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Stereochemistry of 9-Arylthioxanthene 10-Oxides and 10,10-Dioxides[1]

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Abstract -- The stereochemistry of 9-arylthioxanthene 10-oxides and 10,10-dioxides were studied by the nmr spectroscopy. The conformation was elucidated.

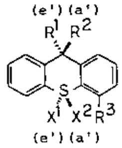
Current interest in rotational barriers and conformational studies in fluorene and 9,10-dihydroanthracene derivatives[2] has led us to investigate the stereochemical studies of 9-arylthioxanthene 10-oxides and 10,10-dioxides. The sulfoxides and sulfones in this communication were synthesized to study the chemistry of 9,10-disubstituted 10-thiaanthracenes.[3,4]

Ternay and Evans have discussed the stereochemistry of 9-alkylthioxanthene 10-oxides and 10,10-dioxides.[5] However, investigations on the chemistry of 9-arylthioxanthene derivatives are little known.

The conformation of 9-arylthioxanthene 10-oxides was made clear by the detailed nmr studies. The nmr spectral data were summarized in Table 1. Conformation of the 9-aryl group was determined by the fact that the anisotropic effect of 9-aryl group caused the upfield shift of the proximal peri protons (H_1 and H_8) and that the thioxanthene ring shielded the protons or the substituents of the 9-aryl group.

Four isomers (A - D) are possible for 9-arylthioxanthene 10-oxides from conformational and configurational point of view. In the conformer C, the 9-aryl group is pseudoaxial (a') and the sulfinyl oxygen atom is pseudoequatorial (e'). Therefore, protons of the 9-aryl group especially 2'- and 6'-protons are considered to be shielded by the thioxanthene ring. Compound 2 showed the nmr signals of 2'- and 6'-protons and 3'-, 4'- and 5'-protons at δ 6.78 - 7.02 and 7.02 - 7.29, respectively. The assignment was drawn from the spectra of 9-pentadeuteriophenylthioxanthene 10-oxides (3 and 4). When the 9-phenyl group and the sulfinyl oxygen atom occupy the a' conformation, namely in the conformer A, the sulfinyl

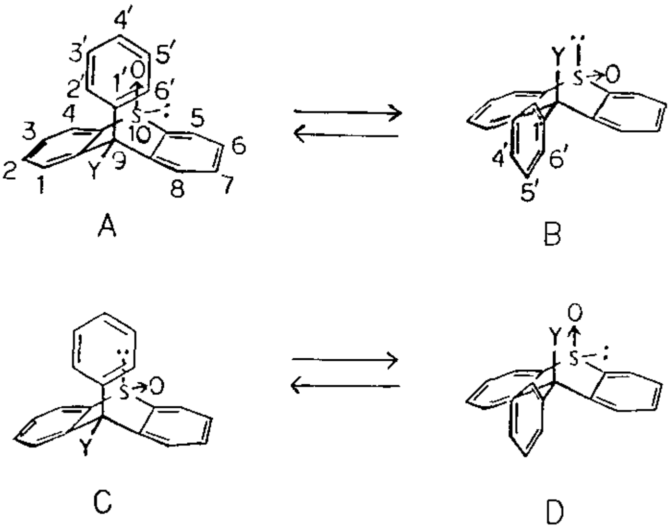
Table 1. NMR Spectral Data of 9-Arylthioxanthene 10-Oxides in $CDCl_3$ and C_6D_6[a)]



Compd No.	R^1 b)	R^2 b)	R^3	X^1	X^2	$H_{1,8}$ (mc) c)	$H_{4,5}$ (mc) c)	$H_{4,5}$ in C_6D_6 (mc) c)	$\Delta_{H_{4,5}}$ d)	H_9 ($W_{1/2}$Hz)	other absorptions	preferred conformation
1	C_6H_5	H	H	O	-:	6.90-7.13 (7.02)	7.85-8.17 (8.01)	8.00-8.29 (8.15)	-0.14	4.83 (2.8)		B g)
2	H	C_6H_5	H	O	-:	-- e)	7.83-8.15 (7.99)	7.92-8.22 (8.07)	-0.08	5.52 (2.1)	6.78-7.02($H_{2',6'}$) 7.02-7.29($H_{3',4',5'}$)	C g)
3	C_6D_5	H	H	O	-:	6.86-7.13 (7.00)	7.82-8.15 (7.99)	8.01-8.31 (8.16)	-0.17	4.83 (2.7)		B
4	H	C_6D_5	H	O	-:	-- e)	7.81-8.14 (7.98)	7.93-8.22 (8.08)	-0.10	5.52 (1.5)		C
5	H	C_6H_5	Me	-:	O	-- e)	7.72-8.10 (7.91)	7.55-7.85 (7.70)	0.21	5.37 (3.0)		A
6	C_6H_5	Pr^i	H	O	-:	6.60-6.80 (6.70)	7.90-8.13 (8.02)	8.10-8.35 (8.23)	-0.21	--		B
7	Pr^i	C_6H_5	H	O	-:	-- e)	7.79-8.06 (7.93)	7.87-8.22 (8.05)	-0.12	--	6.49-6.84($H_{2',6'}$) 6.88-7.21($H_{3',4',5'}$)	C
8	Mes	H	H	-:	O	6.94-7.23 (7.09)	7.90-8.20 (8.05)	7.70-7.97 (7.84)	0.21	6.28 (3.8)	1.88($Me_{2',6'}$) 2.39($Me_{4'}$)	D
9	Dur	H	H	-:	O	6.92-7.23 (7.08)	7.91-8.20 (8.06)	7.70-7.97 (7.84)	0.22	6.43 (2.9)	1.77($Me_{2',6'}$) 2.32($Me_{3',5'}$)	D
10	Dur	H	Me	-:	O	6.73- f)	7.90-8.19 (8.05)	7.68-7.92 (7.80)	0.25	6.46 (3.5)	1.18($Me_{6'}$), 2.21($Me_{2'}$) 2.37($Me_{3',5'}$)	D
11	H	C_6F_5	H	O	-:	-- e)	7.91-8.25 (8.08)	8.07-8.36 (8.22)	-0.14	6.22 (2.1)		C

a) Chemical shifts (δ) are reported in parts per million downfield from Me_4Si. b) Pr^i = isopropyl; Mes = mesityl; Dur = 2,3,5,6-tetramethylphenyl. c) The center of the multiplet resulting from these protons. d) Δ = ASIS value = $\delta_{CDCl_3} - \delta_{C_6D_6}$. e) The upfield shifts of $H_{1,8}$ were not observed. f) The downfield side of the absorption was obscured by the absorption of the other aromatic protons. g) Reference 4.

group deshields protons of the 9-aryl group. Consequently, the definitive upfield shift cannot be observed in compound 5. In conformers B and D in which the 9-aryl group exists in the e' array, peri protons (H_1 and H_8) of the thioxanthene ring

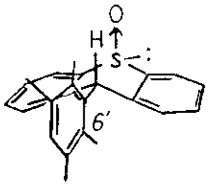


are expected to be shielded by the 9-aryl group. The upfield shift of H_1 and H_8 was observed in compounds 1, 3, 6, 8, 9 and 10. Since the conformer D has the a' sulfinyl group, the 9a' proton should be considerably deshielded relative to the 9e' proton in compound 1. Compounds 8, 9 and 10 showed this downfield shift.

The conformation of the sulfinyl oxygen atom was determined by aromatic solvent induced shifts (ASIS) which were applied to determine the conformation of the sulfinyl oxygen atom of 9-alkylthioxanthene 10-oxides by Ternay and Evans.[5] In the thioxanthene system the ASIS value ($\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$) showed negative for the e' sulfinyl oxygen atom and positive for the a' conformation. Compounds 5, 8, 9 and 10 have the a' sulfinyl oxygen atoms and compounds 1, 2, 3, 4, 6, 7 and 11 take the 10e' conformation.

The nmr spectra of 9-arylthioxanthene 10-oxides in C_6D_6 exhibited the absorption of the H_4 and H_5 protons at higher than δ 7.9 and lower than δ 8.0 due to the deshielding by 10a' and 10e' sulfinyl oxygen atoms, respectively. 9-Aryl-4-methylthioxanthene 10-oxide (5) prefers that conformation in which the sulfinyl oxygen atom is a'.

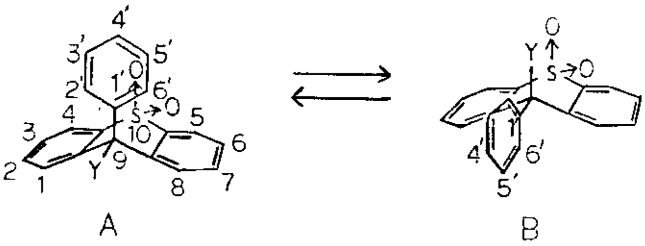
When both 2'- and 6'-protons of the 9-aryl group were substituted by methyl groups the rotation about C_9-$C_{1'}$ bond was hindered and 6'-methyl group is packed just



under the thioxanthene ring and hence affected by the anisotropy of the thioxanthene ring. Therefore, the signal of the 6'-methyl group appeared at quite a high field.

A pair of stereoisomers isolated (B and C) cannot be the conformers by ring inversion.

On the other hand, the stereoisomerism of 9-arylthioxanthene 10,10-dioxides were examined in relation to the sulfoxides. Here, two isomers (A and B) arising from ring inversion may exist in 9-arylthioxanthene 10,10-dioxides.

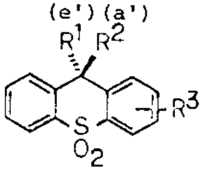


In the conformer B, H_1 and H_8 should be shifted to the upfield since the 9-aryl group is e' and faces H_1 and H_8, while this upfield shift would not be observed in the conformer A. (see Table 2)

Compound <u>21</u> having a substituent of a methyl group at C_1-position is believed to assume the conformation A and the other dioxides existed in the isomer B.

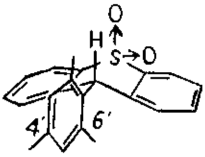
9-Mesityl- and 9-(2,3,5,6-tetramethylphenyl)thioxanthene 10,10-dioxides showed a methyl absorption (6'-methyl) at quite a high field (δ 1.23 - 1.97) as observed in the corresponding sulfoxides.

Table 2. NMR Spectral Data of 9-Arylthioxanthene 10,10-Dioxides in $CDCl_3$ a)



Compd No.	R^1 b)	R^2	R^3	$H_{1,8}$ (mc) c)	$H_{4,5}$ (mc) c)	other absorptions	preferred conformation
12	C_6H_5	H	H	7.09- d)	7.98-8.30(8.14)	7.35(C_6H_5)	B
13	C_6D_5	H	H	7.09-7.30(7.20)	7.98-8.30(8.14)		B
14	Mes	H	H	6.87-7.21(7.04)	8.13-8.43(8.28)	1.33($Me_{6'}$), 2.40($Me_{4'}$), 2.45($Me_{2'}$)	B
15	Mes	H	3-Et	6.77- d)	8.11(H_4) 8.17-8.40(8.29)	1.36($Me_{6'}$), 2.40($Me_{4'}$), 2.45($Me_{2'}$)	B
16	Mes	H	3-Pr	6.75- d)	8.08(H_4) 8.13-8.42(8.28)	1.35($Me_{6'}$), 2.40($Me_{4'}$), 2.45($Me_{2'}$)	B
17	Mes	OH	H	7.03-7.35(7.19)	8.04-8.35(8.20)	1.97($Me_{2',6'}$), 2.33($Me_{4'}$)	B
18	Dur	H	3-Pr	6.75- d)	8.13(H_4) 8.18-8.44(8.31)	1.23($Me_{6'}$), 2.21($Me_{2'}$), 2.37($Me_{5'}$) 2.43($Me_{3'}$)	B
19	C_6F_5	H	H	6.83-7.23(7.03)	8.07-8.46(8.27)		B
20	C_6F_5	H	3-Me	6.79(H_1) 6.78-7.03(6.91)	7.95(H_4) 7.99-8.30(8.15)		B
21	H	C_6F_5	1-Me	-- e)	7.85-8.20(8.03)		A

a) Chemical shifts (δ) are reported in parts per million downfield from Me_4Si. b) Mes = mesityl; Dur = 2,3,5,6-tetramethylphenyl. c) The center of the multiplet resulting from these protons. d) The downfield side of the absorption was obscured by the absorption of the other aromatic protons. e) The upfield shifts of $H_{1,8}$ were not observed.



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