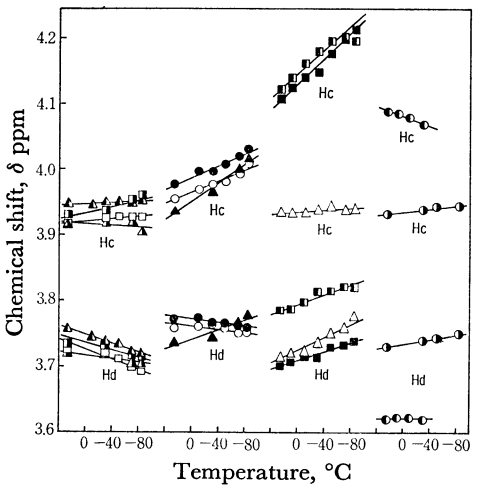
TABLE 1. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THE METHYLENE PROTONS OF THE **1** COMPOUNDS, IN ACETONE-d_6 AT 26 °C

Compd.	Chemical shifts, δ ppm				Geminal, Hz		Vicinal, Hz				r	θ
	H_a	H_b	H_c	H_d	J_{ab}	J_{cd}	J_{ac}	J_{bd}	J_{ad}	J_{bc}	J_{ad}/J_{bc}	(degree)
I	4.995	4.784	3.949	3.755	8.4	8.9	6.4	6.7	8.4	4.5	1.87	12.0
IIa	4.915	4.560	4.108	3.702	8.0	9.3	6.9	6.6	4.4	7.9	1.80[a]	−11.3
IIb	4.968	4.732	3.919	3.722	8.5	8.9	6.4	6.8	8.3	4.4	1.89	12.2
IIc	4.958	4.713	3.916	3.722	8.3	8.9	6.5	6.9	7.8	4.9	1.59	9.0
IIIa	4.864	4.508	3.936	3.713	8.3	9.1	6.9	7.1	5.1	7.0	1.37[a]	−6.2
IIIb	4.975	4.747	3.927	3.733	8.6	9.0	6.4	6.7	8.5	4.3	1.98	13.1
IIIc	4.935	4.660	3.934	3.731	8.3	9.0	6.4	6.6	7.0	5.7	1.23	4.0
IV	5.005	4.790	3.937	3.737	8.4	8.9	6.3	6.8	8.6	4.2	2.05	13.8
Va	4.930	4.563	4.123	3.785	7.9	9.3	6.9	6.7	4.2	8.3	1.98[a]	−13.1
Vb	5.031	4.824	3.975	3.772	8.5	8.8	6.3	6.8	8.8	4.0	2.20	15.2
Vc	5.016	4.800	3.955	3.758	8.4	8.8	6.3	6.8	8.5	4.3	2.00	13.5
VI	5.013	4.829	4.092	3.621	8.6	8.6	5.8	6.9	10.3	2.3	4.48	28.6

a) Values for J_{bc}/J_{ad}

Chemical Shifts. The chemical shifts for the methylene protons, H_a, H_b, H_c, and H_d, at several low temperatures are shown in Figs. 1-a and 1-b. From these observations, it is clear that the chemical shifts of the methylene protons of the **1** compounds are dependent on the temperatures, moving either to a lower or a higher field with a decrease in the temperature.





Figs. 1-a and 1-b. Temperature-dependence of the chemical shifts of the methylene protons of the **1** compounds.
Group 1a ◭, I; □, IIb; ◭, IIc; ◨, IIIb
Group 1b ▲, IV; ●, Vb; ○, Vc
Group 2 ■, IIa; △, IIIa; ◧, Va
Group 3, 4 ◑, IIIc; ◐, VI

In the previous paper,[1] we proposed that the conformations of the **1** compounds could be divided roughly into several groups on the basis of their well-defined patterns of the appearance of the methylene-proton signals, the ratios (r values) of the vicinal coupling constants (that is, J_{ad}/J_{bc} or J_{bc}/J_{ad}), their torsion angles, and the data of the solvent-shift studies in benzene (Table 2). In this present study, the characteristic properties of these groups are reflected in the temperature-dependence of their methylene-proton chemical shifts. In particular, with a decrease in the temperature the H_b proton shifts of the IIa, IIIa, and Va compounds in Group 2 move markedly toward a higher field in comparison with those of other H_b protons. This interesting feature may be caused by the presence of an *o*-substituent.

TABLE 2. CLASSIFICATION OF THE CONFORMATIONS OF THE **1** COMPOUNDS

Group		R	r value	θ°
1	1a	H, *m*-CH_3, *p*-CH_3, *m*-OCH_3	1.59—1.89[a] (1.8—2.2)[b]	9.0—13.1 (11—15)
	1b	*p*-Br, *m*-Cl, *p*-Cl	2.00—2.20 (1.9—2.2)	13.5—15.2 (12—15)
2		*o*-CH_3, *o*-OCH_3, *o*-Cl	1.37—1.98 (1.3—1.8)	−6.2——13.1 (−5——11)
3		*o*-OCH_3, *p*-OCH_3	1.23—1.37 (1.2—1.3)	−6.2—+4.0 (−5—+4)
4		tri-Cl	4.48 (4.7)	28.6 (≥30)

a) The values in upper line are obtained in this study.
b) The values obtained in the previous paper[1] are shown in parentheses.

Geminal Coupling. Two geminal coupling constants of the **1** compounds have been determined in this study; they were found not to vary significantly in the temperature range of 111 °C. This phenomenon means that the angle of neither H_a–C_5–H_b nor H_c–C_4–H_d changes, not even at low temperatures.

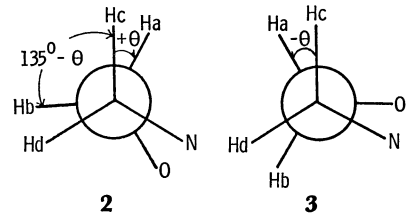
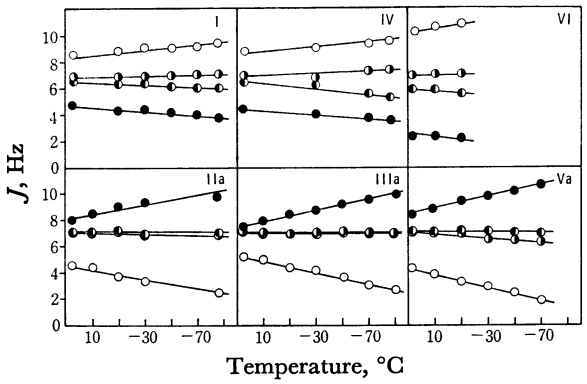
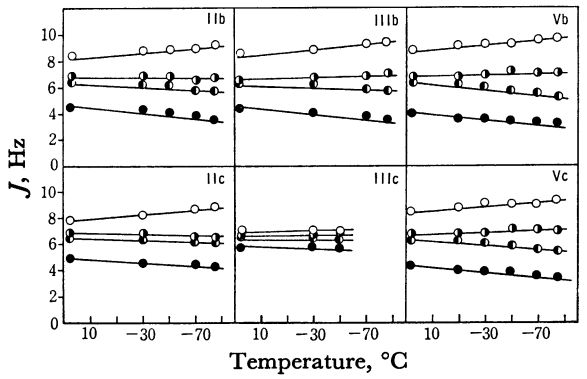


Fig. 2. Diagrams of **2** and **3** forms of the parts of methylene protons of **1**.
Dihedral angle (ϕ) = 135 °± Torsion angle (θ).

Vicinal Coupling. As has been discussed in our previous study,[1] the vicinal coupling data for the four methylene protons of the **1** compounds corroborate the explanations that the distortions of the compounds with an *m*- or *p*-substituent are in the direction of the **2** projection (in Fig. 2), while those with an *o*-substituent cause distortion toward the **3** projection. Furthermore, the r values, J_{ad}/J_{bc} for the **2** projection and J_{bc}/J_{ad} for the **3** projection, have been found to be nearly independent of the electronegativity of the substituent and of other factors, and to be dependent only on each dihedral angle. It was, therefore, possible to determine the conformational effects by means of the r value.

Figures 3-a and 3-b show the vicinal coupling constants, J_{ad}, J_{bd}, J_{ac}, and J_{bc}, of the **1** compounds at various low temperatures. The value of J_{ad} or J_{bc} increased with a decrease in the temperature, whereas J_{bc} or J_{ad} decreased with a decrease in the temperature. These figures clearly show that the values of J_{ad} and J_{bc} of the **1** compounds change almost linearly with the temperatures in the range from 26 to −85 °C. When the two straight lines for J_{ad} and J_{bc} are extended, the





Figs. 3-a and 3-b. Vicinal coupling constants of the **1** compounds at various temperatures.
○, J_{ad}; ◑, J_{bd}; ◐, J_{ac}; ●, J_{bc}

two lines intersect around 6.3, are symmetrical with respect to the line which is parallel with the x-axis, and pass through the point of 6.3 on the y-axis. That is, the average value of J_{ad} and J_{bc} obtained from the experimental data (118 pieces) of all the **1** compounds is 6.331. The results indicate that, at each intersection point, the values of both J_{ad} and J_{bc} are the same and are very close to 6.3 Hz; therefore, their r value becomes 1.000.

In the case of the well-known Karplus equation ($90 \leq \theta \leq 180°$), the curve passes through the inflection point at 135°.[4] From our results presented above that the increasing and decreasing straight lines are symmetrical and show the same gradient, it is possible to get a rough idea of the value of the projection angle of a CH_2 group—that is, the angles of H_a–C_5–H_b and H_c–C_4–H_d. (Fig. 2). We therefore suggest that, in the case of the oxathiazolidine ring, the projection angle is no longer 120°, but is close to the value of 135°, corresponding to the above inflection point.

On the other hand, the projection angle of a CH_2 group in the five-membered rings, must be larger than the 120° in the six-membered rings. At present, it is not possible to obtain an accurate value of the projection angle in the five-membered rings. However, it was necessary to estimate the size of this angle. Usually the value of 120° in the six-membered rings has been used for the calculation of Karplus-type equations of the five-membered rings.[1,5-7]

On the basis of the above observations and the results of the previous investigation,[1] we may set the following parameters of the Karplus equation by means of a "trial

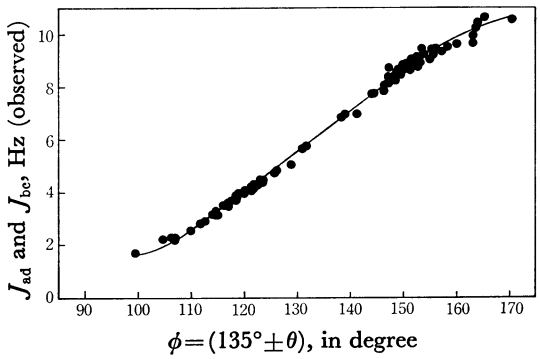
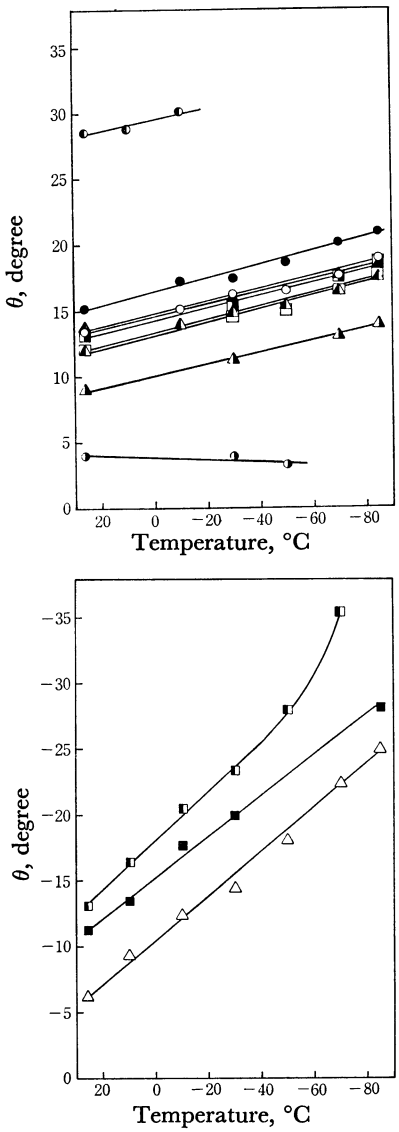


Fig. 4. Plots of the observed vicinal coupling constants, J_{ad} and J_{bc}, of all the **1** compounds at various temperatures *vs.* the dihedral angles.
——, Calculated curves by Karplus eq.
●, J_{ad} or J_{bc}; number of dots in this figure is 118 pieces.



Figs. 5-a and 5-b. Temperature dependence of the torsion angles of the **1** compounds.
Group 1a: ▲, I; □, IIb; ▲, IIc; ◨, IIIb
Group 1b: ▲, IV; ●, Vb; ○, Vc
Group 2: ■, IIa; △, IIIa; ◧, Va
Group 3: ◑, IIIc
Group 4: ◐, VI

and error" procedure;

$$r = (J_{ad}/J_{bc}) \text{ or } (J_{bc}/J_{ad})$$
$$= \frac{5.3-\cos(135+\theta)+4.3\cos 2(135+\theta)}{5.3-\cos(135-\theta)+4.3\cos 2(135-\theta)}$$
$$+45^\circ \geq \theta \geq -45^\circ$$

After setting the above parameters, we evaluated the correlation among the θ, J, and r values. Then, the torsion angles can be obtained from the observed values of J_{ad} and J_{bc} by using this relation. Figure 4 shows the plots of the observed vicinal coupling constants, J_{ad} and J_{bc}, of all the **1** compounds at various low temperatures *vs.* the dihedral angles obtained by means of the above procedure. The experimental data clearly fall on the calculated Karplus curve for the above parameters.

Torsion Angles at Low Temperatures. The torsion angles of the **1** compounds at 26 °C are shown in Table 1. Figures 5-a and 5-b show the data at various low temperatures. The values of θ increased with the decrease in the temperature, except in the IIIc compound. As can be seen in these figures, the compounds belonging each group show a similar tendency toward increasing the torsion angle. These findings indicate that each group shows a sterically different feature.

References

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