The Structure of Thianthrenium Biscarbethoxymethylide and the Corresponding Sulfoxide

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Thianthrene reacts with one equivalent of diethyl diazomalonate to form the monosulfonium ylide thianthrenium biscarbethoxymethylide. Single crystal X-ray and ^{13}C-nmr establish the conformation as pseudo-equatorial (e') in both the solid state and solution. The angle of fold between aryl rings is 135.7°, the nearly-planar malonylide fragment bisecting this angle. The carbonyl oxygen of the endo carbethoxy group is anti to the nonbonding electron pair on sulfur. The methylide carbon resonates at 50 ppm. The aromatic solvent induced shift (ASIS) technique indicates that thianthrene S-oxide also is e'.

9,10-Dihydroanthracene (**1**) and its sulfur-containing heterologs are folded about an imaginary line containing the *meso* positions (*i.e.*, C9 and C10 in **1**). The corresponding sulfoxides, sulfonium salts, and so forth, also are folded about this line and, by virtue of the substituent on sulfur, can exist in two possible conformations: pseudo-axial (a') and pseudo-equatorial (e'). This is illustrated for thianthrene S-oxide (**2**).
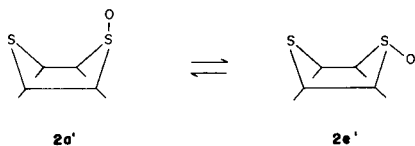
It is clear that the preferred conformation of the sulfinyl oxygen in sulfoxides of this type depends upon several factors including (a) the nature of the other *meso* substituent, (b) the presence of aryl substituents adjacent ("peri") to the sulfinyl sulfur and (c) specific interactions between the medium and the sulfinyl group. These effects are nicely illustrated in the thioxanthene (**3**) system. First, thioxanthene 10-oxide (**4**) is e' (1) while phenoxathiin sulfoxide (**5**) is a' (2). The second factor is responsible for the a' conformation of 1,4-dimethylthioxanthene S-oxide (**6**) (3). The third factor explains the conformational change (e' to a') undergone by **4** in going from deuteriochloroform to trifluoroacetic acid (1b) or upon addition of halogen to solutions of **4** in carbon tetrachloride (1a).

The ability for one *meso* atom to influence the geometry at the *meso* sulfinyl group (*e.g.*, **4**, *vs.* **5**) makes it imperative to treat individual conformationally-restricted diaryl sulfur systems independently. It is known that *cis*-thianthrene disulfoxide (*cis*-**7**) exists preferentially in the

di-e' conformation in both the solid state (4) and in solution (5). The corresponding trans isomer (*trans*-**7**) must be a', e' (6). Combining these data with the known (7) thermal isomerization of *trans*-**7** to *cis*-**7** indicates that the sulfinyl oxygen prefers the e' array when the other *meso* substituent is, itself, a sulfinyl moiety (either a' or e'). Of course, this does not demand that divalent sulfur at one *meso* position forces a sulfinyl group at the other *meso* position to occupy the e' orientation.

Table 1

Crystal and Experimental Data of Thianthrenium
Biscarbethoxymethylide

Chemical formula	$C_{19}H_{18}O_4S_2$	
Formula Weight	374.45	
Crystal system	Triclinic	
Space group	P$\bar{1}$	
Unit cell dimensions	a = 8.092(1) Å	α = 95.55(2)°
	b = 10.389(2)	β = 108.17(1)
	c = 11.374(2)	γ = 104.09(1)
	V = 865.6(3) Å^3	
Density (calculated)	1.436 g cm^{-1}	
Number of molecules per unit cell	2	
X-radiation used for data collection	$\lambda(CuK_\alpha)$ = 1.5418 Å	
Linear absorption coefficient	$\mu(CuK_\alpha)$ = 28.79 cm^{-1}	
Total number of reflections with $2\theta < 130°$	2901	
Number of reflections with I > 3σ(I)	2179	
Disagreement index, R	0.071	
Crystal size	0.29 × 0.11 × 0.04 mm	

Several reports describing the stereochemistry of sulfonium ylides derived from thioxanthene and thioxan-

Table 2

Torsion Angles and Ring Puckering Parameters

The Central Ring:

Torsion Angles:

C(14)-S(9)-C(11)-C(12)	−43.3°
S(9)-C(11)-C(12)-S(10)	−0.9
C(11)-C(12)-S(10)-C(13)	47.7
C(12)-S(10)-C(13)-C(14)	−50.1
S(10)-C(13)-C(14)-S(9)	5.8
C(13)-C(14)-S(9)-C(11)	40.5

Ring Puckering Parmaters:

	Ideal Boat Conformation
$q_2 = 0.805$ Å	$q_2 = Q$
$q_3 = -0.045$	$q_3 = 0$
$Q = 0.807$	$\phi_2 = 0°$
$\phi_2 = 2.2°$	$\theta = 90°$
$\theta = 93.2°$	

The Ylide Group-Torsion Angles:

C(12)-S(10)-C(15)-C(16)	125.9°
C(12)-S(10)-C(15)-C(19)	−58.1
C(13)-S(10)-C(15)-C(16)	−124.5
C(13)-S(10)-C(15)-C(19)	51.6
S(10)-C(15)-C(16)-O(1)	176.4
S(10)-C(15)-C(16)-O(2)	−4.1
S(10)-C(15)-C(19)-O(3)	13.9
S(10)-C(15)-C(19)-O(4)	−165.6
O(1)-C(16)-C(15)-C(19)	0.8
O(1)-C(16)-O(2)-C(17)	−1.2
C(15)-C(16)-O(2)-C(17)	179.3
O(2)-C(16)-C(15)-C(19)	−179.7
C(16)-O(2)-C(17)-C(18)	173.1
O(3)-C(19)-C(15)-C(16)	−170.5
O(3)-C(19)-O(4)-C(20)	−2.5
C(15)-C(19)-O(4)-C(20)	177.0
O(4)-C(19)-C(15)-C(16)	10.1
C(19)-O(4)-C(20)-C(21)	−81.7

Figure 1. ORTEP drawing of one molecule of thianthrenium biscarbethoxymethylide (12).

Figure 2. Bond lengths (Å) and bond angles (°) of thianthrenium biscarbethoxymethylide (e.s.d.'s in parenthesis).

thone have appeared recently (8) and suggest that they have the same conformation as do the corresponding sulfoxides. Thus, thioxanthenium biscarbomethoxymethylide (8) is e' while 1,4-dimethylthioxanthenium biscarbomethoxymethylide (9) is a' (8). Furthermore, both thioxanthone S-oxide (10) and thioxanthonium biscarbomethoxymethylide (11) (8c,d) possess slightly folded structures with the substituent on sulfur occupying the e' array (10).

This report presents the conformation of 2 and the structurally-related thianthrenium biscarbethoxymethylide (12) in solution and the single crystal X-ray structure of 12.

Results and Discussion.

It has been shown (11) that the confomation of conformationally-restricted diaryl sulfoxides can be determined using the ASIS technique (Aromatic Solvent Induced Shift). Specifically, benzene induces a downfield shift of
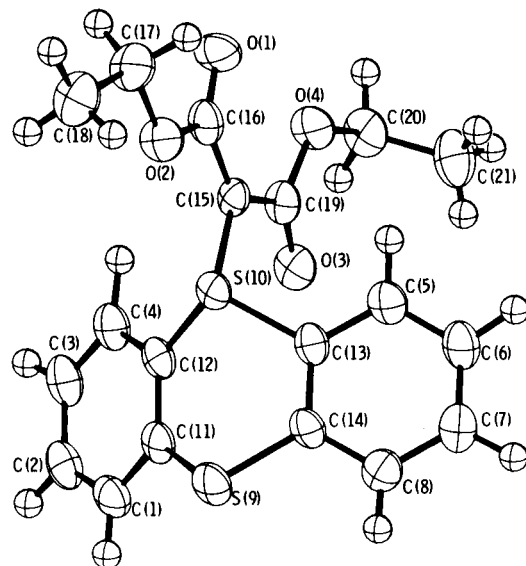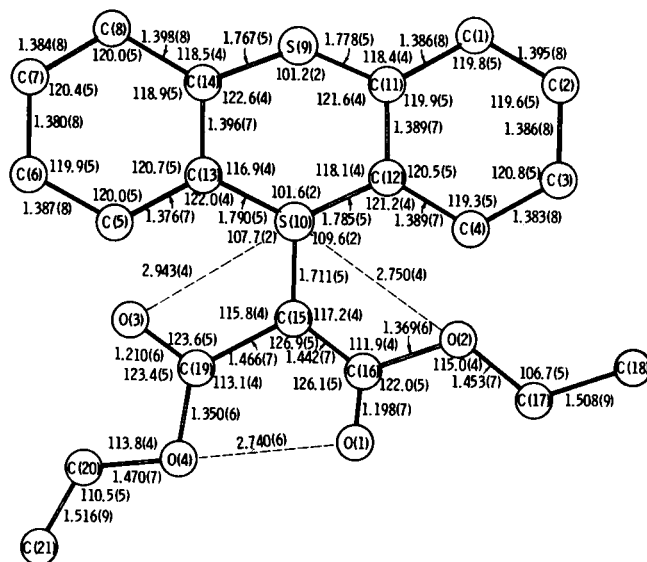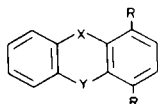
the proximal peri protons when solvating an e' sulfinyl group but an upfield shift of these same protons when solvating an a' sulfinyl group (12). This is precisely the behavior observed for 2. Thus, protons peri to the sulfinyl groups of 2 move from ~7.8 to ~8.1 ppm in going from chloroform to benzene. This indicates that the oxygen is e' (11).

	X	Y	R
1	CH$_2$	CH$_2$	H
2	S	SO	H
3	CH$_2$	S	H
4	CH$_2$	SO	H
5	O	SO	H
6	CH$_2$	SO	CH$_3$
7	SO	SO	H
8	CH$_2$	S-C(CO$_2$CH$_3$)$_2$	H
9	CH$_2$	S-C(CO$_2$CH$_3$)$_2$	CH$_3$
10	C=O	SO	H
11	C=O	S-C(CO$_2$CH$_3$)$_2$	H
12	S	S-C(CO$_2$C$_2$H$_5$)$_2$	H
13	S	S	H
14	CD$_2$	S-C(CO$_2$C$_2$H$_5$)$_2$	H

Table 3

Least-squares Planes and the Displacements of Atoms from the Plane

Equation of Planes: Ax + By + Cz = D, where x, y, z are in Å refer to the Crystallographic axes

Plane	A	B	C	D
(a)	−0.7250	−0.1412	0.8498	3.0818
(b)	−0.8249	−0.3379	0.2572	1.7951
(c)	−0.8336	−0.2671	0.5936	2.0716
(d)	0.1990	0.1776	0.7849	1.7346

Dihedral angles between the least-squares planes

Planes	Dihedral angle
(a) and (b)	135.7°
(a) and (d)	110.9
(b) and (d)	113.2
(c) and (d)	91.5

Displacements in Å from the least-squares planes

Plane

C(1)	−0.008	C(5)	−0.001	C(11)	−0.015	S(10)	−0.007
C(2)	0.001	C(6)	−0.009	C(12)	0.015	C(15)	0.024
C(3)	0.005	C(7)	0.015	C(13)	−0.015	C(16)	−0.009
C(4)	−0.005	C(8)	−0.012	C(14)	0.015	C(19)	−0.009
C(11)	0.009	C(13)	0.004	S(9)	0.637 (a)	O(1)	−0.055 (a)
C(12)	−0.002	C(14)	0.002	S(10)	0.756 (a)	O(2)	0.030 (a)
S(9)	0.119 (a)	S(9)	0.054 (a)			O(3)	0.188 (a)
S(10)	0.124 (a)	S(10)	0.224 (a)			O(4)	−0.292 (a)
						C(17)	−0.016 (a)
						C(18)	0.211 (a)
						C(20)	−1.768 (a)
						C(21)	2.447 (a)

(a) Indicates atoms excluded from the calculation of the least-squares planes.

Thianthrenium biscarbethoxymethylide, **12**, was prepared by reacting thianthrene with diethyl diazomalonate. The identification of the atoms and configuration of the molecule are shown in the ORTEP drawing (13) in Figure 1. The bond lengths and bond angles, with their standard deviations, are shown in Figure 2. Salient crystal data are presented in Table 1. The central ring is in a boat conformation as shown by the ring torsion angles and the Cremer and Pople (14) puckering parameters in Table 2. The methylide carbon is in the e' conformation; torsional angles involving the methylide fragment are included in Table 2. The least-square plane of the ylide group involving S(10), C(15), C(16) and C(19) is nearly perpendicular to the plane of the central ring involving C(11), C(12), C(13) and C(14) (Table 3). While one of the ester fragments has a planar configuration within the ylide groups, the other deviates from the plane significantly. These deviations are included in Table 2. That the two benzene rings are planar is shown by the least-squares planes in Table 3. The angle of fold between these planes is 135.7°. This is not very different from the value reported for *trans*-7 (133°) (6) but is somewhat larger than the value for thianthrene, **13** (128°) (15).

The two C-C bonds involving the methylide carbon are 1.466(7) and 1.422(7)Å, consistent with greater double bond character in the latter. The corresponding carbonyl groups possess lengths of 1.210(6) and 1.198(7)Å, respectively. The mean value of the two C-S bond lengths not involving the ylide group is 1.773(5), which is less than the mean value of the two C-S bond lengths involving the ylide group (1.788(5)Å). The corresponding length in **13** is reported to be 1.76Å (16) and 1.77Å (17).

The C-S bond length outside the ring is 1.711(5)Å which is similar to what has been reported for 9,9-dideuteriothioxanthenium biscarbethoxymethylide (**14**), 1.706(8)Å (8d). Interestingly, the two C-S-C angles within the central ring are equal and are similar to the value (100°) reported for **13** (16,17).

The carbonyl oxygen of the endo ester group is anti to the nonbonding electron pair on sulfur. The separation, 2.943(4) corresponds closely to that found in **14** (2.935Å) and in **11** (2.932Å). The ether-like oxygen of the exo ester fragment of **12** (O(2)) shows a significant intramolecular contact with sulfur (2.750(4)Å) and in **11** (2.733Å). In general, the orientation of the atoms within the malonylide fragment, relative to the heterocyclic ring, are quite similar in **12** and **14**. This geometry permits the nonbonding electron pairs on the ether-like oxygen of the exo ester group to straddle the nonbonding electron pair on sulfur and a nonbonding electron pair of the endo carbonyl oxygen to approach anti to that electron pair.

The closest intermolecular contact is between O(3) and C(8), 3.162Å.

Thus far, it appears that the preferred conformation (*i.e.*, a' *vs.* e') of thioxanthene sulfoxides, thioxanthenium methylides, phenoxathiin sulfoxides and thianthrene disulfoxides is the same in the solid state and in noninteracting solvents (*e.g.*, chloroform) (18). Since it already has been demonstrated (8c,d) that the chemical shift of the methylide carbon can be used to assign conformation (a' *vs.* e') to thioxanthenium methylides, we have examined the ^{13}C nmr spectrum of **12** in deuteriochloroform. The methyl and methylene carbons resonate 14.2 and 59.5 ppm, respectively. The isochronous carbonyl carbons occur at 165.6 ppm while the methylide carbon occurs at 49.7 ppm. All of these values are close to the corresponding resonances in **14** (14.0, 59.0, 165.8 and 53.8 ppm) (8d) and support the view that **12**, like **14**, is e'. They also indicate reltively rapid rotation about the S^+-$\underline{C}$ bond.

In summary, it is concluded that divalent sulfur, unlike divalent oxygen (2), causes a sulfinyl oxygen and a sulfonium methylide to exist preferentially in the e' geometry in these conformationally-restricted diaryl sulfur systems.

EXPERIMENTAL

Thianthrenium Biscarbethoxymethylide (**12**).

Thianthrene (2.0 g, 9.2 mmoles) was reacted with diethyl diazomalonate (3.0 g, 16 mmoles) and 60 mg of anhydrous copper sulfate. The reaction mixture was stirred at 140° for 1 hour under a nitrogen atmosphere. After cooling to room temperature the reaction product was dissolved in hot chloroform (50 ml) and the copper sulfate removed by filtration. Removal of the solvent from the filtrate afforded a solid contaminated with an oil. The oil was removed by washing with 6 × 10 ml of hexane to afford 2.6 g of crude ylide, mp 195-202°. This solid was dissolved in 30 ml of chloroform and the solvent allowed to partially evaporate. After several days, thianthrenium biscarbethoxymethylide (0.81 g, 2.2 mmoles, 24% yield), mp 202-204°, deposited as a white, crystalline solid. (Crystals for the X-ray study were produced in 95% ethanol).

X-ray Analysis.

Single crytals of the title compound were grown from ethanol solution in the form of clear prisms. The unit cell parameters and intensity data were measured on a Syntex P2$_1$ computer controlled diffractometer. The crystal data were summarized in Table 1. A $\theta/2\theta$ scanning mode with graphite monochromatic CuK$_\alpha$ was used in the intensity measurements. A reflection was considered as observed if the intensity was greater than three times its standard deviation, and the standard deviation was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and Polarization factors, and no absorption corrections were applied.

The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement technique (19). The refinement was carried out by the block-diagonal least-squares method with anisotropic temperature factors. Most of the hydrogen positions were located on a difference Fourier synthesis, and the rest were calculated with reasonable bond lengths and bond angles with respect to the atoms to which they are bonded. The isotropic temperature factors were used for the hydrogen atoms in the refinement. The weight of the reflection was assigned as $1/[\sigma(F)]$ (20) where $\sigma(F)$, the standard deviation of structure amplitude, was calculated from counting statistics. The quantity $\Sigma w\{||Fo| \cdot |Fc||\}^2$ was minimized. The final disagreement index, $R = (\Sigma ||Fo| \cdot |Fc|/\Sigma|Fo|)$ was 0.071. The atomic scattering factors used for sulfur, oxygen, and carbon atoms were those from International Tables for X-ray Crystallography (20). For hydrogen, the values

given by Stewart, Davidson, and Simpson (21) were used. The final positional and thermal parameters are given in a table deposited with the Cambridge Crystal Data File.

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