DITHIOLANE AND DITHIANE: NEW CHIROPTICAL GROUP FOR DETERMINATION OF ABSOLUTE CONFIGURATION AT α- AND β-POSITIONS TO THE GROUPS BY CD

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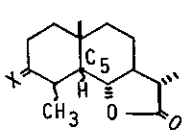
Dithiolane and dithiane, known as dithioacetals, have been famous protective group for carbonyl and found in some papers with CD measurement failed so far to find a rule. We found at first a empirical rule between CD signs at 237 and 252 nm and absolute configurations at α- and β-positions to dithiolane(1) group of tetrahydro-ℓ-α-santonin derivatives without exception. Some dithianes(2) and oxathiolanes(3) derivatives were examined for utilization of the rule with its scope and limitation.

Ligand field theory and molecular orbital method(CNDO/II) were applied to the problem to clarify the mechanism of the rule using atom coordinates from X-ray crystallography as the same as that of coordination metal.

Results: 1) All the CD signs in dithioacetals(1 and 2) at 237 and 252 nm well corresponded to absolute configurations of α- and β-positions to the group; plus and minus signs for rectus(R) and sinister(S), respectively. 2) Although the distance between symmtric carbons and bivalent sulfurs in dithioacetals were about 2.8 Å. for α- and 3.2 Å for β-positions in solid state, the strengths of two interactions were almost same as some examples shown in Table 1. 3) C_{2v} symmetry for bivalent sulfur indicated that electronic exitation from lone pair(b_1) to exited stats(a_1 and a_2) should be allowed in UV(or CD) absorption, probably to three d-orbitals (d_z^2, $d_{x^2-y^2}$ and d_{xy}). 4) MO calculation(CNDO/II) for those dithiolanes and dithianes indicated that the contribution from d_z^2 and $d_{x^2-y^2}$ for CD absorption at 237 and 252 nm have been estimated to be approximately 20 %.

Table 1.



X=		Absolute configurations at C_4	Absolute configurations at C_5	Amplitudes[θ] at 237 nm	Amplitudes[θ] at 252 nm
[S,S]X	1a	S	S	-2,920	-2,800
	1b	R	S	+3,500	-1,380
	1c	R	R	+6,320	+6,130
	1d	S	R	-2,450	+1,730
<S,S>X	2b	R	S	+9,050	-3,800
	2d	S	R	-1,800	+6,300