chloride, 71912-38-4; β-(4-bromophenylseleno)ethyl chloride, 57878-10-1; β-(4-chlorophenylseleno)ethyl chloride, 57878-09-8; β-(4-(trifluoromethyl)phenylseleno)ethyl chloride, 71912-39-5; β-(4-nitrophenylseleno)ethyl chloride, 57878-11-2; 4-methoxyphenyl vinyl ether, 4024-19-5; 4-methylphenyl vinyl ether, 1005-62-5; phenyl vinyl ether, 766-94-9; 4-fluorophenyl vinyl ether, 351-93-9; 4-bromophenyl vinyl ether, 1005-61-4; 4-chlorophenyl vinyl ether, 1074-56-2; 3-chlorophenyl vinyl ether, 1005-41-0; 4-nitrophenyl vinyl ether, 940-14-7; 4-methoxyphenyl vinyl sulfide, 16411-17-9; 4-methylphenyl vinyl sulfide, 16336-54-2; phenyl vinyl sulfide, 1822-73-7; 4-fluorophenyl vinyl sulfide, 64287-53-2; 4-bromophenyl vinyl sulfide, 16411-18-0; 4-chlorophenyl vinyl sulfide, 16411-16-8; 4-(trifluoromethyl)phenyl vinyl sulfide, 64287-55-4; 4-nitrophenyl vinyl sulfide, 42150-17-4.

A Nuclear Magnetic Resonance Study of Solvent Effects on the Conformational Preference of Thioxanthene *S*-Oxides

A. L. Ternay, Jr.,* J. Herrmann, and B. A. Hayes

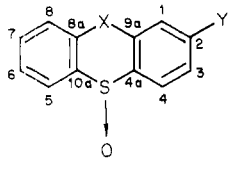
Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019

P. Joseph-Nathan*

Departamento de Quimica del Centro Investigacion y de Estudios Avanzados, Instituto Politicnico Nacional, Apartado Postal 14-740, Mexico 14, D.F., Mexico

Received July 12, 1979

Most stereochemical studies of thioxanthene *S*-oxides and related 6,6,6-tricyclic systems[1] have been conducted in weakly interacting or noninteracting solvents.[2] In general, it appears that the conformation favored in the solid state is also preferred in such solvents. For example, we have shown[3] that phenoxathiin *S*-oxide (1) possesses



1, X = O; Y = H
2, X = CH(CH$_3$); Y = H
3, X = NH; Y = H
4, X = CH$_2$; Y = H
5, X = CH$_2$; Y = Cl

a pseudoaxial (a′) sulfinyl oxygen both in the solid state and in solution.[4] Also, *cis*- and *trans*-9-methylthioxanthene *S*-oxides (*cis*- and *trans*-**2**) have a similar conformations (i.e., e′ S–O) in the solid state and in solution.[5] Phenothiazine *S*-oxide (**3**) appears to have an a′ sulfinyl oxygen both in the solid and in solution.[6] We now report what appears to be the first observation of the solvent dependence of the preferred conformation of a thioxanthene *S*-oxide (i.e., a conformationally restricted diaryl sulfoxide) ascribed to a specific interaction between the sulfinyl oxygen and the solvent.

Table I. ^{1}H NMR Chemical Shifts (ppm) of Thioxanthenes[a,f]

compd	C9-Ha′	C9-He′	R(a′/e′)[b,c]
4	4.70	4.21	1.5 (1.3)
6	4.73	4.27	1.8 (1.9)
7	4.53	4.82	1.4 (1.5)
8	1.55[d]	2.09[e]	

[a] CF_3CO_2H solvent. [b] Ratio of average bandwidth at half-height of a′ and e′ signals. [c] Value in parentheses for $CDCl_3$ as solvent. [d] a′ CH_3 ($CDCl_3$), 1.36 ppm. [e] e′ CH_3 ($CDCl_3$), 1.98 ppm. [f] From Me_4Si.

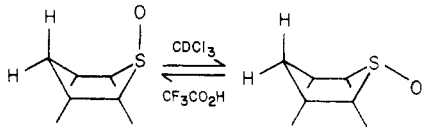
Table II. ^{13}C Chemical Shifts (ppm) of Phenoxathiin *S*-Oxide (1)[a,b]

solvent	C1	C2	C3	C4	C4a	C9a
$CDCl_3$	124.6	133.5	118.5	130.6	123.5	149.1
CF_3CO_2H	127.2	137.7	120.9	132.6	118.4	151.9

[a] Carbon numbering used in this table is shown in the structure in the text. [b] From Me_4Si.

In thioxanthene *S*-oxide (**4**), 2-chlorothioxanthene *S*-oxide (**5**), and related *S*-oxides lacking a substituent at both C4 and C5, the preferred conformation in weakly interacting solvents (e.g., $CDCl_3$, C_6D_6) is one in which the sulfinyl oxygen is pseudoequatorial (e′). In light of the results of our studies of **1** and **3** and of the greater hindrance in the e′ position, such results are somewhat surprising. Because of this difference between compounds such as **4** and **5** *and* **1** and **3**, we have attempted to determine if **4**, and related systems, can be forced to alter conformational preference by increasing the effective size of the sulfinyl oxygen.[7]

In the thioxanthene ring system C9-Ha′ is broadened (bandwidth at half-height) in comparison to C9-He′. This broadening, due to long-range coupling to aryl protons, permits ready distinction between e′ and a′ protons. In **4** and **5** the a′ proton appears upfield of the e′ proton. This



4a′ **4e′**

is the display expected when the sulfinyl oxygen is e′.[2] In compounds containing a substituent at C4 (which forces the sulfinyl oxygen into the a′ position), the (still-broadened) a′ C9-H is deshielded by the now pseudoaxial sulfinyl group. We now report a similar alteration in the spectra of **4** and **5** simply by changing the solvent from $CDCl_3$ or C_6D_6 to CF_3CO_2H, suggesting that the conformation is changed from e′ to a′.[8]

The view that association with the solvent (hydrogen bonding) alters the conformation of the sulfinyl oxygen is supported by the spectrum of 4-methylthioxanthene *S*-oxide (**6**), where S–O is a′ (in all solvents) by virtue of repulsions with C4-CH_3. In CF_3CO_2H the chemical shifts of C9-H in **6** are virtually identical with those of **4** in CF_3CO_2H (Table I). The ratio of the bandwidth at half-height of the C9-H's of **6** is nearly the same in $CDCl_3$

(1) These structures may be thought of as conformationally restricted diaryl sulfoxides.
(2) Ternay, A. L., Jr.; Evans, S. A. *J. Org. Chem.* **1974**, *39*, 2941. Evans, S. A.; Ternay, A. L., Jr. *Ibid.* **1975**, *40*, 2993 and references cited therein.
(3) Chen, J. S.; Watson, W. H.; Austin, D.; Ternay, A. L., Jr. *J. Org. Chem.* **1979**, *44*, 1989.
(4) An earlier report, assigning phenoxanthiin *S*-oxide the e′ conformation is apparently in error: Lumbroso, H.; Montando, G. *Bull. Soc. Chim. Fr.* **1964**, 2119.
(5) Ternay, A. L., Jr.; Ens, L.; Herrmann, J.; Evans, S. A. *J. Org. Chem.* **1969**, *34*, 940.
(6) Chu, S. S. C.; Ternay, A. L., Jr., to be submitted for publication. See, also: Vázquez, S.; Castrillon, J. *Spectrochim. Acta, Part A* **1974**, *30*, 2021.
(7) Complexation of sulfoxides with halogens can lead to altered conformation preferences: Ternay, A. L., Jr.; Herrmann, J.; Harris, M.; Hayes, B. R. *J. Org. Chem.* **1977**, *42*, 2010. However, the structural details of these complexes are unreported.
(8) We have observed that thioxanthenium bis(carbomethoxy)-methylide, like **4**, exists in the e′ array in $CDCl_3$. Its C9-H signals resemble those of **4**: Ternay, A. L., Jr.; Craig, D.; O'Neal, H. R., submitted for publication.

0022-3263/80/1945-0189$01.00/0

Table III. Chemical Shifts of Aromatic Carbons[a,b] of Thioxanthene S-Oxide (4) in Acidic Solvents

% CD_3CO_2D	% CF_3COOH	C4a	C9a	C1	C2	C3	C4
0	100	133.5	139.3	131.3	135.3	129.7	131.0
20	80	134.5	138.6	130.9	134.5	129.3	130.4
30	70	135.6	137.8	130.7	133.9	129.0	129.6
40	60	136.1	137.5	130.5	133.6	128.9	128.9
60	40	137.8	136.1	129.9	132.6	128.6	127.7
80	20	138.4	135.5	129.6	132.2	128.4	127.1
100	0	140.1	134.4	129.0	131.3	128.0	125.9

[a] Spectra determined on a Varian XL-100A-FT-16K at 25.2 MHz. C1 was ascribed from gated decoupling and C4 from selective decoupling. [b] From Me_4Si.

and CF_3CO_2H. Correctness of the a′ and e′ assignments in CF_3CO_2H are further supported by the deshielding effect of chlorine upon e′ C9-H in 1-chloro-4-methylthioxanthene S-oxide (7) (Table I).

Although the solvent change $CDCl_3$ to CF_3CO_2H has its most dramatic effect upon the protons bonded to C9, the ^{13}C NMR spectra of 4 in a series of solvents reveals only minor deshielding of C9. However, C9 does appear farthest downfield in CF_3CO_2H (solvent/ppm: Me_2SO-d_6/34.4; C_6D_6/35.5; $CDCl_3$/35.5; CD_3CO_2D/35.7; CF_3CO_2H/36.0).

Solvent change has a dramatic effect on the chemical shift of the carbons (C4a and C10a) directly bonded to the sulfinyl group (solvent/ppm: C_6D_6/143.3; $CDCl_3$/141.7; Me_2SO-d_6/141.4; CD_3CO_2D/140.1; CF_3CO_2H/133.5). That this *shielding* partially reflects a change in the conformation of the sulfinyl group is supported by the *comparative* insensitivity of the spectrum of 1 with respect to solvent. Since 1 is already in the a′ array, a change in going from $CDCl_3$ to CF_3CO_2H should not lead to a conformational change of the sulfinyl moiety.[9] In 1, C4a goes upfield (but only by 5 ppm) in going from $CDCl_3$ to CF_3CO_2H.

Furthermore, the chemical shift of those carbons once removed from the sulfinyl group of 1 (C4 and C9a in Table II) are affected only slightly by TFA while the corresponding carbons of 4 are influenced considerably (Table III).

Our tentative[10] assignments of the various carbons in 1 are shown in Table II. These data suggest, among other things, that the heterocyclic oxygen is not extensively hydrogen bonded in CF_3CO_2H.

In order to more clearly see the effect of hydrogen bonding upon the spectra of 4, we have examined the ^{13}C NMR spectrum of 4 in a series of mixed acids (CF_3CO_2H/CD_3CO_2D). These data (Table III) clearly show the effect of increasing acidity upon the chemical shift of those carbons closest to the sulfinyl group.

Finally, conversion of the sulfinyl oxygen from an e′ to an a′ array might be difficult if an a′ substituent were present at C9 because of transannular strain between a′ substituents at C9 and S. The existence of such transannular strain in an appropriately substituted system could be demonstrated by the *absence* of the solvent effect under discussion. 9,9-Dimethylthioxanthene S-oxide (8) must have an a′ methyl group regardless of the conformation of the sulfinyl group and, therefore, should not alter conformation (S–O e′ to a′) upon changing the solvent from chloroform to trifluoroacetic acid. Compound 8 has an e′ sulfinyl group in $CDCl_3$,[5] and any alteration should deshield the a′ C9-CH_3 group. In fact, the methyl groups of 8 are rather insensitive to this solvent change (Table I).

Experimental Section

All of the compounds used in this study have been described by us previously[2,5] or are commercially available. ^{13}C NMR spectra were determined on a Varian XL-100A-FT-16K at 25.2 MHz. ^1H NMR spectra were recorded on a Varian HA-100.

Acknowledgment. The research at The University of Texas was funded by Grant No. Y-484 of the Robert A. Welch Foundation. Purchase of the HA-100 was funded, in part, by a grant from the Research Corp.

Registry No. 1, 948-44-7; 4, 10133-81-0; 6, 61689-16-5; 7, 61689-17-6; 8, 19019-06-8.

(9) It might, however, represent a bulk solvent effect and/or an effect of protonation upon the anisotropy of the sulfinyl group. A simple, "inductive-effect" argument should lead to a deshielding.

(10) A detailed study of ^{13}C NMR spectra of conformationally restricted diaryl sulfur compounds will be the subject of a future paper by G. Martin and A. L. Ternay, Jr.