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

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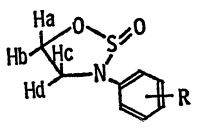
Proton magnetic resonance spectroscopy has been used to investigate the conformations of a series of 3-aryl-1,2,3-oxathiazolidine 2-oxides. Their conformations were assigned on the basis of the vicinal coupling constants between four methylene protons at the C-4 and C-5 positions. The oxathiazolidine 2-oxides prefer twist-envelope forms, and their conformations vary with both the situation and the nature of the ring substituent. Postulated collision complexes based on the data of the observed solvent-shifts can also be explained in terms of the differences in the conformations.

Recently, considerable attention has been directed to the elucidation of the conformations of heterocyclic compounds by NMR spectroscopy. However, only a few studies have been reported on the stereochemistry of the 1,2,3-oxathiazolidine 2-oxides. For example, Deyrup and Moyer reported that the sulfoxide bond was known to have an acetylenic-like anisotropy and that, therefore, the NMR spectra of the two isomeric 4- or 5-substituted 3-*t*-butyl-1,2,3-oxathiazolidine 2-oxides permitted the assignment of *cis* and *trans* geometry.[1] On the other hand, we ourselves have reported that twelve new 3-aryl-5-methyl- and 3-aryl-5-chloromethyl-1,2,3-oxathiazolidine 2-oxides have been prepared in good yields, and the configurations of their stereoisomers have been discussed on the basis of the NMR spectral data.[2] In continuation of our previous reports concerning the formation of 3-aryl-1,2,3-oxathiazolidine 2-oxides and their NMR and mass spectra,[3,4] this paper will report the results of NMR analyses of a series of 3-aryl-1,2,3-oxathiazolidine 2-oxides (**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
IIIb, R=*m*-OCH_3
IIIc, R=*p*-OCH_3
IV, R=*p*-Br
Va, R=*o*-Cl
Vb, R=*m*-Cl
Vc, R=*p*-Cl
VI, R=2,4,6-tri-Cl

Experimental

Measurements. All the boiling and melting points are uncorrected. All the NMR spectra were determined at 100- and 60-MHz with Japan Electron Optics Model JNM-PS-100 and JNM-3H-60 spectrometers respectively. The chemical shifts were reported in ppm downfield from the internal TMS (δ). The coupling constants were determined from the spectra with a 270 Hz sweep width and a sweep time of 0.5—1.0 Hz/s. The IR spectra were recorded on a Shimadzu Model 27-G grating spectrophotometer on a KBr disk for the solid materials or a NaCl plate for the liquid materials. The glc analysis was carried out on a Shimadzu gas chromatograph, Model GC-5AP$_3$T, using a 2.15-m column packed with silicone SE-30 (10 wt%). The percentage composition of the product was estimated by means of the relative peak areas (uncorrected).

Compounds. A series of **1** was prepared by the reaction of the corresponding *N*-sulfinylanilines with ethylene oxide in the presence of lithium chloride as a catalyst, and was purified by distillation or recrystallization, as has been described in our previous papers.[2,3] The above reaction conditions and the properties of the compounds thereby obtained are listed in Table 1.

Results and Discussion

Sulfoxide Bond. The IR spectra of all the **1** compounds showed a characteristic band of the S=O group at 1155—1172 cm^{-1} (Table 1). In trimethylene sulfites, the S=O group prefers to be axial,[5] and the same conformational preference is found in six-membered ring sulfoxides.[6,7] The assignment of the axial and equatorial S=O groups has been made on the basis of the positions of the S=O stretching bands in trimethylene sulfites: 1190 cm^{-1} for an axial oxygen and 1230 cm^{-1} for an equatorial oxygen. In the case of ethylene sulfite, the position of the S=O stretching band 1193 cm^{-1} (neat) to 1214 cm^{-1} (cyclohexane) indicates a predominance of pseudoaxial conformers.[8] If this consideration can be extended to the **1** compounds, and assuming an equilibrium between pseudoaxial and pseudoequatorial conformers, the position of the S=O stretching bands of **1**, 1172 (neat) to 1182 cm^{-1} (carbon tetrachloride) would indicate a predominance of pseudoaxial conformers. An inspection of the molecular model also reveals that the **1** compounds exist in pseudoaxial conformers.

Methylene Protons. The NMR spectra of the methylene protons of the IIa, IIIc, IV, and VI compounds are shown in Fig. 1. All the **1** compounds displayed similar sets of methylene-proton multiplets of the representative ABCD pattern. That is, the two well-separated multiplets of an unequal height and width correspond to the two protons at the 5 position, while the other ones further upfield correspond to the protons at the 4 position.[2] Besides, according to S=O bond anisotropy, which exerts a stronger deshielding effect at the *cis*-position than at the *trans*-position,[1,2] the NMR signals of the H_a and H_c protons can be assigned multiplets in a lower field than those of H_b and H_d respectively.

The appearance of the NMR spectra of **1** gave well-defined patterns for the methylene-proton signals. We have, therefore, segregated the spectra into four types—A, B, C, and D, as can be seen in Fig. 1. The signals of Compounds I, IIb, IIc, IV, Vb, and Vc may all be

Table 1. Data for the 3-aryl-1,2,3-oxathiazolidine 2-oxides

Compd. No.[a]	Reaction conditions		Yield %	Mp °C or Bp(mmHg)	IR (S=O) cm^{-1}	Elementary analysis (%), (Calcd value)				
	Temp., °C	Time, hr				C	H	N	S	halogen
I	50	8	90	45.0—46.8	1172	—	—	—	—	
IIa	45	13	74	79(0.1)	1162	71.20[b] (71.49)	8.66 (8.67)	9.12 (9.26)	—	
IIb	50	4	60	38.2—38.8	1161	54.60 (54.80)	5.61 (5.62)	7.15 (7.10)	16.22 (16.25)	
IIc	30	7	47	74.8—75.6	1169	—	—	—	—	
IIIa	40	6	80	120—125(0.1)	1157	64.07[b] (64.65)	7.91 (7.84)	8.10 (8.38)	—	
IIIb	30	13	10	34.0—36.0	1163	50.77 (50.69)	5.36 (5.20)	6.60 (6.57)	14.81 (15.03)	
IIIc	15	16	65	52.8—53.2	1163	50.83	5.25	6.62	14.72	
IV	50	7	60	87.5—88.2	1155	36.93 (36.66)	3.14 (3.08)	5.41 (5.34)	12.19 (12.23)	30.96 (30.48)
Va	20	14	47	58.0—59.9	1162	55.84[b] (55.99)	5.88 (5.87)	8.15 (8.16)		20.59 (20.67)
Vb	50	5	86	84.7—85.0	1161	44.07 (44·14)	3.65 (3.70)	6.44 (6.43)	14.82 (14.73)	16.29 (16.29)
Vc	50	5	79	68.5—71.5	1158	—	—	—	—	—
VI	45	4	50	115.3—115.8	1165	33.48 (33.53)	2.07 (2.11)	4.90 (4.89)	11.11 (11.19)	37.50 (37.12)

a) IIa, IIb, IIIa, IIIb, IIIc, IV, Va, Vb, and VI are newly-prepared compounds. b) These compounds are unstable even at room temp. and easily decompose by exposure to air. Therefore, the values of the elementary analyses were obtained for the corresponding *N*-(*β*-hydroxyethyl)aniline.[2]

Table 2. NMR spectral data of the compounds, **1**.[a]

Compd. No.	Chemical Shifts, δ ppm							
	H_a	H_b	H_c	H_d	CH_3 or OCH_3	Aromatic ring proton[c]	H_a-H_b	H_c-H_d
I	4.89	4.55	3.77	3.52	—	6.82—7.35 (m)	0.34	0.25
IIa	4.82	4.41	4.00	3.49	2.36	7.05—7.26 (m)	0.41	0.51
IIb	4.85	4.51	3.72	3.49	2.27	2,4,6 : 6.62—6.82 5 : 7.10, J=7.5	0.34	0.23
IIc	4.86	4.50	3.74	3.49	2.29	2,6 : 6.84, J=8.3 3,5 : 7.05, J=8.3	0.36	0.25
IIIa	4.82	4.44	3.84	3.57	3.92	6.99 (s) 6.80—7.20 (m)	0.38	0.27
IIIb	4.86	4.52	3.73	3.50	3.73	2,4,6 : 6.42—6.60 (m) 5 : 7.12 (q)	0.34	0.23
IIIc	4.76	4.39	3.72	3.46	3.63	2,6 : 6.87 or 6.66 3,5 : 6.66 or 6.87	0.37	0.26
IV[b]	4.99	4.64	3.80	3.57	—	2,6 : 6.87, J=8.5 3,5 : 7.37, J=8.5	0.35	0.23
Va	4.84	4.44	3.95	3.65	—	7.04—7.46 (m)	0.40	0.30
Vb[b]	4.96	4.62	3.79	3.57	—	2,4,6 : 6.82—7.04 (m) 5 : 7.19	0.34	0.22
Vc	4.87	4.52	3.72	3.46	—	2,6 : 6.78, J=8.5 3,5 : 7.15, J=9.0	0.35	0.26
VI[b]	5.06	4.70	3.99	3.51	—	7.43 (s)	0.36	0.48

a) The data refer to 0.5 mmol/ml solutions in CCl_4 unless otherwise indicated. Chemical shifts are believed to be significant to ±0.02 ppm and coupling constants to ±0.2 Hz. b) Data for $CDCl_3$ (30%)—CCl_4 solution. c) Coupling constant, Hz.

considered to belong to Type A. Similarly, those of Compounds IIa, IIIa, and Va appear to belong to Type B, and those of IIIb and IIIc, to Type C. Only the signal of VI belongs to a different Type, D.

The NMR spectra of **1** are of an almost pure first-order type, and all the coupling constants can be obtained by inspection. Small second-order effects can be observed on the basis of a comparison of the peak pattern at 100 MHz with that of 60 MHz. Theoretically, one of these methylene protons is individually split to octet lines because of coupling with the three other protons. Computor simulations of the observed signals were carried out using the five-spin system (No. 396) of the Japan Electron Opt. Co., Ltd., program.

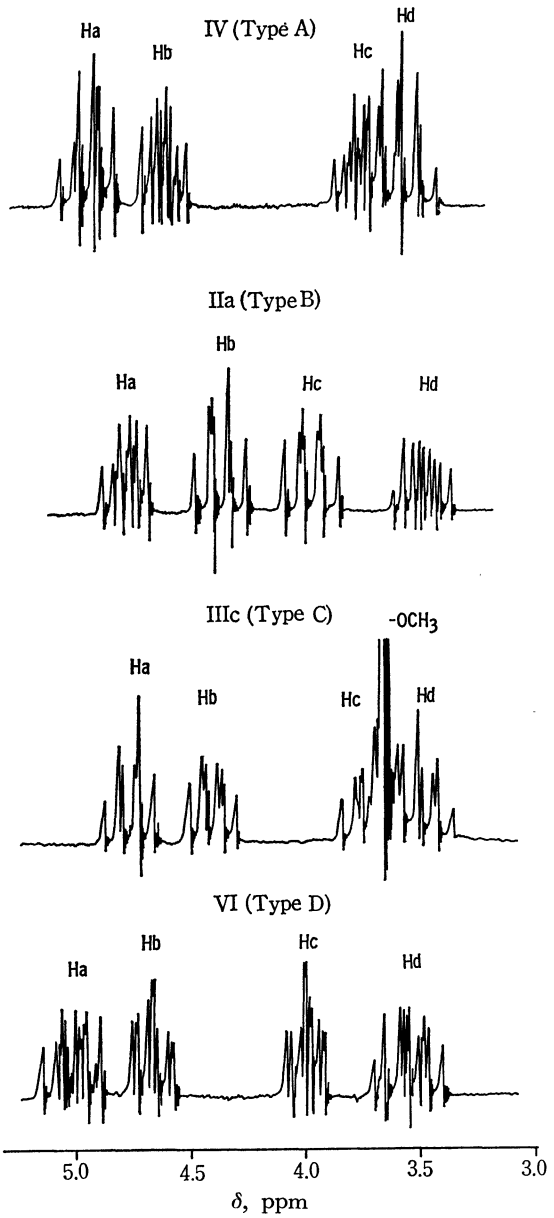


Fig. 1. 100 MHz NMR spectra of the methylene protons of **1** in CCl_4.

The agreement between the observed and calculated spectra was excellent. The NMR spectral data are listed in Table 2, while their coupling constants are summarized in Table 3.

As can be seen in Table 2, the differences between the chemical shift values for the geminal protons (H_a-H_b and H_c-H_d, δ ppm) may be due to the conformation of the oxathiazolidine ring. In the case of the compounds of Types A and C, the values of H_a-H_b and H_c-H_d are 0.34—0.37 and 0.22—0.26 ppm respectively. On the other hand, in the compounds of Types B and D, the above values are 0.36—0.41 and 0.27—0.51 ppm respectively. From the above results, it may be thought that the conformations of **1** vary with both the situation and the nature of the ring substituent, and that it is possible to distinguish them by the appearances of their methylene-proton signals.

Geminal Coupling. Two geminal coupling have been determined in this study (in Table 3); they were found to be in agreement with the values obtained for the other 3-aryl-5-methyl-1,2,3-oxathiazolidine 2-oxides (J_{cd}=8.3—8.8 Hz).[2]

Vicinal Coupling and Stereochemistry. In view of the results of the present investigation, the relevant distortions from the idealized stereochemistry of the **1** system, in which H_a is completely eclipsed by H_c and in which H_b is also eclipsed by H_d, involve torsional changes about the C-4 and C-5 bonds. These changes are most likely to be of two kinds, represented by the projections of **2** and **3** in Fig. 2.

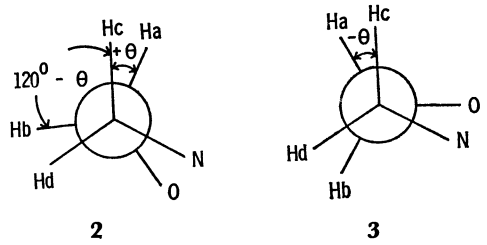
A comparison of the pairs of entries in Table 3, where the electronegativities of the substituents are the same or similar, but where the substituents differ in position, leads to some suggestions. Thus, the much greater J_{ad} constants for Compounds IIb, IIc, IIIb, IIIc, Vb, and Vc than those of IIa, IIIa, and Va suggest that the distortions of the compounds with an *m*- or *p*-substituent are in the direction of the **2** projection, while those with *o*-substituents cause a distortion toward the **3** projection.

Williamson[9] and Laszlo and Schleyer[10] reported that the magnitudes of coupling constants between protons on adjacent saturated carbon atoms vary significantly with

TABLE 3. THE DATA OF THE COUPLING CONSTANS[a] FOR THE METHYLENE PROTONS OF **1**

Compd. No.	Coupling Constants, Hz						J_{ad}/J_{bc} (r value)	θ (degree)	
	Geminal		Vicinal					A=8	A=7
	J_{ab}	J_{cd}	J_{ac}	J_{ad}	J_{bc}	J_{bd}			
I	8.5	8.5	6.6	8.9	4.1	7.0	2.2	15	12
IIa	7.8	9.0	7.2	4.5	7.9	6.8	1.8[b]	−11	−9
IIb	8.5	8.6	6.6	8.2	4.3	6.9	1.9	12	10
IIc	8.6	8.4	6.5	8.4	4.7	6.6	1.8	11	9
IIIa	8.4	8.9	7.1	5.4	7.1	7.0	1.3[b]	−5	−4
IIIb	8.6	8.6	6.5	8.5	4.1	7.0	2.1	14	11
IIIc	8.4	8.3	6.8	6.8	5.5	6.7	1.2	4	4
IV	8.4	8.6	6.5	8.6	4.1	6.9	2.1	14	11
Va	7.9	8.9	7.1	4.5	8.0	6.9	1.8[b]	−11	−9
Vb	8.4	8.4	6.6	8.8	4.0	6.9	2.2	15	12
Vc	8.4	8.4	6.6	8.2	4.3	6.8	1.9	12	10
VI	8.4	8.2	6.0	10.3	2.2	6.8	4.7	≥30	27

a) Coupling constants are believed to be significant to 0.2 Hz. b) Values for J_{bc}/J_{ad}.



2 3

Fig. 2. Diagrams of **2** and **3** forms of the parts of methylene protons of **1**.
Dihedral angle (ϕ) = 120°±torsion angle (θ).

changes in the electronegativity (ER) of the adjacent substituent and that the internal chemical shifts for the same protons also depend on the ER of the substituent. From this literature, values of approximately 1—2 ppm/ER unit for the chemical shift and 1—1.5 Hz/ER for the coupling constant are given. Such values, which can be obtained from Tables 2 and 3, are quite small in comparison with the values mentioned above. Besides, the plots of J vicinal *vs.* ER of **1** showed a considerable scatter. There seems to be no unequivocal correlation between the ER and the coupling constant. These facts indicate that the chemical shifts and the coupling constants in the series of **1** do not depend on the ER of the ring substituent. Furthermore, the nature of our system assures the constancy of other variables, for example, the C–C bond length and the H–C–C angle. It is, therefore, probable that the vicinal coupling constants of **1** depend only on each dihedral angle.

Assuming, as is mentioned above, that the most important factor determining the magnitude of the vicinal coupling constant is the dihedral angle, one may conclude that the J_{trans}(J_{ad} or J_{bc}) in **1** is more sensitive to distortions from perfect eclipsing than J_{cis} (J_{ac} or J_{bd}) because of the shape of the Karplus function. In this series of 12 compounds, J_{ad} varies from 4.5 to 10.3 Hz, and J_{ac} varies from 6.0 to 7.2 Hz (Table 3).

When the envelope conformation and various other conformational extremes are considered, there is found to be a wide range of variability in the stereochemical relationships between methylene protons of **1**. For the molecule existing in the ideal envelope conformation, the coupling constants, J_{ad} and J_{bc}, correspond to the dihedral angles of approximately 120 and 120° respectively. In this case, the ratio (r) of J_{ad} to J_{bc} in the five-membered ring of **1** is close to 1.0. On the other hand, Lambert[11] reported that the ratio (R) of the average $^3J_{trans}$ to the average $^3J_{cis}$ in the six-membered ring compounds is nearly independent of the ER of the substituents and become a direct measure of the conformational effects, and that the ratio was close to 2.0 for the molecules in the perfect-chair conformation. In our system, a further inspection of molecular model reveals that a decrease in θ will decrease J_{ad} (Projection **2** in Fig. 2) or J_{bc} (Projection **3**), whereas it will increase J_{bc} (Projection **2**) or J_{ad} (Projection **3**). Thus, the coupling constant caused by each torsion angle, θ, is given by the following Karplus eq.:[12]

$$r = (J_{ad}/J_{bc}) \text{ or } (J_{bc}/J_{ad}) = \frac{A - B\cos(120+\theta) + C\cos 2(120+\theta)}{A - B\cos(120-\theta) + C\cos 2(120-\theta)} \quad (1)$$

For the above eq. (1), a reasonable set of empirical parameters, $A=+7$, $B=+1$, and $C=+5$,[12] was employed. Then we attempted to use the $A=+8$ parameter in eq. (1) in order to get good results. The changes in θ caused by the distortions and the corresponding changes in J and r are listed in Tables 4 and 5 ($+30° \geq \theta \geq -30°$).

The tortion angles corresponding to the calculated r values (in Table 5) with the best agreement with the observed r values (Table 3) were found out to be as is shown in Table 3. Figure 3 shows the plots of the observed vicinal coupling constants *vs.* the dihedral angles with the calculated Karplus curves for both of the parameters, $A=+7$ and $A=+8$. In the case of the $A=+8$ parameter, the data clearly fall on the Karplus curve.

Table 4. J values calculated by the Karplus Eq. in Eq. (1)

θ°	J, Hz		θ°	J, Hz	
	A=8	A=7		A=8	A=7
0	6.00	5.00			
1	6.17	5.17	−1	5.84	4.84
4	6.69	5.69	−4	5.36	4.36
5	6.86	5.86	−5	5.21	4.21
10	7.77	6.77	−10	4.51	3.51
11	7.96	6.96	−11	4.39	3.39
12	8.15	7.15	−12	4.26	3.26
13	8.33	7.33	−13	4.15	3.15
14	8.52	7.52	−14	4.04	3.04
15	8.71	7.71	−15	3.93	2.93
20	9.63	8.63	−20	3.48	2.48
25	10.53	9.53	−25	3.16	2.16
30	11.37	10.37	−30	3.00	2.00

Table 5. Correlation between θ and r obtained from Eq. (1)

θ°	r	
	A=8	A=7
0	1.00	1.00
1	1.06	1.07
4	1.25	1.31
5	1.32	1.39
10	1.72	1.93
11	1.81	2.05
12	1.91	2.19
13	2.01	2.33
14	2.11	2.47
15	2.22	2.63
20	2.77	3.48
25	3.33	4.41
30	3.79	5.19

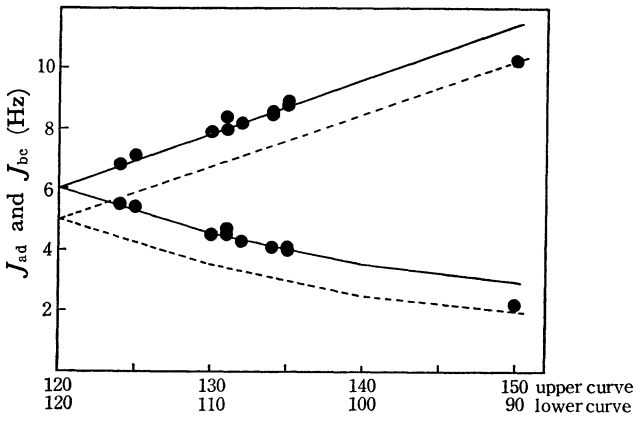


Fig. 3. Plots of the vicinal coupling constants, J_{ad} and J_{bc}, *vs.* the dihedral angles.
Calculated Karplus curves {—— in $A=8$ ---- in $A=7$

From these results, the conformations of **1** may be divided roughly into the following four groups:

Group 1. $\theta=10$—$15°$, $r=1.8$—2.2. The compounds of Type A, —that is, I, IIb, IIc, IV, Vb, and Vc, and IIIb—show this type of conformation.

Group 2. $\theta=-5$——$11°$, $r=1.3$—1.8. The compounds of Type B, IIa, IIIa, and Va, all with an *o*-substituent, show this type of conformation.

Group 3. $\theta=-5$—$+4°$, $r=1.2$—1.3. In IIIa and IIIc (Types B and C respectively), the two methylene groups are nearly eclipsed.

Group 4. $\theta\geq30°$, $r=4.7$. Compound VI, Type D, shows this conformation.

In Group 1, r is approximately 2.0 ± 0.2 (within 10—15%). In Group 3, both the r values are close to 1.0. The r of Group 4 shows an extremely large value; this indicates the presence of severe distortion in VI. Thus, deviations from $r=1$ indicate distortions from the envelope conformation.

It is interesting to compare these conformations with their chemical stabilities. Group 1 and Group 4 compounds are stable at room temperature. On the contrary, Group 2 and Group 3 compounds are unstable even at room temperature and are easily decomposed by water to the corresponding *N*-(β-hydroxyethyl)-anilines, as can be seen in Table 1.

Solvent-shift Studies. The NMR spectral data of **1** in a deuterobenzene solution exhibit benzene-induced shifts, as can be seen in Table 6. The proposed geometry of a benzene–solute collision complex of **1** is shown in Fig. 4. The results furnish considerable information on the stereochemical structure of the collision complex. (1a) In the case of Compounds I, IIb, IIc, and IIIb the solvent-shifts, $\Delta\delta_H$ ppm, for the different protons are in this order: $H_d>H_b>H_c>H_a$.

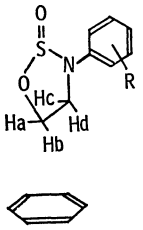


Fig. 4. Proposed geometry of benzene-solute collision complex of the oxathiazolidines.

This fact confirms the finding that the torsion angles in these compounds (Group 1) are found in the 10—15° range. In each compound, the $\Delta\delta_{Ha}$ value is smaller than the other three values; they are approximately 1.5 times H_a. This means that the co-ordinated benzene molecule exists rather closer to the C-4 atom than to the C-5 atom. (1b) On the other hand, Compounds IV, Vb, and Vc, all with a halogen substituent in Group 1, show this order of $\Delta\delta_H$ values; $H_d>H_c>H_b>H_a$. The values of the different four protons are somewhat greater than those of the corresponding protons in (1a) (*e.g.* $\Delta\delta_{Ha}$ in 1b$>\Delta\delta_{Ha}$ in 1a). These facts suggest that the co-ordinated benzene molecule in these compounds (1b) comes closer to the oxathiazolidine ring than with that of the compounds of (1a). (2) In the compounds with an *o*-substituent, IIa, IIIa, and Va, the $\Delta\delta_{Hc}$ values are somewhat smaller than the other three values. This indicates that the sign of the torsion angle of this group is negative compared with that of the compounds in Group 1.

TABLE 6. BENZENE-INDUCED SOLVENT SHIFTS $\Delta=[\delta(CCl_4)-\delta(C_6D_6)]$ FOR THE DIFFERENT PROTONS IN **1**

Compd. No.	Resonance					$(\Delta\delta_{Hc}-\Delta\delta_{Ha})/(\Delta\delta_{max}-\Delta\delta_{min})$
	H_a	H_b	H_c	H_d	CH_3 or OCH_3	
I	0.515	0.780	0.745	0.820	—	0.75
IIa	0.552	0.759	0.481	0.741	0.170	−0.26
IIb	0.475	0.725	0.675	0.760	0.240	0.70
IIc	0.445	0.680	0.605	0.715	0.215	0.59
IIIa	0.510	0.655	0.487	0.701	0.560	−0.11
IIIb	0.461	0.727	0.697	0.772	0.355	0.76
IIIc	0.485	0.770	0.580	0.725	0.390	0.39
IV[a)]	0.720	0.955	1.025	1.105	—	0.79
Va	0.620	0.705	0.520	0.805	—	−0.35
Vb[a)]	0.710	0.940	1.070	1.140	—	0.84
Vc	0.575	0.805	0.900	0.985	—	0.79
VI[a)]	0.590	0.820	0.745	0.730	—	—

a) $\Delta=\delta(CDCl_3(30\%)\text{-}CCl_4)-\delta(C_6D_6)$.

In IIa, the $\Delta\delta_H$ values show the order of $H_b > H_d > H_a > H_c$, and while in IIIa and Va the values show the order of $H_d > H_b > H_a > H_c$. (3) Compounds IIIa and IIIc, with a methoxy substituent, are considered to belong to this section. The $\Delta\delta_{Hb}$ value of IIIa is the smallest of all those of **1**; the value of $\Delta\delta_{Ha} - \Delta\delta_{Hc}$ is also the smallest of those of the compounds with an *o*-substituent,—that is, IIa, IIIa, and Va. In IIIc the $\Delta\delta_{Hd}$ value is relatively small and the value of $\Delta\delta_{Hc} - \Delta\delta_{Ha}$ is the smallest of the compounds in Group 1 and VI. In IIIa, the $\Delta\delta_H$ values show the order of $H_a > H_c$ and $H_d > H_b$, while in IIIc the order is $H_c > H_a$ and $H_b > H_d$. These facts indicate that the torsion angles of IIIa and IIIc are small and have either a positive or a negative sign. This result is quite consistent with the near-ideal envelope conformation of Group 3. (4) Compound VI, with tri-chloro substituents, shows the following effects. (a) The value of $\Delta\delta_{max} - \Delta\delta_{min}$, that is, $\Delta\delta_{Hb} - \Delta\delta_{Ha}$, is 0.230 ppm, the smallest of all those of **1**. (b) $\Delta\delta_{Hc}$ and $\Delta\delta_{Hd}$ are almost the same. From the above facts, we suggest that the co-ordinated benzene molecule exists at almost the same distance from both the H_c atom and the H_d atom.

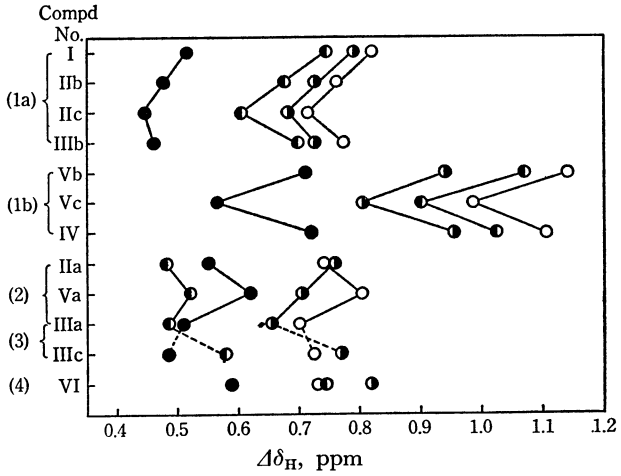


Fig. 5. Solvent-shift changes ($\Delta\delta_H$ obsd) of the methylene protons of **1**.
—●— H_a, —◑— H_b, —◐— H_c, —○— H_d

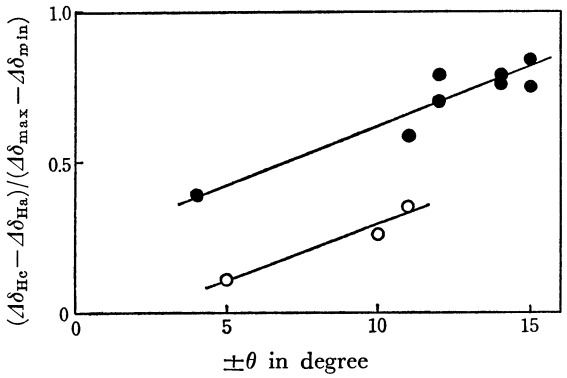


Fig. 6. Relationships between the values of $(\Delta\delta_{Hc} - \Delta\delta_{Ha})/(\Delta\delta_{max} - \Delta\delta_{min})$ and torsion angles θ.
●: I, IIb, IIc, IIIb, IIIc, IV, Vb, and Vc.
○: IIa, IIIa, and Va.

All the above phenomena are easily recognizable in Fig. 5. All the values of $(\Delta\delta_{Hc} - \Delta\delta_{Ha})/(\Delta\delta_{max} - \Delta\delta_{min})$ in **1**, except for VI, gave the proportional relationship with the θ angle, as can be seen in Fig. 6.

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