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Registry No. 1, 13537-82-1; 2, 72952-61-5; 3, 13357-88-5; 4, 13341-72-5; 5, 591-24-2; 8, 15174-78-4; 9, 1919-00-2; 10, 13674-37-8; 12, 22273-97-8; 12 2,4-DNP, 22273-98-9; 13, 72952-62-6; ethyl 2-iodopropionate, 31253-08-4; ethyl 2-bromopropionate, 535-11-5; (±)-menthofuran, 59553-66-1; 2-propanol, 67-63-0.

The Stereochemistry of Thioxanthenium Methylides. Use of 1,4-Dimethylthioxanthenium Methylides as Model Compounds

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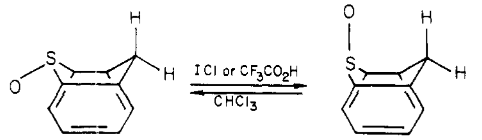
We previously have shown[1] that the preferred conformation of the sulfinyl oxygen in thioxanthene 10-oxide (1)

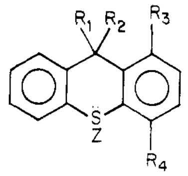


1e′ 1a′

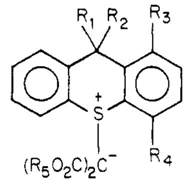
and related thioxanthene 10-oxides (e.g., *cis*- and *trans*-9-methylthioxanthene 10-oxides (*cis*- and *trans*-**2**)) is one in which the sulfinyl oxygen occupies the pseudoequatorial position (e′). More recently, we have demonstrated that complexation of the sulfinyl oxygen of **1** with iodine monochloride[2] or trifluoracetic acid[3] increases the amount of the pseudoaxial conformer (a′).

Since X-ray data[4] suggest that the a′ position is less hindered than the e′ position and since we recently have demonstrated[5] that phenoxathiin sulfoxide (**3**) exists in the a′ array, we now have determined the conformational preference of several ylides derived from thioxanthene in order to assess the effect of increased bulk (i.e., O$^-$ to CR$_2^-$) upon the stereochemistry about sulfur in these systems.

The ylides used in this study are derived from thioxanthene (**4**), 9,9-dideuteriothioxanthene (**5**), 1,4-dimethylthioxanthene (**6**), and 9,9-dideuterio-1,4-dimethylthioxanthene (**7**). We have already shown that a methyl group peri to sulfur (i.e., C4-CH$_3$) forces a proximal sulfinyl to adopt the a′ conformation in various thioxanthene sulfoxides[1b] and that peri methyl groups force C9 alkyl groups into the a′ array in thioxanthenes[6] and 9,10-dihydroanthracenes.[7] The same steric repulsions will be present in ylides derived from **6** and **7** and will permit them to be used as models for ylides having an a′ array. In turn, their spectral parameters can be used to deduce the conformation of "uncongested" ylides derived from **4** and **5**.



	R$_1$	R$_2$	R$_3$	R$_4$	Z
1	H	H	H	H	O
2	CH$_3$	H	H	H	O
4	H	H	H	H	··
5	D	D	H	H	··
6	H	H	CH$_3$	CH$_3$	··
7	D	D	CH$_3$	CH$_3$	··



	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$
8	H	H	CH$_3$	CH$_3$	CH$_3$
9	D	D	CH$_3$	CH$_3$	C$_2$H$_5$
10	H	H	H	H	CH$_3$
11	D	D	H	H	C$_2$H$_5$

1,4-Dimethylthioxanthenium bis(carbomethoxy)methylide (**8**) and 9,9-dideuterio-1,4-dimethylthioxanthenium bis(carbethoxy)methylide (**9**) must, by virtue of their C4-CH$_3$ groups, be constrained to the a′ conformation. This view is supported by the ^{1}H NMR spectra of the C9-CH$_2$ group of **8**. Thus, the a′ proton[8] occurs downfield of the e′ proton (see Table I). This is similar to what is observed when the corresponding sulfinyl group is a′.[1b,3]

Study of **9** permitted analysis of the methylene region of the ethoxy group which might have otherwise been confounded by overlap with the C9-CH$_2$ region. This a′ ethoxy group is characterized by a triplet centered at δ 1.20 (J = 7 Hz) and a quartet centered at δ 4.08 (J = 7 Hz). Deuteration prevented observation of the C9-methylene group; however, it is assumed to be similar to that of **8**.

Thioxanthenium bis(carbomethoxy)methylide (**10**) exhibits a pair of AB doublets for its methylene group which is strikingly different from that of **8**. Thus, the broadened wing of the "AB quartet" (C9-Ha′) is found upfield of the sharper (e′) wing. This argues that the malonyl residue in **10** does not have the same conformation as in **8** and is, therefore, e′. 9,9-Dideuteriothioxanthenium bis(carbethoxy)methylide (**11**) also was prepared and its methyl resonance was observed to be different from that of **9**. This is consistent with the view that **9** and **11** have different geometries.

We conclude that, like the corresponding sulfoxides, ylides **10** and **11** exist in the e′ conformation. Moreover, we have shown that ylides **8** and **9** serve as models for the a′ array, much as do the corresponding sulfoxides. Since hydrogen bonding increases the amount of a′ conformer present in **1**, and since these ylides (**10** and **11**) exist in the e′ array, our current results are consistent with the view that the "effective size" of the hydrogen-bonded sulfinyl

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[8] Identified by its relative broadness.[1] (The bandwidth at half-height of the more intense peak of the downfield portion of the AB quartet was approximately 1.5 times as large as the comparable peak of the upfield portion.) Long-range coupling to the aryl protons broadens the C9-Ha′.

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Table I. ^{1}H NMR Parameters[a]

compd	C9-H[b]	Ar-CH$_3$	*C*-alkyl	Ar-H
8	4.65, 3.97	2.35, 2.52	3.62	6.8–7.6
9		2.37, 2.55	1.20,[c] 4.08[d]	6.9–7.8
10	3.91, 4.31		3.60	7.2–7.8
11			0.93,[c] 4.02[d]	7.2–7.9

[a] Deuteriochloroform solvent; 36 °C. Chemical shifts in parts per million downfield from internal Me_4Si.
[b] Chemical shifts for H_A and H_B of a pair of AB doublets calculated by using $|\nu_A - \nu_B| = (|\nu_1 - \nu_4| \times |\nu_2 - \nu_3|)^{1/2}$; $J = 18$ Hz. The broader resonance (Ha′) is given first.
[c] CH_2CH_3; $J = 7$ Hz. [d] CH_2CH_3; $J = 7$ Hz.

group (and the sulfinyl group bonded to halogens) is greater than that of the dialkylmalonyl residues under dicussion.

Experimental Section[9]

9,9-Dideuterio-1,4-dimethylthioxanthene (7). 1,4-Dimethylthioxanthene (1.5 g, 6.6 mmol) was added to 20 mL of CH_3OD which had been reacted with a pea-sized piece of sodium; the reaction mixture was refluxed for 48 h. The solvent was then removed and the residue washed with deuterium oxide and dried to afford 1.5 g (6.6 mmol, 100%) of the desired product, mp 78–80 °C. The ^{1}H NMR exhibited only those peaks due to aryl H and aryl CH_3.

Diethyl Diazomalonate. This compound was prepared according to literature methods[10] in 69% yield.

Dimethyl Diazomalonate. This compound was prepared similarly to diethyl diazomalonate and was obtained in 77% yield.[10,11]

9,9-Dideuteriothioxanthenium Bis(carbethoxy)methylide (11).[12] A mixture of 9,9-dideuteriothioxanthene[13] (2.0 g, 10.2 mmol), diethyl diazomalonate (1.7 g, 9.3 mmol), and anhydrous copper(II) sulfate was heated for 4 h at 90–95 °C. After the solution was cooled, chloroform was added and the insoluble residue removed by filtration. The solvent was then removed (nitrogen stream) and the residue recrystallized from benzene/ethyl acetate (2:1) to afford 1.5 g (4.2 mmol, 45%) of colorless crystals, mp 191–192 °C.[14]

9,9-Dideuterio-1,4-dimethylthioxanthenium Bis(carbethoxy)methylide (9).[12] A mixture of 9,9-dideuterio-1,4-dimethylthioxanthene (1.1 g, 5.0 mmol), diethyl diazomalonate (1.8 g, 9.9 mmol), toluene (1 mL), and anhydrous copper sulfate (200 mg) was heated for 4 h at 100 °C under a nitrogen atmosphere. After the mixture was cooled, the product was suspended in chloroform and filtered. The filtrate was concentrated to a brown oil and then triturated with hexane (15 × 2 mL) and methanol (2 × 1 mL) to afford 230 mg (12%) of **9**, mp 160–162 °C.

Thioxanthenium Bis(carbomethoxy)methylide (10).[12] A mixture of thioxanthene (2.0 g, 10 mmol), dimethyl diazomalonate (3.5 g, 22 mmol), and anhydrous copper(II) sulfate (0.060 g, 0.38 mmol) was heated at 90–95 °C for 3 h. After the solution was cooled, the reaction mixture was triturated with chloroform and the insoluble residue removed by filtration. Removal of the solvent (nitrogen stream) followed by recrystallization of the residue (2:1 benzene/ethyl acetate) afforded 0.64 g (2.0 mmol, 20%) of **10**, as colorless crystals, mp 203–204 °C.

1,4-Dimethylthioxanthenium Bis(carbomethoxy)methylide (8).[12] A mixture of 1,4-dimethylthioxanthene (3.0 g, 13 mmol), dimethyl diazomalonate (4.0 g, 25 mmol), naphthalene (2.0 g), and anhydrous copper sulfate (100 mg) was heated for 4 h at 100 °C under a nitrogen atmosphere. After the mixture was cooled, the solvent (naphthalene) was removed by trituration with hexane (6 × 20 mL). The resulting green solid was suspended in chloroform and filtered. After evaporation of the solvent, the residue was triturated with hexane (6 × 50 mL) and then recrystallized from benzene/ethyl acetate (2:1) to afford 1.6 g (4.5 mmol, 35%) of **8** as fine white crystals; mp 194–198 °C. Further trituration with hexane (4 × 2 mL) raised the mp to 198–199 °C.[15]

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Registry No. 4, 261-31-4; 5, 24624-33-7; 6, 17394-13-7; 7, 72844-60-1; 8, 72844-61-2; 9, 72844-62-3; 10, 72447-77-9; 11, 72844-63-4; diethyl diazomalonate, 5256-74-6; dimethyl diazomalonate, 6773-29-1.

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[9] Melting points were obtained by using a Mel-Temp apparatus and a Büchi melting point device and are corrected. Boiling points are uncorrected. New compounds (8–11) gave satisfactory analyses (C, H, S) and their NMR spectra were completely consistent with assigned structures. Homogeneity was established by TLC (silica gel) or recrystallization to a constant melting point and NMR spectrum. NMR spectra were recorded on Varian Models T-60 and HA-100.

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[12] The method is adopted from Ando, W.; Yagihara, T.; Tozune, S.; Imai, I.; Suzuki, J.; Toyama, T.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1972**, *37*, 1721. We have observed significant increase in yields by using toluene as a "solvent" for this reaction.

[13] Prepared quantitatively, by reacting thioxanthene with an excess of CH_3OD and $NaOCH_3$.

[14] Since this work was completed, this structure conformation has been confirmed by X-ray crystallography (W. H. Watson and A. L. Ternay, Jr., in preparation).

[15] When conducted in the absence of solvent, the reaction afforded the isomeric dimethyl 9-(1,4-dimethylthioxanthenyl)malonate, mp 123–124 °C. The structure of this a′-substituted thioxanthene was established by X-ray crystallography (W. H. Watson, in preparation).

Natural-Abundance ^{15}N Nuclear Magnetic Resonance Spectroscopy. Unambiguous Evidence for Lack of Influence of Lone-Pair Orbital Orientation on Piperidine ^{15}NH Chemical Shifts

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Recently, Duthaler et al. reported that ^{15}N chemical shifts of *N*-methylpiperidines appear to depend on the configuration of the N substituent, but those of the NH-substituted piperidines do not.[1] The latter inference was based on the existence of a simple linear correlation between the piperidine ^{15}N shifts and the ^{13}C shifts of hydrocarbon analogues. Such a correlation might not have been expected because piperidines thought to have predominantly axial as well as those with predominantly equatorial N–H bonds were included among the data. However, because direct evidence for the N–H configurations was lacking, the above inference is uncertain.

We report here explicit evidence that piperidine ^{15}N chemical shifts are indeed independent of N–H conformation. This conclusion is based on comparison of the 8-methyl-*trans*-decahydroquinolines 1 and 2[2] with the

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