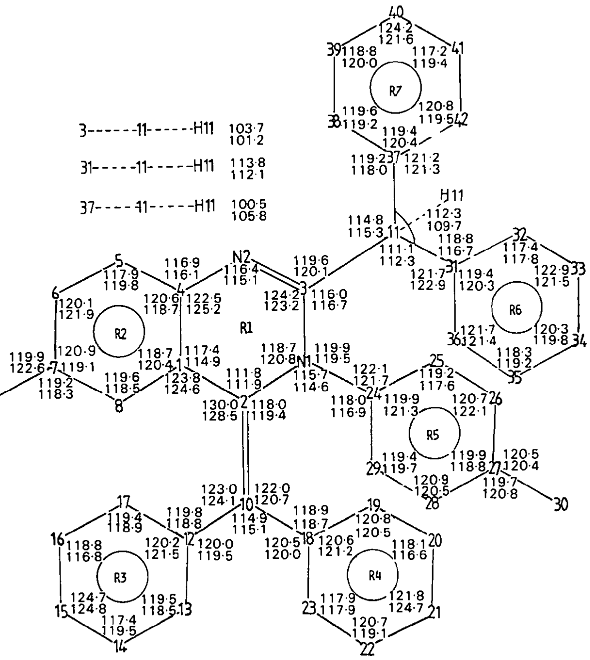


Fig. 4. Bond angles (°) for molecules *A* (upper) and *B* (lower) with average e.s.d. 1·0°.

C(24) away from C(10) and C(11) and the substituents have, where possible, attained a staggered conformation, several relatively short intramolecular non-bonded distances still persist. There does not appear to be any intramolecular non-bonded π interaction except, possibly, between *R*4 and *R*6, which overlap and approach fairly closely [C(31)—C(19) 3·70 (4), 4·00 (5) Å], but as the rings are far from parallel [61 (2), 56 (2)°] this seems unlikely. *R*1 bond lengths indicate little delocalization and apart from C(1)—C(4), which is common to *R*2, the most significant deviation from integral bonding is N(1)—C(3) [1·39 (1), 1·39 (1) Å]. These bond lengths contrast with those in the planar quinazoline structure (Huiszoon, 1976), where C—N range from 1·31 to 1·37 Å and C—C are 1·40 and 1·41 Å. However, the difference is not so great where C(2) has achieved sp^2 hybridization by double bonding externally to the quinazoline frame, *e.g.* in tricycloquinazoline (Iball & Motherwell, 1969), where the quinazoline forms part of a larger planar system, the bonds vary from those of the title molecule by less than 2 σ. Incomplete delocalization is also seen in planar quinazolinone derivatives. In the case of 2-phenyl-4(3*H*)-quinazolinone (Holm, Christophersen, Ottersen, Hope & Christensen, 1977), C(2)—N(1) at 1·36 Å is the only significant difference from the title molecule [1·46 (1), 1·44 (1) Å]. However, in 2-phenyl-3-[*p*-(2,2,4-trimethylchroman-4-yl)phenyl]-4(3*H*)-quinazolinone (Gilmore, Hardy, MacNicol & Wilson, 1977), this bond has lengthened to 1·40 Å, possibly because of the substituent on N(1), but at 1·37 Å C(4)—N(2) is significantly reduced [title compound: 1·42 (1), 1·43 (1) Å]. The shortest heavy-atom intermolecular contacts are 3·46 (4), 3·39 (4) Å between C(28) and C(5) at 1−*x*, 2−*y*, 1−*z* (molecule *A*) and −*x*, 2−*y*, −*z* (molecule *B*).

References

Barker, M. W. & Rosamund, J. D. (1974). *J. Heterocycl. Chem.* **11**, 241–243.

Crystal Structure Search and Retrieval (1980). *Instruction Manual.* Daresbury Laboratory, England.

Flowers, W. T. & Halls, A. L. (1981). Presented (by WTF) at the 8th International Heterocyclic Congress, Graz, Austria; Conference Abstracts, p. 127. To be submitted to *J. Chem. Soc. Perkin Trans.* 1.

Flowers, W. T. & Halls, A. L. (1982). *J. Chem. Soc. Perkin Trans.* 1, pp. 1255–1256.

Gilmore, C. J., Hardy, A. D. U., MacNicol, D. D. & Wilson, D. R. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1427–1434.

Holm, A., Christophersen, C., Ottersen, T., Hope, M. & Christensen, A. (1977). *Acta Chem Scand. Ser. B*, **31**, 687–693.

Huiszoon, C. (1976). *Acta Cryst.* B**32**, 998–1003.

Iball, J. & Motherwell, W. D. S. (1969). *Acta Cryst.* B**25**, 882–888.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Sheldrick, G. M. (1976). *SHELX.* A program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1983). C**39**, 643–646

cis-1,4,9-Trimethylthioxanthene 10-Oxide, $C_{16}H_{16}OS$

By Shirley S. C. Chu and Langford Book

School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275, *USA*

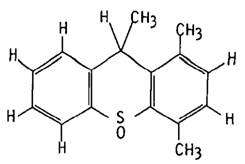
(*Received* 7 *September* 1982; *accepted* 12 *January* 1983)

Abstract. $M_r = 256{\cdot}36$, orthorhombic, $P2_12_12_1$, $a = 15{\cdot}296$ (4), $b = 11{\cdot}662$ (3), $c = 7{\cdot}328$ (2) Å, $V = 1307{\cdot}1$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}303$ Mg m^{-3}, graphite-monochromated Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu =$

0108-2701/83/050643-04$01.50

1·950 mm^{-1}, $F(000) = 544$, $T = 298$ K, $R = 0·044$ for 1248 observed reflections. Single crystals of the title compound were obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry, University of Texas at Arlington. The 9-methyl and 10-oxide groups are both in the 'boat-axial' conformation with respect to the central ring of the thioxanthene ring system.

Introduction. The determination of the crystal structure of the title compound (I) is a continuation of the study of the effects of nonbonded interaction between the *meso* and *para* substituents on the conformation and configuration of thioxanthene derivatives. The crystal structures of *cis* and *trans* isomers of 2,4,9-trimethylthioxanthene 10-oxide (Chu, Rosenstein & Ternay, 1979; Chu, Grant, Napoleone, Ternay & Massah, 1981), and the *cis* and *trans* isomers of 9-ethyl-2,4-dimethylthioxanthene 10-oxide (Chu, Napoleone, Massah & Ternay, 1981; Chu & Napoleone, 1982) have been determined. The conformation and configuration of the 1,4-dimethyl substituted 9-alkylthioxanthenes will provide further information on the comparative effects of the *para*-methyl and 9-alkyl substituents on the conformation of the sulfinyl oxygen. The crystal structure of 1,4,9-trimethylthioxanthene 10-oxide is presented in this paper. The crystal structures of 9-ethyl- and 9-isopropyl-substituted 1,4-dimethylthioxanthene 10-oxides are discussed in the succeeding papers (Chu & Napoleone, 1983; Book, Chu & Rosenstein, 1983).



(I)

Experimental. Single crystals obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry, University of Texas at Arlington, unit-cell parameters by least-squares analysis of 15 reflections with 2θ from 47 to 100°, $P2_12_12_1$ deduced from systematic absences ($h00$ absent with h odd, $0k0$ absent with k odd, $00l$ absent with l odd), Syntex $P2_1$ automatic diffractometer, crystal $0·36 \times 0·36 \times 0·35$ mm, $\theta/2\theta$ scanning mode, 1280 independent reflections with $2\theta < 130°$, 1248 observed, $I > 3\sigma(I)$; three standard reflections measured after every 50 reflections showed a random variation of less than 5% in intensity; Lorentz–polarization corrections, no absorption or extinction corrections, direct methods, *MULTAN* (Germain, Main & Woolfson, 1971), refinement by block diagonal least squares (Shiono, 1971), anisotropic, most of the hydrogen positions located in a difference Fourier synthesis, except some of those associated with the methyl groups which were calculated with respect to the atoms to which they are bonded, isotropic temperature factors for hydrogen atoms, $w = 1/[\sigma(F)]^2$, $\sigma(F)$ from counting statistics, $\sum w\{\|F_o| - |F_c\|\}^2$ minimized; since the structure has a noncentrosymmetric space group, the absolute configuration of the molecule was determined by the application of anomalous-scattering factor for S atom; $R = 0·044$ for the parameters and the configuration shown in Table 1* and Fig. 1, respectively, $R_w = 0·051$, $S = 0·97$, maximum height in final difference Fourier synthesis is 0·15 e Å^{-3}, $R = 0·053$ and $R_w = 0·060$ for the mirror-related structure, atomic scattering factors for sulfur, oxygen, and carbon were from *International Tables for X-ray Crystallography* (1962), for hydrogen, from Stewart, Davidson & Simpson (1965).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38362 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

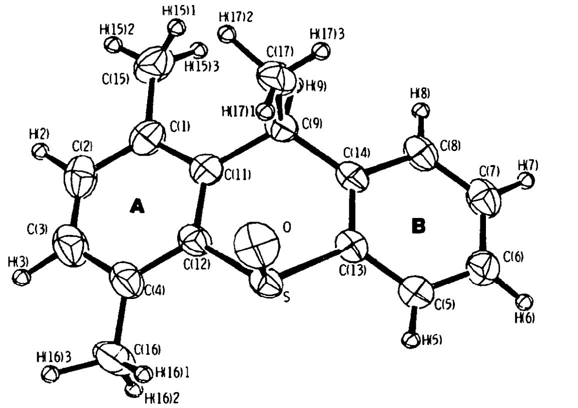
Discussion. The atomic parameters are given in Table 1 and identification of the atoms and the configuration of the molecule are shown in Fig. 1. Similarly to other

Table 1. *Atomic coordinates* ($\times 10^4$) *for non-hydrogen and* ($\times 10^3$) *for hydrogen atoms and thermal parameters*

The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B (Å^2)
S	3703 (1)	3130 (1)	4592 (1)	3·05 (3)
O	3720 (2)	2486 (2)	2807 (5)	4·10 (14)
C(1)	6260 (3)	4077 (3)	4921 (6)	3·16 (17)
C(2)	6553 (3)	3301 (4)	6220 (6)	3·85 (20)
C(3)	5988 (3)	2534 (4)	7049 (6)	4·26 (22)
C(4)	5107 (3)	2508 (4)	6625 (6)	3·49 (19)
C(5)	2653 (3)	4999 (4)	4565 (7)	3·50 (18)
C(6)	2432 (3)	6131 (4)	4233 (6)	3·79 (19)
C(7)	3051 (3)	6846 (4)	3446 (6)	3·67 (18)
C(8)	3876 (3)	6452 (3)	3029 (6)	3·06 (17)
C(9)	5032 (3)	4907 (3)	3012 (5)	2·65 (16)
C(11)	5376 (2)	4077 (3)	4450 (5)	2·55 (15)
C(12)	4819 (2)	3282 (3)	5302 (5)	2·70 (15)
C(13)	3485 (3)	4603 (3)	4144 (5)	2·77 (15)
C(14)	4114 (3)	5316 (3)	3407 (5)	2·51 (15)
C(15)	6910 (3)	4889 (4)	4062 (8)	4·33 (21)
C(16)	4507 (3)	1672 (4)	7589 (7)	4·75 (24)
C(17)	5090 (3)	4378 (4)	1073 (6)	3·89 (20)
H(2)	724 (3)	340 (4)	649 (6)	4·8 (12)
H(3)	621 (3)	206 (4)	797 (7)	5·8 (12)
H(5)	227 (3)	444 (4)	505 (7)	5·2 (12)
H(6)	190 (2)	648 (3)	476 (5)	3·0 (9)
H(7)	297 (3)	772 (3)	327 (6)	4·2 (11)
H(8)	429 (3)	700 (4)	264 (7)	5·3 (12)
H(9)	546 (3)	570 (5)	293 (9)	8·7 (17)
H(15)1	691 (4)	495 (5)	280 (11)	10·9 (21)
H(15)2	748 (4)	469 (4)	428 (8)	7·4 (15)
H(15)3	687 (3)	576 (4)	421 (7)	6·8 (15)
H(16)1	408 (4)	137 (5)	662 (10)	12·2 (23)
H(16)2	421 (4)	201 (6)	850 (10)	13·6 (24)
H(16)3	482 (3)	81 (5)	798 (8)	8·0 (17)
H(17)1	472 (2)	360 (3)	92 (6)	3·9 (10)
H(17)2	578 (3)	418 (3)	76 (6)	4·5 (11)
H(17)3	491 (3)	484 (4)	24 (7)	5·7 (13)



C(9)–C(11)–C(12)–S	5·3 (5)	S–C(13)–C(14)–C(9)	−2·6 (5)
C(11)–C(12)–S–C(13)	−37·4 (4)	C(13)–C(14)–C(9)–C(11)	−37·6 (5)
C(12)–S–C(13)–C(14)	36·4 (4)	C(14)–C(9)–C(11)–C(12)	35·7 (5).

Fig. 1. *ORTEP* drawing (Johnson, 1965) of one molecule of the title compound. The torsion angles (°) around the central ring are also shown.

thioxanthenes, the central ring in the title compound is in a boat conformation. The puckering parameters (Cremer & Pople, 1975) of the central ring are $q_2 = 0{\cdot}588$, $q_3 = 0{\cdot}067$ Å, $Q = 0{\cdot}592$ Å, $\varphi_2 = 178{\cdot}7°$, and $\theta = 96{\cdot}5°$. For ideal boat conformation, these values are $q_2 = Q$, $q_3 = 0$ Å, $\varphi_2 = 180°$, and $\theta = 90°$. The torsion angles around the central ring are shown in Fig. 1. In the title compound, the 9-methyl and 10-oxide groups are both in the boat-axial conformation. It has been shown that the 10-oxide group prefers the boat–equatorial conformation when the 9-alkyl substituent is a methyl group (Jackobs & Sundaralingam, 1969). That the boat-axial conformation was preferred in the title compound and in the *cis* isomer of 2,4,9-trimethylthioxanthene 10-oxide (Chu, Rosenstein & Ternay, 1979) is due to the nonbonded interaction between the sulfinyl oxygen and the *para*-methyl [at C(4)] substituent. This result demonstrates that the *para*-methyl substituent has a larger effect than the 9-axial methyl substituent in governing the conformation of the sulfinyl oxygen.

The equations of the least-squares planes of the two benzo rings are $-2{\cdot}86\,(3)x + 7{\cdot}79\,(2)y + 5{\cdot}278\,(9)z = 3{\cdot}98\,(2)$ and $4{\cdot}77\,(3)x + 3{\cdot}03\,(2)y + 6{\cdot}697\,(6)z = 5{\cdot}84\,(1)$ (where *x*, *y*, and *z* are in fractional coordinates) for rings *A* and *B*, respectively. The deviations of atoms range from 0·001 (5) to 0·007 (6) Å and 0·004 (6) to 0·013 (5) Å for plane *A* and plane *B*, respectively. The deviations of the two methyl substituents on the benzo ring, C(15) and C(16), from plane *A* are 0·006 (8) and 0·036 (8) Å, respectively. The folding angle between the planes of the two benzo rings is 140·7 (1)° compared to that of 147·3° in *cis*-2,4,9-trimethylthioxanthene 10-oxide. The smaller folding angle in the title compound is due to the nonbonded interaction between the 9-methyl and *para*-methyl substituents.

The bond lengths and angles with their standard deviations are shown in Fig. 2. Similarly to other *para*-methyl substituted thioxanthene 10-oxides (Chu, Rosenstein & Ternay, 1979; Chu & Napoleone, 1982), there is a slight lengthening of the C(12)–S bond length on the side of the benzo ring with the *para*-methyl substituents. The two C–S–O bond angles are also significantly different and the difference is primarily due to the interaction between the sulfinyl oxygen and the 9-methyl substituent, both being in the boat-axial conformation. This can be deduced from the fact that the larger C–S–O bond angle is on the side of the benzo ring without *para*-methyl substituents. Furthermore, the nonbonded distance of 2·44 (4) Å between O and H(17)1 is much shorter than the nonbonded distances of 3·13 (7) and 3·29 (7) Å between O and H(16)1 and O and H(16)2, respectively. The C–H bond lengths range from 0·86 to 1·15 Å (mean 1·00 Å) with a r.m.s. standard deviation of 0·05 Å. The C–C–H bond angles involving benzene rings range from 112 to 125° (mean 119°), and the C–C–H and H–C–H bond angles involving tetrahedral C atoms range from 92 to 127° (mean 109°). The standard deviation of these bond angles is 3°. A stereoscopic

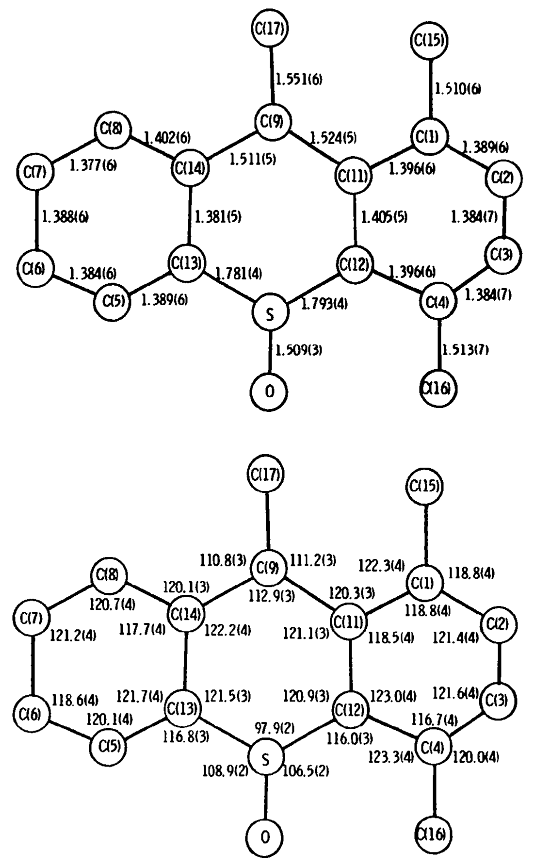


Fig. 2. Bond lengths (Å) and angles (°) of the title compound with e.s.d.'s in parentheses.

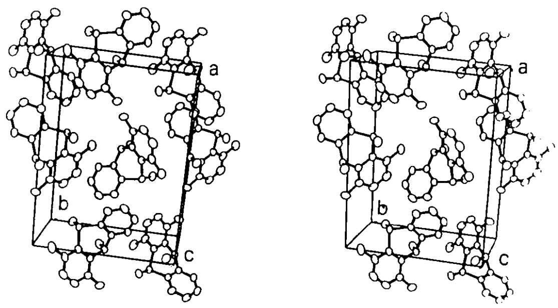


Fig. 3. The molecular packing of the title compound in a unit cell.

diagram of the packing of the molecules in the crystal is shown in Fig. 3. The closest intermolecular contact not involving hydrogens is 3·460 (6) Å between O and C(15).

This research was supported by the Robert A. Welch Foundation, Houston, Texas. The authors wish to thank Dr A. L. Ternay Jr of the University of Texas at Arlington for kindly supplying the crystals.

References

BOOK, L., CHU, S. S. C. & ROSENSTEIN, R. D. (1983). *Acta Cryst.* C**39**, 648–650.

CHU, S. S. C., GRANT, W. K., NAPOLEONE, V., TERNAY, A. L. JR & MASSAH, F. (1981). *Acta Cryst.* B**37**, 1948–1950.

CHU, S. S. C. & NAPOLEONE, V. (1982). *Acta Cryst.* B**38**, 2288–2290.

CHU, S. S. C. & NAPOLEONE, V. (1983). *Acta Cryst.* C**39**, 646–648.

CHU, S. S. C., NAPOLEONE, V., MASSAH, F. & TERNAY, A. L. JR. (1981). *Acta Cryst.* B**37**, 775–777.

CHU, S. S. C., ROSENSTEIN, R. D. & TERNAY, A. L. JR (1979). *Acta Cryst.* B**35**, 2430–2433.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.

JACKOBS, J. & SUNDARALINGAM, M. (1969). *Acta Cryst.* B**25**, 2487–2496.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SHIONO, R. (1971). Tech. Rep. 49. Crystallography Department, Univ. of Pittsburgh.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1983). C**39**, 646–648

cis-9-Ethyl-1,4-dimethylthioxanthene 10-Oxide, $C_{17}H_{18}OS$

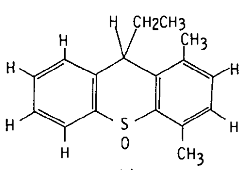
BY SHIRLEY S. C. CHU AND VERA NAPOLEONE

School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275, *USA*

(*Received* 7 *September* 1982; *accepted* 12 *January* 1983)

Abstract. $M_r = 270{\cdot}40$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}578\ (1)$, $b = 10{\cdot}243\ (1)$, $c = 12{\cdot}987\ (2)$ Å, $V = 1407{\cdot}1\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}276$ Mg m^{-3}, graphite monochromated Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 1{\cdot}844$ mm^{-1}, $F(000) = 576$, $T = 298$ K, $R = 0{\cdot}036$ for 1281 observed reflections. Single crystals of the title compound were obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry, University of Texas at Arlington. The 9-ethyl and 10-oxide groups are both in the 'boat-axial' conformation with respect to the central ring of the thioxanthene ring system.

Introduction. The determination of the crystal structure of the title compound (I) is a continuation of the study of the effects of nonbonded interaction between the *meso* and *para* substituents on the conformation and configuration of the thioxanthene ring system. The



(I)

crystal structure of *cis*-1,4,9-trimethylthioxanthene 10-oxide (Chu & Book, 1983) has been determined. The present study will provide comparative information on the effect of varying the size of the 9-alkyl substituent.

Experimental. Single crystals obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry, University of Texas at Arlington, unit-cell parameters by least-squares analysis of 15 reflections with 2θ from 57 to 90°, $P2_12_12_1$ deduced from systematic absences ($h00$ absent with h odd, $0k0$ absent with k odd, $00l$ absent with l odd), Syntex $P2_1$ automatic diffractometer, crystal $0{\cdot}35 \times 0{\cdot}21 \times 0{\cdot}47$ mm, $\theta/2\theta$ scanning mode, 1363 independent reflections with $2\theta < 130°$, 1281 observed, $I > 3\sigma(I)$; three standard reflections measured after every 50 reflections showed a random variation of less than 3% in intensity; Lorentz–polarization corrections, no absorption or extinction corrections; structure determination, refinement, atomic scattering factors, computer programs were the same as those described in the preceding paper (Chu & Book, 1983); structure also belongs to noncentrosymmetric space group as in the *cis*-9-methyl derivative of 1,4-dimethylthioxanthene 10-oxide (Chu & Book, 1983), absolute configuration

0108-2701/83/050646-03$01.50