

Stereochemistry of organic compounds(19) : On the optical contribution and ¹H-NMR of cyclic derivatives of diethyl d-tartrate

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著者(英語)	Koko Satsumabayashi, Yoko Nishida, Kiyoshi Tanemura
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Stereochemistry of Organic Compounds XIX¹⁾

On the Optical Contribution and ¹H-NMR of Cyclic Derivatives
of Diethyl *d*-Tartrate

Koko SATSUMABAYASHI, Yoko NISHIDA
and Kiyoshi TANEMURA

The Nippon Dental University, School of Dentistry at Niigata,
Hamaura-cho, Niigata 951, JAPAN

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In our earlier studies^{2,3)}, we reported the conformation of tartrate derivatives having dioxolanes. And in the previous paper¹⁾, it has been reported as to the optical contribution of 1,3-dioxolanes having spiro-unionized cyclohexyl derivatives. As a result, the CD spectra assigned to the $n \rightarrow \pi^*$ transition of the carbonyl groups on cyclohexyl derivatives were split up into two opposite signs. Recently, the optical and chiroptical studies on various hetero cyclic compounds were reported⁴⁻¹¹⁾.

In this paper further investigations were carried out with newly synthesized dioxolanes assembled by phenyl derivatives (Compounds I~V), together with the cyclohexyl derivatives (Compounds VI~VIII)¹⁾. The compounds employed are shown in Fig. 1.

Measurements were made with these compounds on their rotatory dispersion (RD), circular dichroism (CD), and ultraviolet absorption (UV) spectra, using ethanol (EtOH) as polar and tetrahydrofuran (T.H.F.) as nonpolar solvents, as well as proton nuclear magnetic resonance (¹H-NMR) spectra.

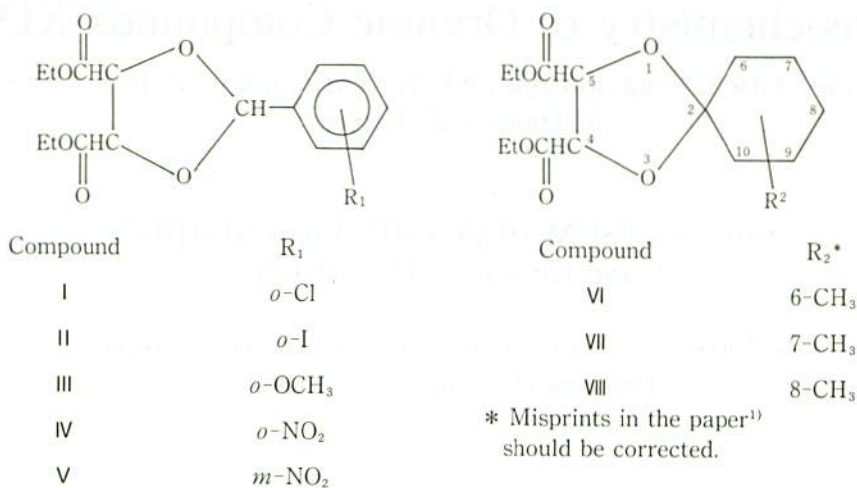


Fig. 1 Structures of cyclic derivatives of *d*-Tartrates examined.

Results and Discussion

In Figures 2, 3, 4, 5 and 6 are given the CD, RD and UV curves of Compounds I, II, III, IV and V respectively. Figure 7 for comparison, shows the CD, RD and UV curves of Compounds VI~VIII¹⁾. The respective data is shown in Table 1. As is clear from Figs. 2~6 and Table 1, the CD and RD values are affected by the different polarity of the solvent. Since the C-C bond between the dioxolane and benzene rings can rotate freely, this seems to indicate that the preferable conformations differ from the solvents. On the other hand, the CD and RD values of Compounds VI~VIII (Fig. 7) are not affected by the differences in the solvents. This is in harmony with the rigid structures of cyclohexyl rings assembled to the dioxolane rings. The CD curves of Compounds I~VIII in ethanol and in tetrahydrofuran are shown respectively in Figs. 8 and 9. All compounds except IV show positive Cotton effects in longer wavelength regions and negative Cotton effects in shorter wavelength regions, while Compound IV shows two positive Cotton effects. The energy level of the C=O group will be considered in the molecular orbitals (Fig. 10). Judging from the energy level, the negative Cotton effects of I~III and V~VIII are due to the $n \rightarrow \pi^*$ of this transition of the C=O group. The weak positive CD bands shown in the longer wavelength regions are due to

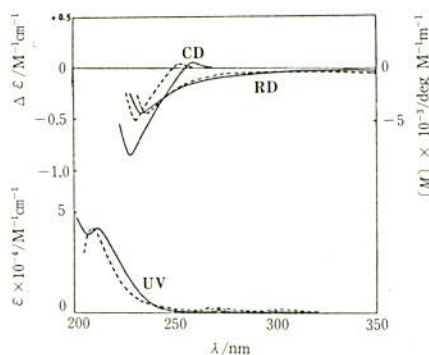


Fig. 2 CD, RD and UV of Compound I: — in EtOH; ---- in T.H.F.

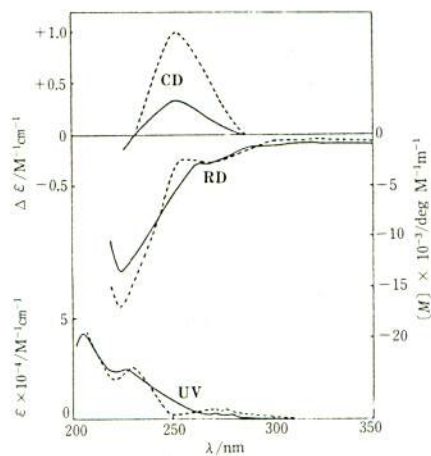


Fig. 3 CD, RD and UV of Compound II: — in EtOH; ---- in T.H.F.

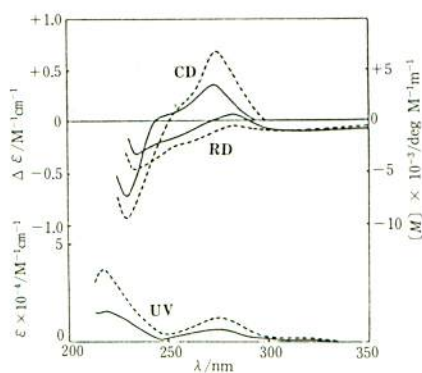


Fig. 4 CD, RD and UV of Compound III: — in EtOH; ---- in T.H.F.

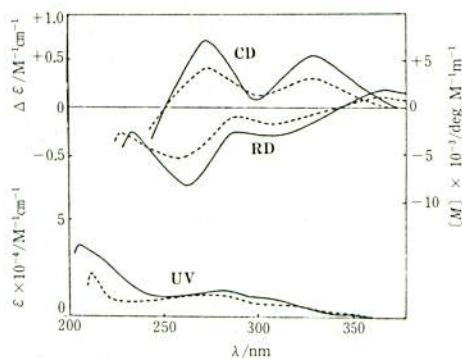


Fig. 5 CD, RD and UV of Compound IV: — in EtOH; ---- in T.H.F.

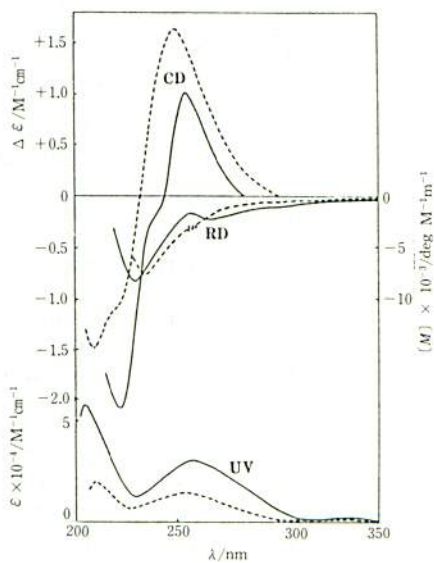


Fig. 6 CD, RD and UV of Compound V: — in EtOH; ---- in T.H.F.

Table 1 Data of CD, RD and UV spectra in EtOH and T.H.F.

Compound	spectrum	solvent	$\lambda_{\max}/\text{nm}(\Delta\epsilon/M^{-1}\text{cm}^{-1}; [M]/\text{deg } M^{-1}\text{m}^{-1}; \epsilon/M^{-1}\text{cm}^{-1})$
I	CD	EtOH	258(+0.0339), 228(-0.870)
		THF	252(+0.0172), 231(-0.530)
	RD	EtOH	234(-4560)
		THF	237(-4590)
	UV	EtOH	273(1490), 213(40200)
		THF	~308(305 shoulder), 273(1400), 266(1630), 211(40400)
II	CD	EtOH	253(+0.342), 225>(negative)
		THF	253(+1.05), 230>(negative)
	RD	EtOH	264(-2280), 225(-13200)
		THF	255(-2300), 224(-16400)
	UV	EtOH	271(2200), 228(24700), 206(43000)
		THF	273(4170), 231(25600)
III	CD	EtOH	274(+0.367), 230(-0.755)
		THF	276(+0.664), 230(-0.961)
	RD	EtOH	310(-441), 285(+593), 235(-3430)
		THF	302(-473), 284(-244), 234(-4860)
	UV	EtOH	~308(101 shoulder), 276(5370), 216(15700)
		THF	~320(235 shoulder), 276(11800), 218(38000)
IV	CD	EtOH	330(+0.458), 274(+0.712)
		THF	330(+0.302), 275(+0.412)
	RD	EtOH	367(+1930), 308(-3340), 288(-2610), 264(-8630), 234(-2870)
		THF	366(+1050), 310(-1930), 288(-1020), 260(-5760), 228(-2880)
	UV	EtOH	306(9390), 282(13600), 206(37600)
		THF	~320(5040 shoulder), 284(9840), 258(10400), 213(22500)
V	CD	EtOH	255(+1.01), 222(-2.12)
		THF	250(+1.65), 210(-1.47)
	RD	EtOH	314(-566), 264(-2660), 258(-1330), 230(-8480)
		THF	235(-7870)
	UV	EtOH	~328(1120 shoulder), 260(32000), 206(59600)
		THF	~330(258 shoulder), 258(14800), 211(20600)
VI	CD	EtOH	234(+0.112), 203(-0.645)
		THF	237(+0.148), 210(-0.515)
	RD	EtOH	228(-2840)
		THF	250(-319), 225(-2320)
	UV	EtOH	~310(9.86 shoulder), 273(116), ~223(403 shoulder)
		THF	266(253)
VII	CD	EtOH	239(+0.0485), 212(-0.773)
		THF	242(+0.0709), 212(-0.833)
	RD	EtOH	229(-3780)
		THF	230(-3510)
	UV	EtOH	278(74.9), 271(76.3), ~215(610 shoulder)
		THF	280(130), 271(143)
VIII	CD	EtOH	239(+0.0885), 210(-0.994)
		THF	242(+0.0745), 212(-0.821)
	RD	EtOH	250(-1460), 230(-3690)
		THF	230(-3380)
	UV	EtOH	~360(10.0 shoulder), 274(414), ~226(535 shoulder)
		THF	267(823)

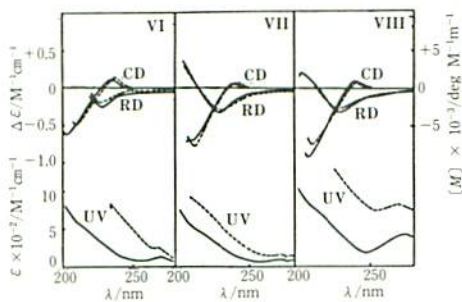


Fig. 7 CD, RD and UV of Compound VI~VIII: — in EtOH; - - - in T.H.F.

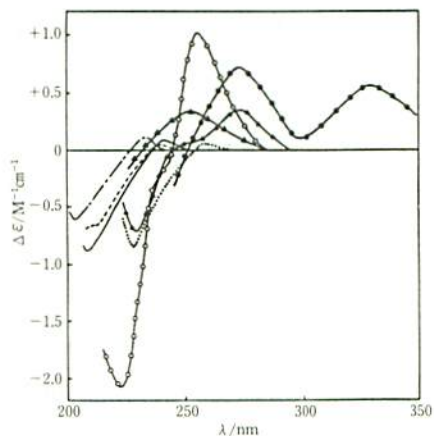


Fig. 8 CD of Compound I~VIII in EtOH: I, -○-○- II, -●-●- III, -◆-◆- IV, -○-○- V, - - - VI, - - - VII, — VIII

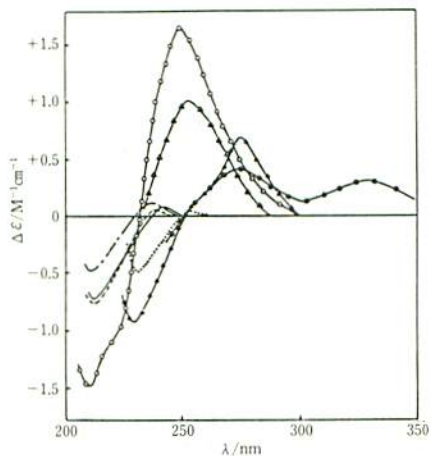


Fig. 9 CD of Compound I~VIII in T.H.F.; I, -○-○- II, -●-●- III, -◆-◆- IV, -○-○- V, - - - VI, - - - VII, — VIII

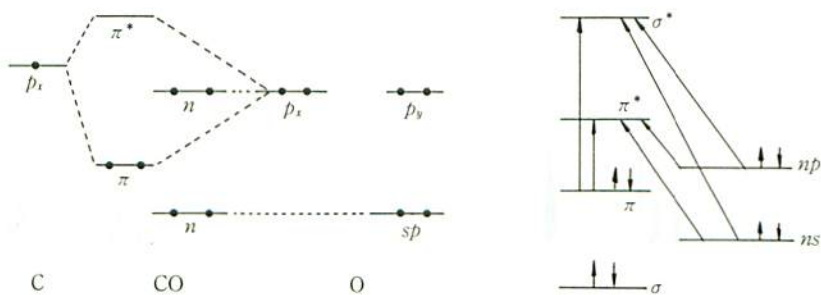


Fig. 10 Energy-level and molecular orbital energy diagrams of C=O.

the exciton band¹²⁾ formed by the coupling of the two carbonyl groups. Furthermore, it is considered that the positive Cotton effect at 330 nm shown only in Compound IV is due to the steric hindrance between the nitro group and the oxygen atom in dioxolane ring. In Compound IV the antibonding electrons of O-atom seem to bring about orbital interaction with *o*-NO₂ chromophore, and cause a positive CD band at 330 nm. It should be noted that the sign of the Cotton effect to assigned to the inherent $n \rightarrow \pi^*$ transition is negative below 230 nm.

Next, to investigate the ring conformation ¹H-NMR spectra were employed. The NMR spectra of all the compounds are illustrated in Figs. 11~18, and this data is listed in Tables 2 and 3. In the NMR spectra, all the compounds are observed to have the characteristic absorptions based upon all protons. As may be seen in Table 2 and Figs. 11~15, the two protons of the ring methines are observed as the AB-type patterns. Therefore, the dihedral angles of H_A-C-C-H_B are calculated by applying Shimizu's equation, $J_{AB} = C + A|\cos\theta|$ as already reported^{2,3)}. The results are given in Table 4. As is evident in Table 4, the conformations of all the compounds are nearly

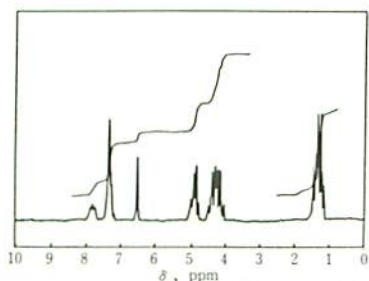


Fig. 11 NMR of Compound I.

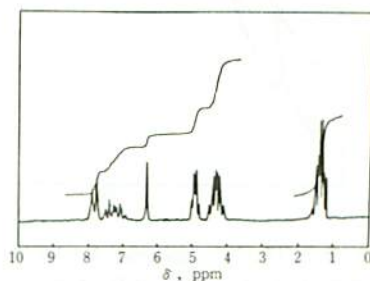


Fig. 12 NMR of Compound II.

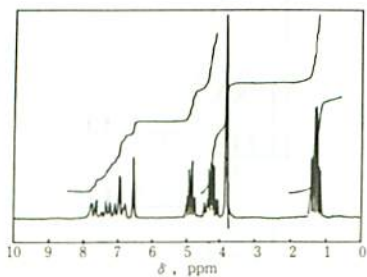


Fig. 13 NMR of Compound III.

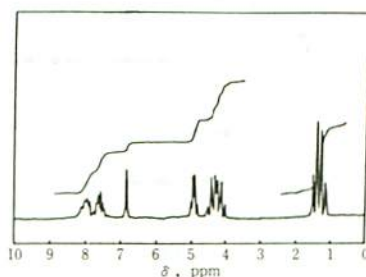


Fig. 14 NMR of Compound IV.

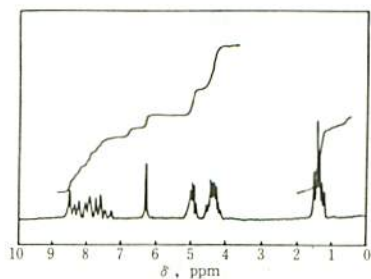


Fig. 15 NMR of Compound V.

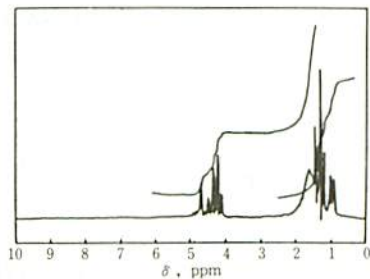


Fig. 16 NMR of Compound VI.

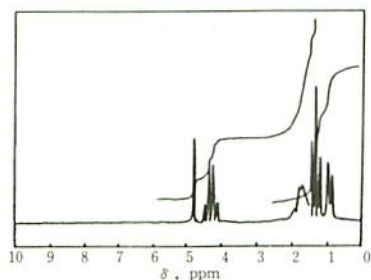


Fig. 17 NMR of Compound VII.

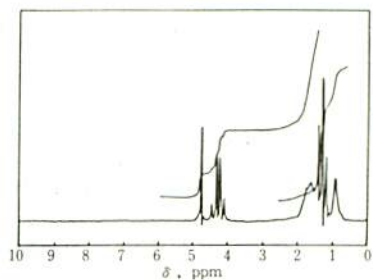


Fig. 18 NMR of Compound VIII.

Table 2 ¹H-NMR data of all Compounds I ~ V (δ)

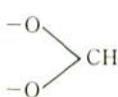
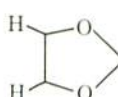


Compound	ArH				
I	7.24-7.50(2 H, m) 7.68-8.02(1 H, m)	6.52(1 H, s)	4.83(1 H, d) 4.96(1 H, d)	4.25(2 H, q) 4.33(2 H, q)	1.28(3 H, t) 1.35(3 H, t)
II	6.90-7.57(2 H, m) 7.70-8.00(1 H, m)	6.30(1 H, s)	4.85(1 H, d) 4.97(1 H, d)	4.26(2 H, q) 4.34(2 H, q)	1.30(3 H, t) 1.38(3 H, t)
III	6.76-7.83(4 H, m)	6.54(1 H, s)	4.81(1 H, d) 4.95(1 H, d)	4.24(2 H, q) 4.30(2 H, q)	1.27(3 H, t) 1.32(3 H, t) 3.80(3 H, s)
IV	7.46-8.20(4 H, m)	6.81(1 H, s)	4.86(1 H, d) 4.96(1 H, d)	4.22(2 H, q) 4.34(2 H, q)	1.22(3 H, t) 1.37(3 H, t)
V	7.43-8.60(4 H, m)	6.28(1 H, s)	4.87(1 H, d) 4.99(1 H, d)	4.30(2 H, q) 4.36(2 H, q)	1.33(3 H, t) 1.40(3 H, t)

Table 3 $^1\text{H-NMR}$ data of all Compounds VI~VIII (δ)

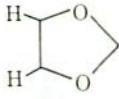



Compound					
VI	4.69(2 H, s)	4.26(4 H, q)	1.30(6 H, t)	1.16-2.10(9 H,m)	0.96(3 H, d)
VII	4.76(2 H, s)	4.27(4 H, q)	1.30(6 H, t)	1.16-2.10(9 H,m)	0.94(3 H, d)
VIII	4.75(2 H, s)	4.26(4 H, q)	1.30(6 H, t)	1.10-2.01(9 H,m)	0.95(3 H, br s)

Table 4 Chemical shifts and dihedral angles of Compounds I~V

Compound	Chemical shift (δ)	J_{AB} (Hz)	θ
I	4.83	4.00	53°
	4.96		
II	4.85	3.60	58°
	4.97		
III	4.81	4.20	51°
	4.95		
IV	4.86	3.20	61°
	4.96		
V	4.87	4.10	52°
	4.99		

identical, where the two carboxylate groups are in the trans-form and, in all cases, show the half-chair form¹³⁾. In Compound IV the dihedral angle indicates the largest of all. This fact shows that the twisting of the five-membered ring in Compound IV is the greatest of all, and so this result can be correlated with the CD band at 330 nm. In Compound II the angle shows the second largest by the steric hindrance of bulky substituent on the ortho-position, but there does not exist an optically active CD band around 330 nm because of the absence of the π -orbital. Moreover, two ethyl groups within the ester groups are not equivalent, that is to say, two ester groups are situated in different environments.

On the other hand, in the cases of Compounds VI~VIII the spin-spin coupling of ring

methines are not observed, and the signals from two ethyl groups are not split. From this fact it can be deduced that in the cases of Compounds VI~VIII, two hydrogens and two ester groups attached to the asymmetric carbons are situated in the same environments because of the $1C \rightleftharpoons C1$ equilibrium of cyclohexyl rings. This explains smaller optical contribution for Compounds VI~VIII compared with Compounds I~V.

From the results of the $^1\text{H-NMR}$ spectra, the conformation of all compounds is given in Fig. 19. This conformer has a negative chirality, and the sign of Cotton effect assigned to the inherent $n \rightarrow \pi^*$ transition of $\text{C}=\text{O}$ is in accordance with this chirality.

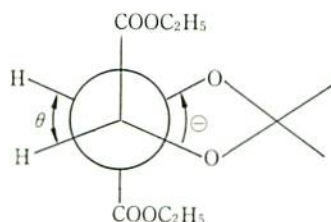


Fig. 19 Conformation of Compounds I~VIII.

Experimental

Materials: The samples were prepared according to the methods described in the literature¹⁴⁾ with a slight modification.

Diethyl *o*-chlorobenzylidene *d*-tartrate (Compound I).

Colorless needles; mp 34–35°C.

Diethyl *o*-iodobenzylidene *d*-tartrate (Compound II).

Pale yellow liquid; bp 198°C/6 Torr.

Diethyl *o*-methoxybenzylidene *d*-tartrate (Compound III).

Colorless liquid; bp 200–202°C/5 Torr.

Diethyl *o*-nitrobenzylidene *d*-tartrate (Compound IV).

Colorless needles; mp 60°C.

Diethyl *m*-nitrobenzylidene *d*-tartrate (Compound V).

Colorless needles; mp 42–43°C.

Measurements: The RD and CD were measured in ethanol and tetrahydrofuran at 20–25°C, in the wavelength region from 200 nm to 600 nm with JASCO ORD/UV-5

type optical rotatory dispersion recorder. The UV spectra were measured with the same conditions as the RD and CD Measurements by Hitachi Model 320 Spectrophotometer. The NMR spectra were recorded on a Hitachi, Model R-24B, at room temperature in CDCl_3 as a solvent. Chemical shifts are in ppm (δ) from SiMe_4 as the internal standard and J -values are given in Hz .

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