

Stereochemistry of organic compounds(2) : Conformation of oxazolidinone derivatives

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Stereochemistry of Organic Compounds II.
Conformation of Oxazolidinone Derivatives

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有機化合物の立体化学 II

オキサゾリデノン誘導体の
コンホメーション

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概 要

前報では光学活性な五員環ジオキサソラノンに 220nm 辺に $n \rightarrow \pi^*$ 遷移による大きな Cotton 効果を示し、その符号が Klyne の五員環ラクトンに適用されたラクトンセクター則第一投影によって説明可能であることを述べた。更に、Cotton 効果への寄与の大小は、五員環平面の歪みと相関し、節平面からはずれた O 原子がどのセクターに入りこむかによって説明してよいことを述べた。

一方、カルボニル基に隣接した α -位のアシメ炭素はフェニル基をもつ S-配置の炭素であり、フェニル基の benzenoid band が 250~270nm に 3 つの peak をもつ弱い負の Cotton 効果を示すことがわかった。

さて、本報では引き続き五員環の conformation を調べるため、異った種類の五員環ラクトンを合成し、その旋光寄与を調べた。まず、L-アミノ酸をトシル化し、ホルムアルデヒドを縮合させて環化し、一連の N-トシルオキサゾリデノン誘導体を合成した (I~VI)。この化合物のアシメ炭素は S-配置を有し、五員環に含まれるヘテロ原子は N 原子と O 原子になる。I~VI に観測された 220nm 辺の強い正の Cotton 効果は、異なるヘテロ原子をもっているにもかかわらず、前報と同様、ラクトンセクター則第一投影によって説明すること

ができる。

一方、I~VI では 250~270nm 辺には小さな負の Cotton 効果を含むが全体として正の Cotton 効果で示される、弱い Complex Cotton effects が観測された。脱トシル化した化合物 VII が 250~270nm 辺に吸収をもたず Cotton 効果を示さないことから、これがトシル基によるものであることは明白である。吸収の位置及び強度から遷移の本質は benzenoid band 1L_b と考えることが妥当であるから、これが光学活性吸収帯で示されることは、 $>N-SO_2-\text{C}_6\text{H}_4-CH_3$ 全体が発色団となって C_4^* についたと考えればよいことになる。従って phenyl 基の共役系が N-原子まで伸びたことを示す。ここで S-配置の C_4^* につく 1L_b band を有す基の示す Cotton 効果について考えた。その結果、このような benzenoid band を説明できる法則はなく、コンホメーションとの相関を説明するために、今回、新しくオクタントを設定し、これに Modified Octant Rule と名づけることにした。これによって oxazolidinone 誘導体だけでなく、dioxolanone 誘導体の場合にも、NMR で支持された conformation をうまく説明されることを示した。

Stereochemistry of Organic Compound II.¹⁾
Conformation of Oxazolidinone Derivatives

In the previous paper,¹⁾ we discussed the chirality of the dioxolanones containing the five membered ring which had two oxygen atoms as the hetero atoms. As a result, the observed positive Cotton effects around 220 nm were in good agreement with the prediction of the sector rule by Klyne.²⁾

In the present investigation, the authors have prepared various oxazolidinone derivatives which have an oxygen and a nitrogen atom as hetero atoms with the objective of investigating the ring chirality and the role of the nitrogen atom. For this purpose, the following eight compounds were studied. The compounds I-VII were newly synthesized and the compound VIII was re-examined, for the purpose of comparison.¹⁾

- 4-Methyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (Compound I),
- 4-Isopropyl-*p*-tosyl-1, 3-oxazolidin-5-one (Compound II),
- 4-*sec*-Butyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (Compound III),
- 4-Isobutyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (Compound IV),
- 4-Thiomethoxymethyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (Compound V),
- 4-Thiomethoxyethyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (Compound VI),
- 4-Isobutyl-1, 3-oxazolidin-5-one (Compound VII), and
- 2,2-Dimethyl-5-phenyl-1, 3-dioxolan-4-one (Compound VIII).

Measurements were made with these compounds on their rotatory dispersion (RD), circular dichroism (CD), ultraviolet absorption (UV), infrared (IR) and NMR spectra.

Results and Discussion

The structures of the compounds I-VIII studied are indicated in Fig. 1.

The compounds (I-VII) were obtained by reaction of various L-amino acids with formaldehyde as the scheme in Fig. 2. In the case of the compounds I-VI, the amino groups of amino acids (a) were beforehand protected by tosylation (b),

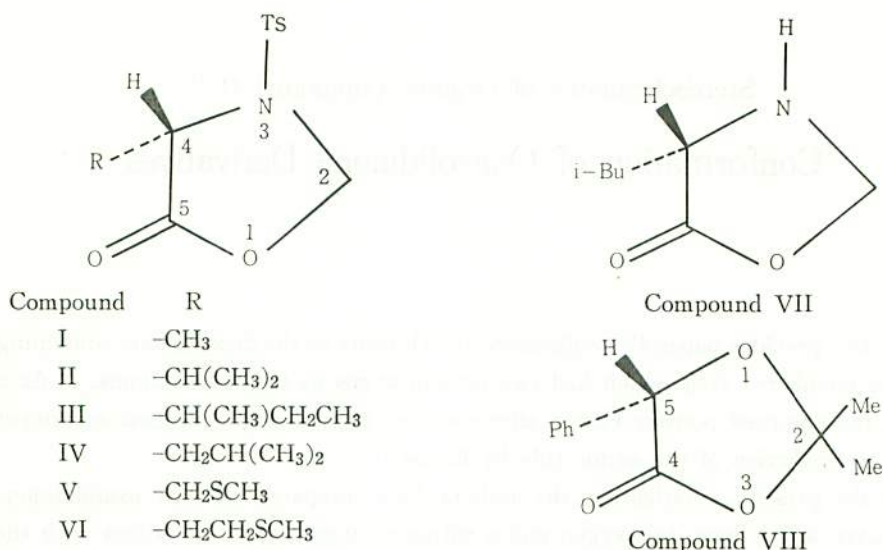


Fig. 1. Structures of all compounds studied.

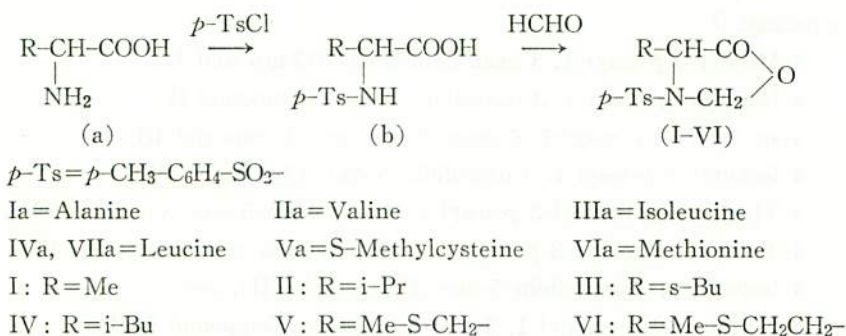


Fig. 2. Syntheses of the compounds I-VI.

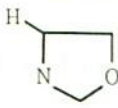
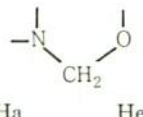
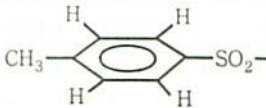
and allowed to react with formaldehyde for 3 hrs in acetic acid at 100°C. The solid products obtained were recrystallized from i-propyl alcohol and analyzed. The compound VII was obtained by detosylation of the compound IV.

Spectral data suggested that the structures were 4-alkyl-3-tosyl-1,3-oxazolidin-5-ones (I-VI), as seen in Table 1 and 2. The infrared spectra exhibited the characteristic absorptions of five membered ketone group at 1814-1774 cm⁻¹ and of ether linkage at 1030-975 cm⁻¹. The nuclear magnetic resonance spectra showed absorptions at δ 5.60-5.11 ppm, assignable to ring methylene protons, at δ 4.25-

Table 1. 4-Alkyl-3-*p*-tosyl-1,3-oxazolidin-5-ones (I-VI)

Compd	R	Mp °C	Yield %	IR, cm ⁻¹ (KBr)			
				C=O	S=O	C-O-C	
I	CH ₃ -	135-136	78	1814	1353	1167	1005
II	(CH ₃) ₂ CH-	74-75	46	1792	1355	1160	1000
III	CH ₃ CH ₂ CH(CH ₃)-	83-85	61	1795	1354	1162	1030
IV	(CH ₃) ₂ CHCH ₂ -	82-83	78	1783	1358	1169	990
V	CH ₃ SCH ₂ -	110-112	67	1780	1362	1168	975
VI	CH ₃ SCH ₂ CH ₂ -	84-86	68	1774	1357	1160	990

Table 2. ¹H-NMR Data of I-VI (δ , ppm)

				R		
		Ha	He			
I	3.99(q, 1)	5.24(d, 1)	5.38(d, 1)	2.46(s, 3) 7.36(d, 2)	7.72(d, 2)	1.54(d, 3)
II	3.85(d, 1)	5.11(d, 1)	5.60(d, 1)	2.42(s, 3) 7.31(d, 2)	7.68(d, 2)	1.10(d, 6) 1.84-2.59(m, 1)
III	3.85(d, 1)	5.11(d, 1)	5.48(d, 1)	2.43(s, 3) 7.28(d, 2)	7.65(d, 2)	0.89-1.26(m, 6) 1.26-2.16(m, 3)
IV	4.04(t, 1)	5.15(d, 1)	5.54(d, 1)	2.42(s, 3) 7.27(d, 2)	7.67(d, 2)	1.00(d, 6) 1.45-2.28(m, 3)
V	4.25(t, 1)	5.33(d, 1)	5.45(d, 1)	2.44(s, 3) 7.30(d, 2)	7.67(d, 2)	2.25(s, 3) 3.06(d, 2)
VI	4.12(t, 1)	5.20(d, 1)	5.46(d, 1)	2.44(s, 3) 7.28(d, 2)	7.67(d, 2)	2.08(s, 3) 2.11-2.70(m, 4)

3.85 ppm, due to ring methine proton, and at δ 2.46–2.42 ppm and 7.72–7.27 ppm, corresponding to tosyl protons. The remaining absorptions are assigned to the alkyl group protons.

Two protons of the ring methylene group are situated in different environments, that is, one is an axial proton (Ha) and the other is equatorial (He). The δ value of He is slightly larger than that of Ha, as is given in Table 2. In general, two substituents, of the neighboring atoms in a saturated cyclic compound, are placed as alternately as possible to decrease the repulsive force of the bulky substituent, which normally prefers the equatorial position. When the alkyl group is stereochemically large enough, the steric repulsion by the large tosyl group occurs, and the two methylene protons are fixed in the axial and equatorial positions. Hence their signals of nuclear magnetic resonance will be observed as typical



Fig. 3. Three patterns of the two protons.

AC-type splitting as seen in Fig. 3. If the alkyl group is small, the two protons are averaged and the signals will be observed as the AB- or A₂-type pattern (Fig. 3). The two protons of the ring methylene group of II, III, IV and VI are split as in the AC pattern, and those of I and V are observed as in the AB. All the NMR spectra of the compounds I-VI are illustrated in Figs. 4-9.

The RD, CD and UV curves of all the compounds are shown in Figs. 10-16. Those curves of the compound VII are shown in Fig. 10, together with those of VIII, in order to illustrate the difference between the dioxolanone ring and the oxazolidinone ring. As is clear from the CD curve, the compound VII exhibits a positive Cotton effect at 217 nm due to the $n \rightarrow \pi^*$ transition of carboxylate group. As both the compounds VII and VIII have L-configurations shown in Fig. 1, it is supposed that the lacton sector projection, applied to the compound VIII¹⁾ with the dioxolanone ring, can also be applied to the compound VII with the oxazolidinone ring. As is evident from Fig. 10, the compound VII has no band around 260 nm, while the compound VIII has the negative complex Cotton effects around 250-270 nm. This indicates that the phenyl group attached to the asymmetric carbon is optically active. As may be seen from Figs. 11-16, all the other compounds, I-VI, exhibit the positive Cotton effects, around 220 nm, attributed to the $n \rightarrow \pi^*$ transition of carboxylate group. The lacton sector projection of the compounds I-VI are indicated in Fig. 17. In Fig. 17, the projection A shows that the five membered ring of the oxazolidinone establishes a planar structure, and the projections B and C indicate distorted five membered rings. In the case of the projection C, the alkyl group R is far from the tosyl group, Ts, in comparison with diagram B. All the projections in Fig. 17 show that the alkyl group, R, attached to the asymmetric carbon falls within the sector of positive contribution, and the observed positive Cotton effects, around 224-232 nm, are in good agreement with the prediction of the sector rule.

Now, we are discussing the CD-values of the $n \rightarrow \pi^*$ band in Table 3. By comparing the $[\theta]_{\max}$ of the compound I through IV, it is apparent that the $n \rightarrow \pi^*$ band experiences a diminution in intensity as well as red shift. These facts can

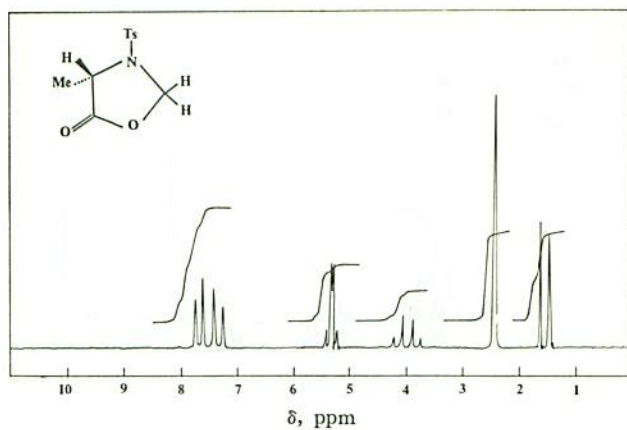


Fig. 4. NMR of Compound I.

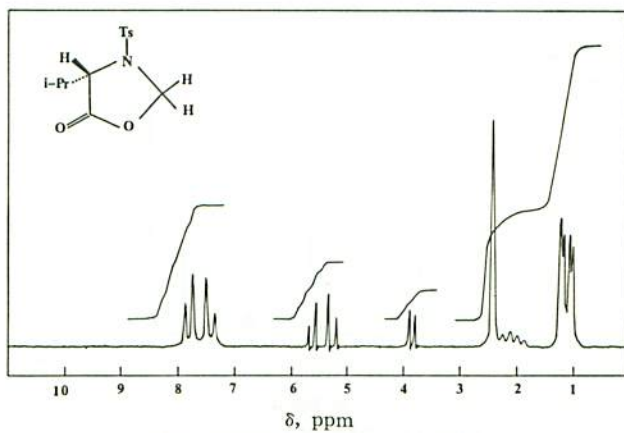


Fig. 5. NMR of Compound II.

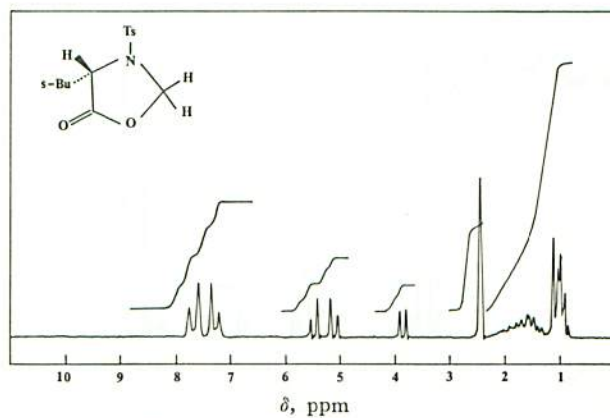


Fig. 6. NMR of Compound III.

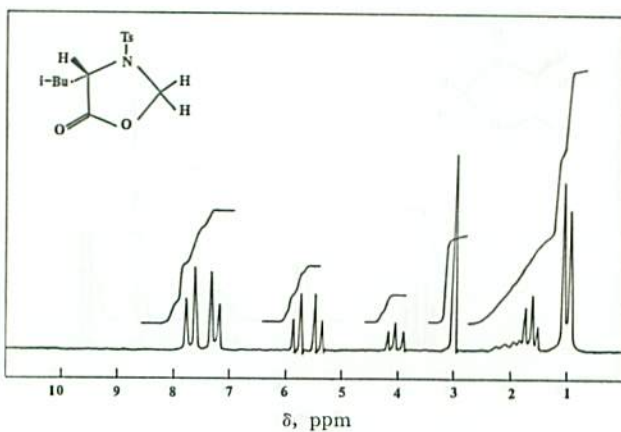


Fig. 7. NMR of Compound IV.

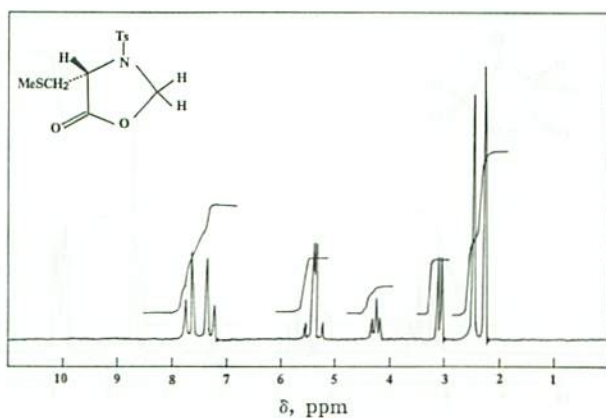


Fig. 8. NMR of Compound V.

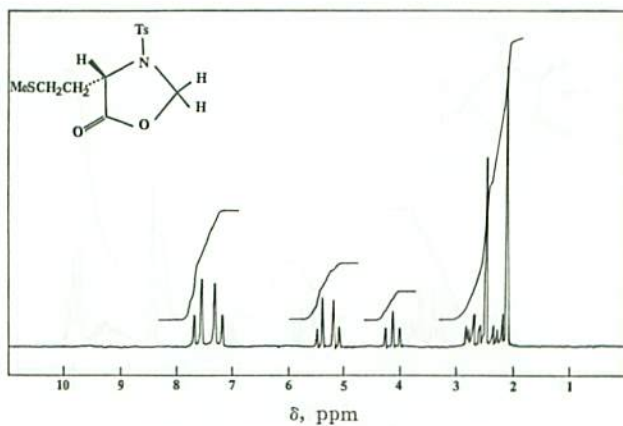


Fig. 9. NMR of Compound VI.

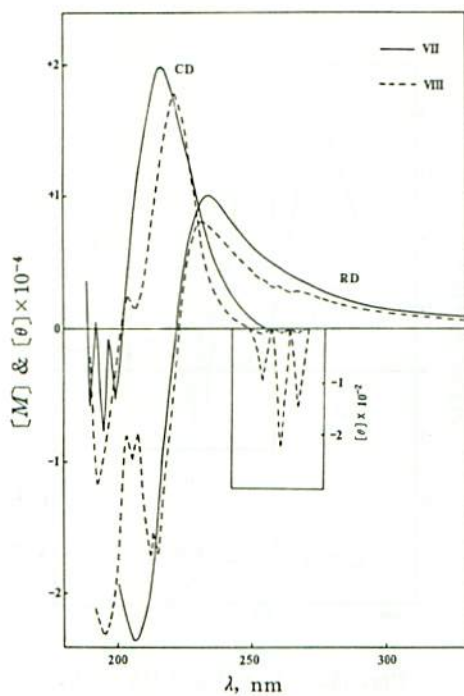


Fig. 10. RD and CD of VII and VIII.

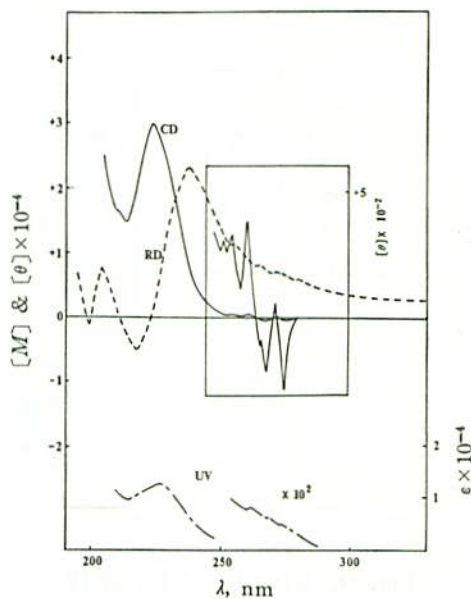


Fig. 11. RD, CD and UV of I.

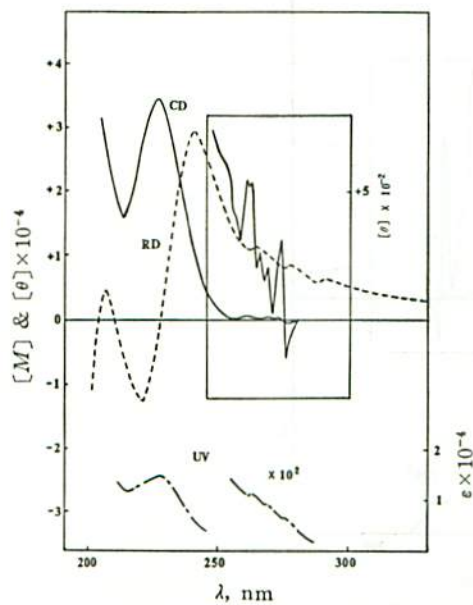


Fig. 12. RD, CD and UV of II.

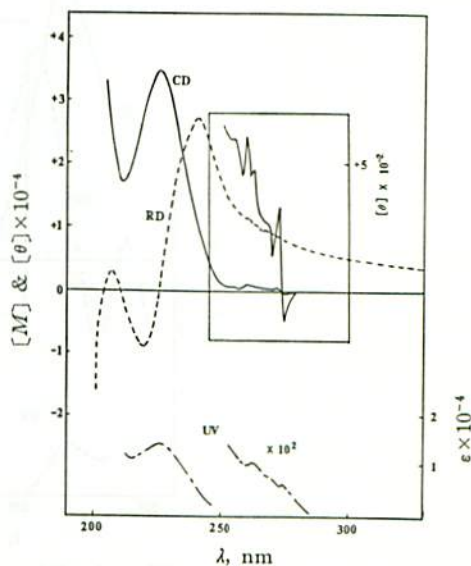


Fig. 13. RD, CD and UV of III.

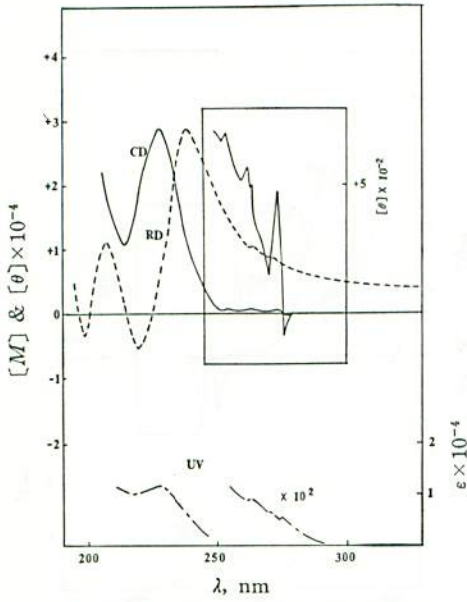


Fig. 14. RD, CD and UV of IV.

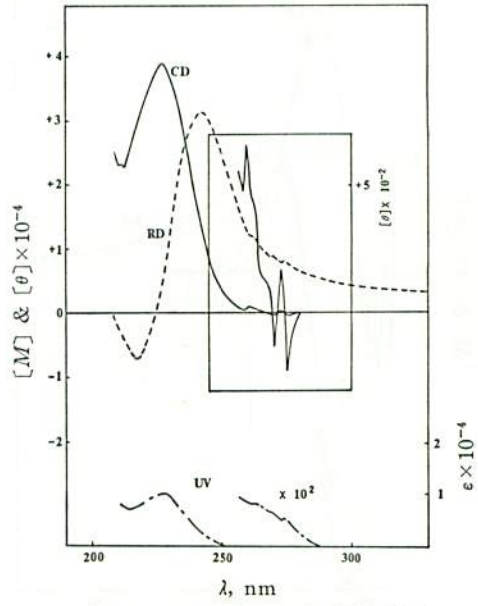


Fig. 15. RD, CD and UV of V.

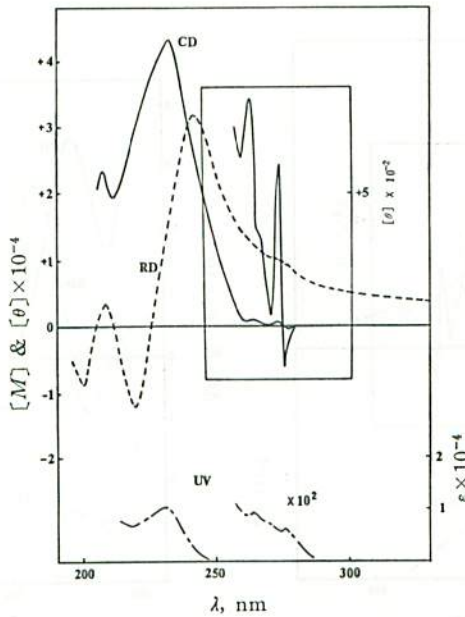


Fig. 16. RD, CD and UV of VI.

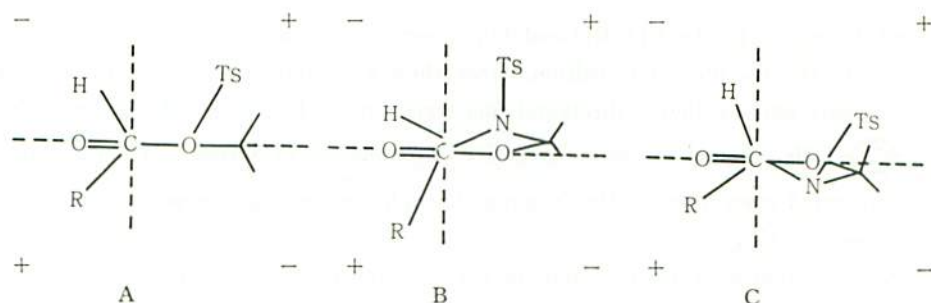


Fig. 17. Sector projection of L-dioxolanone derivatives.

Table 3. CD maximum Values of I-VIII

I-VII		VIII	$[\theta]_{\max}$ (deg mol ⁻¹ cm ²), λ_{\max} , nm				
R'	R''		$n \rightarrow \pi^*$ band	B-band			
I	Me	Ts	+31300(224)	-281(275)	-201(268)	+357(261)	+342(255)
II	i-Pr	Ts	+34300(226)	-223(275)	+308(273)	+286(265)	+546(262)
III	sec-Bu	Ts	+34600(227)	-122(275)	+323(273)	+484(263)	+601(260)
IV	i-Bu	Ts	+28500(228)	-74.0(275)	+495(273)	+575(262)	+706(253)
V	CH ₂ SMe	Ts	+38900(228)	-122(275)	-128(270)	+484(263)	+601(260)
VI	CH ₂ CH ₂ SMe	Ts	+43100(232)	-159(275)	+612(273)	+369(266)	+855(262)
VII	i-Bu	H	+19500(217)				
VIII			+18000(221)	-151(268)	-266(262)	-113(256)	

be interpreted in the following way. Since the five membered rings are distorted, the projections B and C in Fig. 17 are adopted, so that the alkyl group R approaches the nodal-planes in each projection. The values of $[\theta]_{\max}$ by $n \rightarrow \pi^*$ band of the compounds V and VI are larger than those of the compounds I-IV. This fact indicates that the sulfur atom within an alkyl group contributes to a greater positive rotation, as can be expected from the bathochromic shift of the CH₃-S- group. The wavelength of $[\theta]_{\max}$ by $n \rightarrow \pi^*$ band of the compound VII is the shortest of all the compounds. This leads us to believe that the long conjugated systems in the compounds I-VI and VIII lead to absorption of light in the visible region.

Furthermore, discussions will be made about the CD band in the longer wavelength region. As may be seen in Fig. 10, the weak complex Cotton effects around 270 nm of the compound VIII enables one to identify the Cotton effects associated with the ¹L_b phenyl transition or the benzenoid band. As can be seen from Figs. 11-16, all the compounds having the tosyl group exhibit the complex Cotton effects

around 270 nm. In the CD, RD and UV spectra, the bands around 270 nm are assigned to the 1L_b phenyl transition, since they are characterized by their very low intensity and by their vibrational fine structure. Therefore, the group $>N-SO_2-\text{C}_6\text{H}_4-CH_3$ becomes an optically active chromophore as a result of lengthening the conjugated system up to the N-atom through the $-SO_2$ group which is attached to the benzene ring.

We will next consider the signs of these complex Cotton effects due to the 1L_b transition around 250–270nm. Although all the asymmetric carbon atoms of the compounds I-VIII have S-configuration, the signs of the Cotton effects are different, so that the sign of the Cotton effect is not determined by the chirality of the asymmetric carbon.

According to De Angelis et al.,⁴⁾ the aromatic quadrant rule can be applicable to the rigid aromatic compounds containing an asymmetric center adjacent to the aromatic ring. Snatzke et al.⁵⁾ has also proposed a sector rule for the 1L_b band of an aromatic chromophore. However, both rules cannot predict the absolute configuration of the compounds which we investigate since the phenyl group is not rigid. Therefore we will design the new projection in Fig. 18, for the purpose of explaining the signs of the Cotton effects. As can be seen in Fig. 18 a dioxolanone is divided into octants by three mutually perpendicular planes. Fig. 18-A shows the nodal and symmetrical planes. If the dioxolanone derivative is viewed along the $-Z \rightarrow +Z$ axis, the contribution of the group in each quadrant is as shown in Fig. 18-B. According to this rule, the phenyl groups of the compound VIII and the other dioxolanone derivatives,¹⁾ attached to the asymmetric center C_5 , lie in negative octant. The observed negative Cotton effects around 270 nm are provided in the rule. By employing projection similar to the dioxolanone VIII,

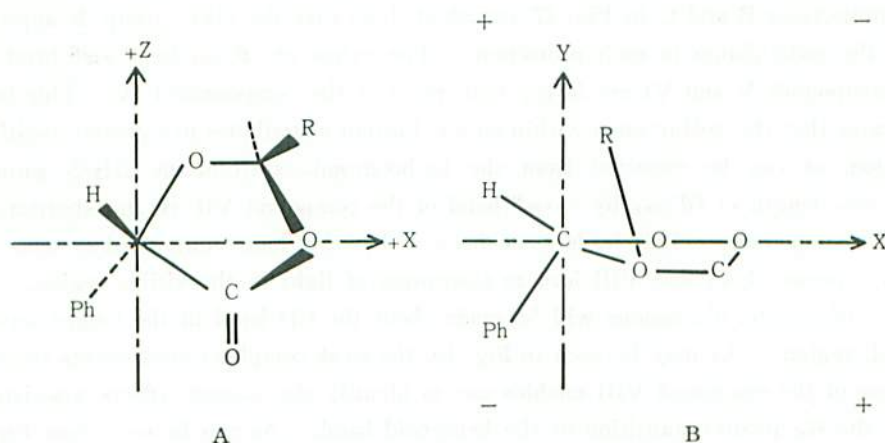


Fig. 18. Modified octant projection for dioxolanones.

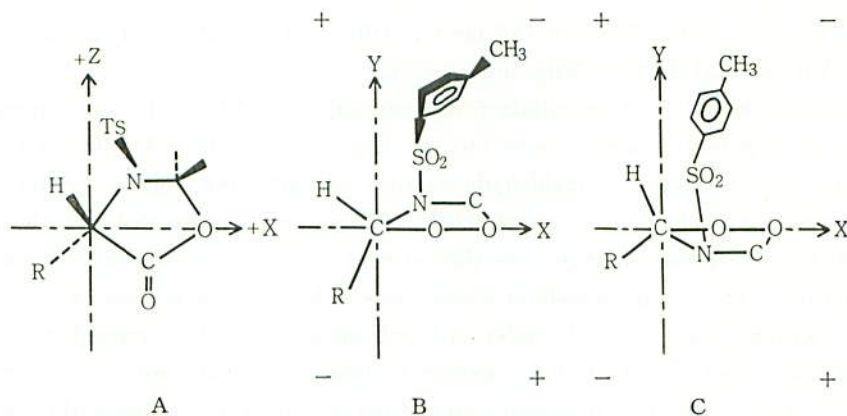


Fig. 19. Modified octant projection for oxazolidinone derivatives.

the modified octant projection, for the oxazolidinone ring, can be shown as seen in Fig. 19. The projection of Fig. 19-B corresponds to the ring structure of Fig. 17-B and Fig. 19-C corresponds to Fig. 17-C. In Fig. 19-B, the $-N-SO_2$ part attached to the asymmetric center C_4 is placed in a negative octant. From this projection, a negative Cotton effect can be expected. At the same time, the aromatic group $-C_6H_4-CH_3$ is situated in the front side of the upper right part. Therefore, the sign of Cotton effect is opposed to that in Fig. 19-B. As mentioned above, the result of NMR spectra of I and V supported the conformation projected in Fig. 19-B.

On the other hand, Fig. 19-C is the projection of the compounds II, III, IV and VI of which methylene protons have the AC pattern. In Fig. 19-C the nitrogen atom enters into the positive octant, therefore major Cotton effects are positive. At the same time, the tosyl group is situated in the rear upper right octant, therefore weak negative Cotton effects are predicted.

To summarize, it is possible to apply the enlarged lacton sector rule by Klyne for the $n-\pi^*$ transition by the $C=O$ group of oxazolidinone derivatives. For the benzenoid band by phenyl group of dioxolanone and oxazolidinone derivatives, we have devised the new modified octant projections.

Experimental

Materials. Alanine (Ia), Valine (IIa), Isoleucine (IIIa), Leucine (IVa, VIIa), S-Methylcysteine (Va), and Methionine (VIa) were obtained commercially. The tosylation of amino acids (a) were carried out with *p*-tosylchloride in the usual manner.³⁾

Ib; mp 138–140°C. IIb; mp 147–148°C. IIIb; mp 132–133°C. IVb; mp 122–124°C. Vb; mp 121–122°C. VIb; mp 84–85°C.

4-Alkyl-3-*p*-tosyl-1, 3-oxazolidin-5-one derivatives (I–VI). To a solution of 0.01 mol of *N-p*-tosyl-L-amino acid (b) in 12.5 ml of acetic acid, 9 g of acetic anhydride and 2 g of 35% formaldehyde aqueous solution were added. After the solution was stirred for 3 hr at about 100°C, 0.25 mol of concentrated sulfuric acid was added. A reaction mixture was then stirred for 0.5 hr, at the same temperature, and 0.9 g of anhydrous sodium acetate was added. The mixture was cooled and the solvent was removed under reduced pressure. The syruped material obtained was added to 150 ml of 5% sodium hydrogen carbonate solution to precipitate the crude product. Recrystallization from isopropyl alcohol gave the results shown in Table 1 and 2.

Measurements. The infrared spectra were measured in a potassium bromide disc using a Hitachi 285 Grating Infrared spectrometer. The nuclear magnetic resonance spectra were recorded with a JNR-PMX spectrometer at room temperature. Chloroform-*d* was used as solvents, and tetramethylsilane was used as an internal reference. The chemical shifts were recorded in values and were followed by the splitting pattern: s, single; d, doublet; t, triplet; q, quarted; m, multiplet.

The rotatory dispersion, circular dichroism and ultraviolet absorption were measured in ethanol at 21–25°C in the wavelength region from 190 nm to 600 nm with a JASCO optical rotatory dispersion recorder of the ORD/UV-5 type.

4-Methyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (I). —The RD and CD were measured at 25°C (*c* 0.1090): $[\alpha]_{589} + 284^\circ$, $[\alpha]_{282} + 2420^\circ$, $[\alpha]_{276} + 2440^\circ$, $[\alpha]_{272} + 2970^\circ$, $[\alpha]_{268} + 2950^\circ$, $[\alpha]_{266} + 3410^\circ$, $[\alpha]_{263} + 3340^\circ$, $[\alpha]_{255} + 4720^\circ$, $[\alpha]_{254} + 4660^\circ$, $[\alpha]_{238} + 9340^\circ$, $[\alpha]_{219} - 2130^\circ$, $[\alpha]_{204} + 3250^\circ$, $[\alpha]_{200} - 147^\circ$, $[\alpha]_{196} + 2620^\circ$, $[\theta]_{278} 0^\circ$, $[\theta]_{275} - 281^\circ$, $[\theta]_{272} + 60.3^\circ$, $[\theta]_{268} - 201^\circ$, $[\theta]_{267} - 90.4^\circ$, $[\theta]_{266} - 101^\circ$, $[\theta]_{261} + 357^\circ$, $[\theta]_{258} + 111^\circ$, $[\theta]_{255} + 342^\circ$, $[\theta]_{253} + 261^\circ$, $[\theta]_{251} + 316^\circ$, $[\theta]_{250} + 261^\circ$, $[\theta]_{224} + 31300^\circ$, $[\theta]_{214} + 15400^\circ$, $[\theta]_{205} + 25600^\circ$. The UV was measured at 25°C in ethanol: $\epsilon_{263-272}$ 856–496, ϵ_{228} 13000.

4-Isopropyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (II). —The RD and CD were measured at 24°C (*c* 0.1030): $[\alpha]_{589} + 243^\circ$, $[\alpha]_{290} + 2290^\circ$, $[\alpha]_{287} + 2020^\circ$, $[\alpha]_{276} + 3070^\circ$, $[\alpha]_{275} + 2830^\circ$, $[\alpha]_{263} + 4040^\circ$, $[\alpha]_{262} + 3880^\circ$, $[\alpha]_{240} + 10500^\circ$, $[\alpha]_{220} - 4350^\circ$, $[\alpha]_{206} + 1650^\circ$, $[\alpha]_{200} - 3960^\circ$, $[\theta]_{278} 0^\circ$, $[\theta]_{275} - 223^\circ$, $[\theta]_{273} + 308^\circ$, $[\theta]_{270} 0^\circ$, $[\theta]_{268} + 207^\circ$, $[\theta]_{267} + 149^\circ$, $[\theta]_{265} + 286^\circ$, $[\theta]_{261} + 202^\circ$, $[\theta]_{262} + 546^\circ$, $[\theta]_{261} + 509^\circ$, $[\theta]_{260} + 546^\circ$, $[\theta]_{258} + 308^\circ$, $[\theta]_{256} + 419^\circ$, $[\theta]_{254} + 573^\circ$, $[\theta]_{226} + 34300^\circ$, $[\theta]_{213} + 15800^\circ$, $[\theta]_{204} + 31800^\circ$. The UV was measured at 25°C in ethanol: $\epsilon_{264-274}$ 1110–642, ϵ_{228} 14500.

4-sec-Butyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (III). —The RD and CD were measured at 24°C (*c* 0.1120): $[\alpha]_{589} + 196^\circ$, $[\alpha]_{272} + 2790^\circ$, $[\alpha]_{271} + 2710^\circ$, $[\alpha]_{267}$

+3190°, $[\alpha]_{266}+3080^\circ$, $[\alpha]_{264}+3610^\circ$, $[\alpha]_{262}+3470^\circ$, $[\alpha]_{261}+3790^\circ$, $[\alpha]_{260}+3730^\circ$, $[\alpha]_{241}+9120^\circ$, $[\alpha]_{221}-2930^\circ$, $[\alpha]_{207}+1140^\circ$, $[\alpha]_{201}-16100^\circ$, $[\theta]_{279} 0^\circ$, $[\theta]_{275}-122^\circ$, $[\theta]_{274} 0^\circ$, $[\theta]_{273}+323^\circ$, $[\theta]_{270}+128^\circ$, $[\theta]_{268}+256^\circ$, $[\theta]_{263}+484^\circ$, $[\theta]_{261}+467^\circ$, $[\theta]_{260}+601^\circ$, $[\theta]_{259}+456^\circ$, $[\theta]_{256}+598^\circ$, $[\theta]_{227}+34600^\circ$, $[\theta]_{212}+16300^\circ$, $[\theta]_{205}+33300^\circ$. The UV was measured at 25°C in ethanol: $\epsilon_{264-274} 1010-582$, $\epsilon_{228} 14200$.

4-Isobutyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (IV). —The RD and CD were measured at 22°C (*c* 0.1050): $[\alpha]_{589}+267^\circ$, $[\alpha]_{270}+2930^\circ$, $[\alpha]_{268}+2840^\circ$, $[\alpha]_{264}+3490^\circ$, $[\alpha]_{262}+3350^\circ$, $[\alpha]_{240}+9660^\circ$, $[\alpha]_{220}-1870^\circ$, $[\alpha]_{207}+3980^\circ$, $[\alpha]_{198}-1300^\circ$, $[\alpha]_{194}+1790^\circ$, $[\theta]_{278} 0^\circ$, $[\theta]_{275}-74.0^\circ$, $[\theta]_{273}+495^\circ$, $[\theta]_{270}+148^\circ$, $[\theta]_{267}+302^\circ$, $[\theta]_{263}+501^\circ$, $[\theta]_{262}+575^\circ$, $[\theta]_{259}+507^\circ$, $[\theta]_{253}+706^\circ$, $[\theta]_{251}+661^\circ$, $[\theta]_{228}+28500^\circ$, $[\theta]_{214}+10300^\circ$, $[\theta]_{205}+22300^\circ$. The UV was measured at 25°C in ethanol: $\epsilon_{264-273} 913-526$, $\epsilon_{227} 11500$.

4-Thiomethoxymethyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (V). —The RD and CD were measured at 25°C (*c* 0.1080): $[\alpha]_{589}+165^\circ$, $[\alpha]_{274}+2850^\circ$, $[\alpha]_{273}+2780^\circ$, $[\alpha]_{269}+3150^\circ$, $[\alpha]_{268}+3100^\circ$, $[\alpha]_{266}+3530^\circ$, $[\alpha]_{265}+3460^\circ$, $[\alpha]_{262}+4260^\circ$, $[\alpha]_{260}+4120^\circ$, $[\alpha]_{243}+11000^\circ$, $[\alpha]_{218}-2630^\circ$, $[\alpha]_{203}-55.6^\circ$, $[\theta]_{278} 0^\circ$, $[\theta]_{275}-216^\circ$, $[\theta]_{274} 0^\circ$, $[\theta]_{273}+170^\circ$, $[\theta]_{270}-124^\circ$, $[\theta]_{268}+124^\circ$, $[\theta]_{262}+448^\circ$, $[\theta]_{260}+664^\circ$, $[\theta]_{258}+479^\circ$, $[\theta]_{228}+38900^\circ$, $[\theta]_{213}+22300^\circ$, $[\theta]_{212}+23200^\circ$, $[\theta]_{210}+22900^\circ$, $[\theta]_{208}+25400^\circ$. The UV was measured at 25°C in ethanol: $\epsilon_{272-256} 513-987$, $\epsilon_{227} 10200$.

4-Thiomethyl-3-*p*-tosyl-1, 3-oxazolidin-5-one (VI). —The RD and CD were measured at 25°C (*c* 0.1060): $[\alpha]_{589}+278^\circ$, $[\alpha]_{276}+2940^\circ$, $[\alpha]_{275}+2920^\circ$, $[\alpha]_{274}+3130^\circ$, $[\alpha]_{273}+3120^\circ$, $[\alpha]_{271}+3280^\circ$, $[\alpha]_{270}+3130^\circ$, $[\alpha]_{241}+10200^\circ$, $[\alpha]_{219}-3920^\circ$, $[\alpha]_{208}+1150^\circ$, $[\alpha]_{200}-2810^\circ$, $[\alpha]_{196}-1430^\circ$, $[\theta]_{278} 0^\circ$, $[\theta]_{275}-159^\circ$, $[\theta]_{273}+612^\circ$, $[\theta]_{270}+33.5^\circ$, $[\theta]_{267}+193^\circ$, $[\theta]_{266}+369^\circ$, $[\theta]_{265}+352^\circ$, $[\theta]_{262}+855^\circ$, $[\theta]_{259}+621^\circ$, $[\theta]_{232}+4310^\circ$, $[\theta]_{211}+19300^\circ$, $[\theta]_{207}+23700^\circ$, $[\theta]_{205}+20300^\circ$. The UV was measured at 25°C in ethanol: $\epsilon_{260-276} 952-574$, $\epsilon_{228} 10600^\circ$.

4-Isobutyl-1, 3-oxazolidin-5-one (VII). —The RD and CD were measured at 24°C (*c* 0.1020): $[\alpha]_{589}+94.1^\circ$, $[\alpha]_{234}+6980^\circ$, $[\alpha]_{207}-16600^\circ$, $[\alpha]_{200}-11200^\circ$, $[\theta]_{258} 0^\circ$, $[\theta]_{217}+19500^\circ$, $[\theta]_{199}-5410^\circ$, $[\theta]_{197}-1340^\circ$, $[\theta]_{195}-9200^\circ$, $[\theta]_{192}+279^\circ$, $[\theta]_{190}-6410^\circ$, $[\theta]_{188}+4180^\circ$.

2,2-Dimethyl-5-phenyl-1, 3-dioxolan-4-one (VIII). —The RD and CD were measured at 21°C (*c* 0.1020): $[\alpha]_{589}+108^\circ$, $[\alpha]_{268}+1410^\circ$, $[\alpha]_{265}+1290^\circ$, $[\alpha]_{261}+1640^\circ$, $[\alpha]_{258}+1570^\circ$, $[\alpha]_{255}+2560^\circ$, $[\alpha]_{253}+2380^\circ$, $[\alpha]_{232}+4160^\circ$, $[\alpha]_{216}-8910^\circ$, $[\alpha]_{215}-7530^\circ$, $[\alpha]_{214}-9260^\circ$, $[\alpha]_{209}-3650^\circ$, $[\alpha]_{208}-6080^\circ$, $[\alpha]_{205}-3800^\circ$, $[\alpha]_{196}-12200^\circ$, $[\theta]_{272} 0^\circ$, $[\theta]_{268}-15.1^\circ$, $[\theta]_{266} 0^\circ$, $[\theta]_{262}-266^\circ$, $[\theta]_{259} 0^\circ$, $[\theta]_{256}-113^\circ$, $[\theta]_{254} 0^\circ$, $[\theta]_{221}+18000^\circ$, $[\theta]_{218}+980^\circ$, $[\theta]_{215}+2560^\circ$, $[\theta]_{194}-12400^\circ$. The UV was measured at 21°C in ethanol: $\epsilon_{257-268} 154-89.5$, $\epsilon_{202-210} 8090-6500$.

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