Quantum Yield Measurements. 3-(*p*-Methoxyphenyl)-3-methyl-1,1-diphenyl-1-pentene. All runs were performed in 750 mL of anhydrous *tert*-butyl alcohol. After photolysis, the solvent was removed in vacuo, the residue taken up in 145 mL of benzene, and tetraphenylethylene added as an internal standard. All runs were analyzed by VPC and peak areas measured by planimetry. For the analysis of the *trans*-2-ethyl-2-methyl-3,3-diphenyl-1-(*p*-methoxyphenyl)cyclopropane, a 168 × 0.6 cm column of 0.5% carbowax 20M on Varaport 30 (100–200 mesh) at 165 °C was employed. For the *cis*-cyclopropane a 183 × 0.6 cm column of 1.0% Apeizon N on Varaport 30 (100–120 mesh) at 180 °C was used.

Run 1. Starting olefin used, 1.48 mmol; 1.35 mEinsteins absorbed; *trans*-cyclopropane formed, 0.0875 mmol; ϕ(trans) = 0.0648; *cis*-cyclopropane formed, 0.0299 mmol; ϕ(cis) = 0.0221; 8.0% conversion.

Run 2. Starting olefin used, 1.48 mmol; 0.968 mEinsteins absorbed; *trans*-cyclopropane formed, 0.0631 mmol; ϕ(trans) = 0.0652; *cis*-cyclopropane formed, 0.029 mmol; ϕ(cis) = 0.216; 5.8% conversion.

Run 3. Starting olefin used, 1.46 mmol; 0.458 mEinsteins absorbed; *trans*-cyclopropane formed, 0.0306 mmol; ϕ(trans) = 0.0667; *cis*-cyclopropane formed, 0.0105 mmol; ϕ(cis) = 0.0230; 2.8% conversion.

Run 4. Starting olefin used, 1.50 mmol; 1.83 mEinsteins absorbed; *trans*-cyclopropane formed, 0.110 mmol; ϕ(trans) = 0.0600; *cis*-cyclopropane formed, 0.0399 mmol; ϕ(cis) = 0.0218; 10.2% conversion.

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Registry No.—**9**, 69652-87-5; (−)-**9**, 65549-74-8; **10**, 759-51-3; **11** isomer A, 69652-88-6; 11 isomer B, 69652-89-7; **12**, 69652-90-0; (−)-**12**, 69652-91-1; (−)-**12** (−)-1-phenethylamine salt, 69685-62-7; **13**, 69652-92-2; (−)-**13**, 69667-90-9; **14**, 69652-93-3; (−)-**14**, 69652-94-4; **15a**, 69652-95-5; (−)-**15a**, 69652-96-6; **15b**, 69652-97-7; (+)-**15b**, 69652-98-8; **16**, 69652-99-9; (−)-**16**, 69667-91-0; **17**, 69653-00-5; (−)-**17**, 69653-01-6; (+)-**17**, 69653-02-7; (−)-**18**, 69653-03-8; (−)-**19**, 53947-69-6; (−)-**20a**, 53750-37-1; (+)-**20b**, 69653-04-9; (+)-methyl *trans*-2-ethyl-2-methyl-3,3-diphenylcyclopropanecarboxylate, 53750-38-2; *p*-anisylmagnesium bromide, 13139-86-1; 2-ethyl-2-methyl-4,4-diphenyl-3-butenoic acid, 69653-05-0; phenyl bromide, 108-86-1.

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(1) This is Paper 118 of our Photochemical Series.
(2) (a) For paper 117 note H. E. Zimmerman, T. P. Cutler, V. R. Fitzgerald, and T. J. Weigt, *Mol. Photochem.*, **8,** 379 (1977); this paper was erroneously labeled paper 110 and referred to a nonexistent *J. Am. Chem. Soc.* communication as paper 109. This communication is to be found as reference 2c. (b) For Paper 116 note H. E. Zimmerman and D. R. Diehl, *J. Am. Chem. Soc.*, **101,** 1841 (1979). (c) Paper 110 of the series: H. E. Zimmerman and T. P. Cutler, *J. Chem. Soc., Chem. Commun.*, 232 (1978).
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Stereochemistry of Phenoxathiin *S*-Oxide

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Phenoxathiin sulfoxide has been found to exist in the pseudoaxial conformation in both the solid state and in solution. Single-crystal X-ray analysis reveals that the heterocyclic ring has a dihedral angle of 152°, with S–O 1.489 (4) Å, S–C 1.775 (5) Å, C–O 1.384 (7) Å, and C–S–C 94.8°. Solution conformation was deduced using the aromatic solvent-induced shift (ASIS) NMR procedure and complexation in the IR.

Compounds such as 9,10-dihydroanthracene (**1**), thioxanthene (**2**), phenothiazine (**3**), thianthrene (**4**), and phenoxathiin (**5**) exist in a folded conformation which is undergoing rapid conformational inversion. Alkyl substituents at the meso position(s) (e.g., C9 and C10 of **1**) normally prefer the a′ array, although molecules with e′ alkyl groups are known.[1-3]

Compounds with sulfur in the meso position (**2**–**5**) can form sulfoxides which, at least in principle, could exist with the sulfinyl oxygen in either the e′ or the a′ array. *cis*-Thianthrene 9,10-dioxide (*cis*-**6**) is more stable then *trans*-thianthrene

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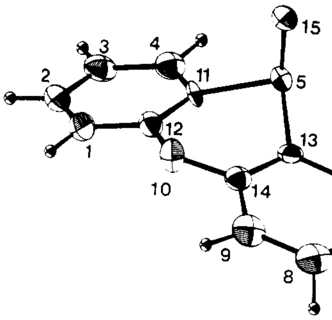
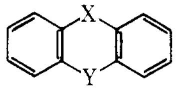


Figure 1. ORTEP drawing of phenoxathiin *S*-oxide. Thermal ellipsoids are drawn at the 50% probability level while hydrogen atoms are represented by spheres of arbitrary size.

dioxide (*trans*-**6**) and exists in the dipseudoequatorial conformation.[4] Thioxanthene 10-oxide (**7**) exists in the e′ conformation in the solid state and in solution.[5,6] Indeed, the preferred conformation of the sulfinyl oxygen in a number of thioxanthene 10-oxides is pseudoequatorial.[5] The exceptions to this rule appear to be those structures which (a) have a large substituent peri to the sulfinyl group (e.g., C4) or (b) are cis isomers possessing a large substituent at C9 (the other meso position). These results are interesting since appropriate single-crystal X-ray data[3] suggest that an e′ sulfinyl oxygen should be *more* hindered than an a′ oxygen in **7** and other related structures. (This view is supported by the observation that **7** changes conformation upon complexation with iodine monochloride[5c] or trifluoroacetic acid.[6])

Based upon an analysis of the infrared spectrum of mercuric chloride, cadmium chloride, and cadmium bromide adducts with **8**, it has been suggested[7] that **8** exists in the a′ conformation in the solid state. Using this technique, these workers also concluded that thioxanthone 10-oxide (**9**) has an a′ sulfinyl oxygen in the solid state. Since Chu has shown[8] that **9** has an e′ sulfinyl oxygen in the solid state, it seemed necessary to define the geometry of **8** in the solid state in an unequivocal manner. Furthermore, Lumbroso and Montaudo[9] have suggested that **8** has an e′ sulfinyl oxygen in solution. Although **8** could have two different conformations in two different states, this would make **8** the first conformationally restricted diaryl sulfoxide to exhibit this property in nonseverely interacting solvents. As a result of these conflicts, we have now examined the conformation of **8** in the solid state (single-crystal X-ray) and in solution (NMR and IR). Based upon results presented below, we conclude that **8** is unlike the simple sulfoxides of **2** or **4** in that it has an a′ sulfinyl oxygen. Furthermore, this conformation is found in both the solid state and in solution. This suggests that the anticipated steric effects are operative in **8** but that electronic effects overwhelm simple steric considerations in the sulfoxides of **2** and **4**.



1, X = CH_2; Y = CH_2
2, X = CH_2; Y = S
3, X = NH; Y = S
4, X = S; Y = S
5, X = O; Y = S
6, X = S(O); Y = S(O)
7, X = CH_2; Y = S(O)
8, X = O; Y = S(O)
9, X = C=O; Y = S(O)

X-ray Analysis. A crystal of dimensions 0.7 × 0.4 × 0.5 mm^3 was prepared by literature methods. The unit cell was found to be monoclinic and room temperature cell dimensions were obtained by a least-squares fit to 15 medium angle reflections. Systematic absences were consistent with space group $P2_1/n$. Intensity data with $2\theta \leq 120°$ were collected on a Syntex $P2_1$ diffractometer using graphite monochromated radiation and a variable scan speed. A periodically monitored reflection showed no significant crystal deterioration. Of the 1300 independent reflections measured, 1190 had intensities greater than $3\sigma(I)$, where $\sigma(I)$ was estimated from counting statistics. Negative measured intensities were assigned the value of zero. Lorentz and polarization corrections were applied, but no absorption corrections were made.

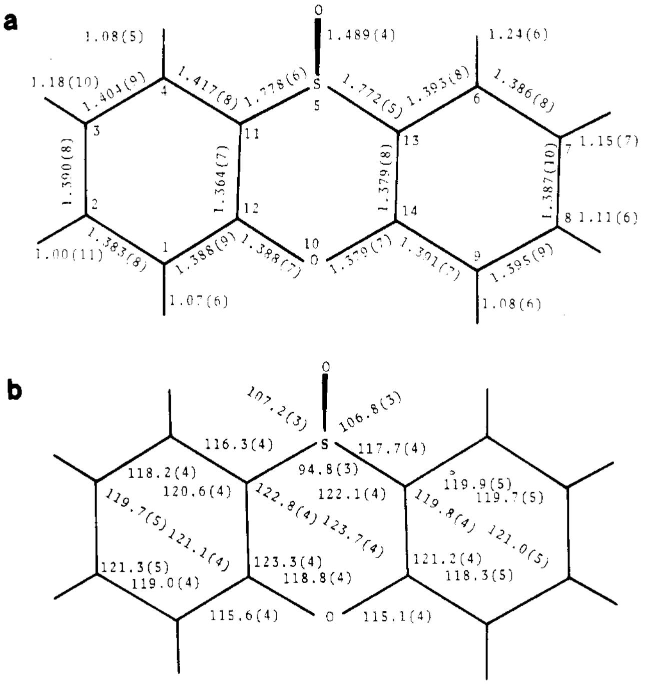


Figure 2. (a) Bond lengths (Å) and (b) valence angles (deg) for phenoxathiin sulfoxide.

The structure was solved by direct methods using MULTAN[10] to calculate phases for the 400 $|E_h|$ values greater than 1.11. The E map computed from the phase set with the highest combined figure of merit revealed clearly all nonhydrogen atoms. Anisotropic least-squares refinement yielded an R value of 0.11, where $R = \Sigma\Delta F_{\text{measd}}/\Sigma|F_{\text{measd}}|$. A difference map calculated with the phases from the last refinement cycle revealed the positions of all H atoms. Least-squares refinement with isotropic H atom thermal parameters lowered the R value to 0.082 for all 1300 reflections. The function minimized was $\Sigma\omega(\Delta F_{\text{measd}})^2$, where $\omega = 1/\sigma^2(F)$. The scattering factors for all atoms were taken from the International Tables for X-ray Crystallography, Vol. IV, 1974.

All parameter shifts during the final cycle were less than 0.0 σ, and a final difference map showed no peak larger than 0.3 e/Å^3. Positional and thermal parameters are available as supplementary material.

Figure 1 shows an ORTEP drawing[11] of **8**, while Figure 2 gives bond angles and distances. The heterocyclic ring is in a boat conformation with the sulfinyl oxygen occupying a pseudoaxial site. Least-squares planes fitted to the two phenyl rings form a dihedral angle of 152°, which is considerably larger than the 138° angle found in **5**,[12] the 133° angle in *trans*-**6**,[13] or any of the thioxanthene sulfoxides,[3] but is comparable to the flattening observed[8] in **9**, where the dihedral angle is 155.7°. The sulfur and oxygen atoms of the heterocyclic ring lie significantly out of the planes of the two phenyl rings, and the structure cannot be considered as simply a folding of a planar molecule along the S $\cdots$ O line. Torsion angles C(7)C(6)C(11)S and C(9)C(12)C(11)S are 173 and −172°, while corresponding angles involving O(1) are 176 and

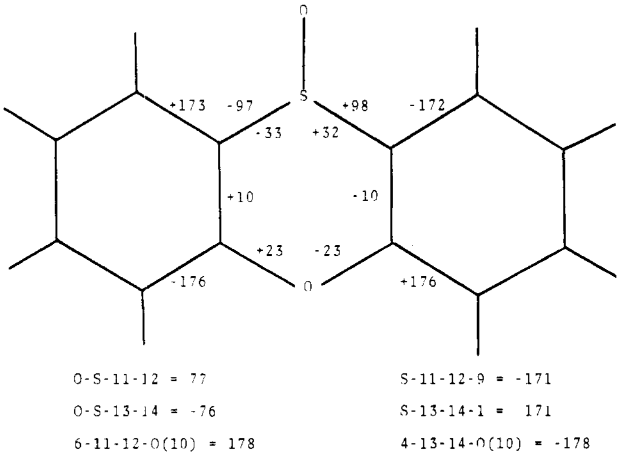


Figure 3. Torsional angles of phenoxathiin sulfoxide. Numbering refers to the labeling in Figures 1 and 2.

−178°. Although the torsion angles around the heterocyclic ring are symmetric with respect to the S(5) ··· O(10) line, C(11)SC(13)C(14) is 32° while C(14)O(10)C(12)C(11) is 23°. These angles are summarized in Figure 3.

The C–S distance of 1.775 (5) Å is considerably longer than the value of 1.752 Å reported for **5**[12] but is comparable with the average value of 1.773 Å reported for **4**,[14] 1.783 Å reported for the axial sulfoxide in *trans*-**6**,[13] and with the three-coordinate thioxanthene sulfoxides which exhibit a mean value of 1.781 Å.[3] The C–S–C angle of 94.8 (3)° is smaller than any reported for the compounds mentioned above; however, the three-coordinate thioxanthene sulfoxides average only 2° larger.[3] The S–O distance of 1.489 (4) Å is equivalent to the value of 1.483 Å for the axial S–O in *trans*-**6** and the corresponding thioxanthene sulfoxide ($S\text{–}O_{av}$ = 1.497 Å). The C–O distance of 1.383 Å is consistent with the 1.388 Å value reported for **5**,[12] but the C–O–C angle has expanded from 111 to 118.8 (4)°, which is consistent with the flattening of the molecule.

NMR and IR Spectra. We have previously shown[5b] that protons peri to sulfur (C4,5-H) in thioxanthenes are shifted downfield if (a) the sulfinyl oxygen is pseudoequatorial (e′) and (b) the solvent is changed *from* deuteriochloroform *to* deuteriobenzene. In contradistinction, C4,5-H's are shifted upfield if (a) the sulfinyl oxygen is pseudoaxial (a′) and (b) the solvent is changed *from* deuteriochloroform *to* deuteriobenzene.

The ASIS technique has now been applied to phenoxathiin sulfoxide in order to assess its conformation in solution. In going from deuteriochloroform to deuteriobenzene we have observed the C4,5-H's to shift upfield (δ 7.94 to 7.68), consistent with an a′ S–O group in solution. This $\Delta\delta$ of 0.26 is consistent with the data reported previously[5b] for the thioxanthene system, where $\Delta\delta$ for an a′ S–O group had a mean value of 0.24 (standard deviation 0.05) and $\Delta\delta$ for an e′ S–O group had a mean value of −0.17 (standard deviation 0.03). Thus, we must conclude that the suggestion by Lumbroso and Montaudo,[9] that phenoxathiin sulfoxide is e′ in solution, is in error and that **8** exists in the same conformation in the solid state and in solution.

We have previously shown[5c] that the IR stretching frequency of the sulfinyl group changes upon complexation with halogens (carbon tetrachloride solvent) and that this change can be used for conformational analyses. In that report we noted in the thioxanthene system an a′ S–O stretching frequency shift to lower values (~60 cm^{-1}) upon complexation with iodine. An e′ S–O group shifted to lower frequency by only about 20 cm^{-1}. Phenoxathiin sulfoxide, upon complexation with iodine, exhibits a $\Delta\nu_{S\text{–}O}$ of 50 cm^{-1},[5c] again arguing for an a′ S–O group rather than an e′ group.

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Registry No.—8, 948-44-7.

Supplementary Material Available: Table I of atomic positional parameters (1 page). Ordering information is given on any current masthead page.

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