References


cis-9-Ethyl-9-methylthioxanthene 10-Oxide

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Abstract. C16H16OS, orthorhombic, Pnam, Z = 4, M r = 256.35, a = 11.249 (1), b = 9.693 (1), c = 11.797 (2) Å, V = 1286.3 (2) Å³, D x = 1.322 Mg m⁻³, λ(Cu Ka) = 1.5418 Å, μ(Cu Ka) = 2.027 mm⁻¹, final R = 0.063. In the cis isomer of the title compound, the 9-ethyl and 10-oxide groups have a cis relation, and both are in a 'boat-equatorial' conformation with respect to the central ring. The two halves of the molecule are related by a mirror plane.

Introduction. Single crystals of the title compound (I) were obtained through the courtesy of Dr Andrew L. Ternay Jr of the Chemistry Department of the University of Texas at Arlington. The crystals are transparent prisms. The unit-cell parameters were obtained from a least-squares analysis of 15 reflections with 2θ values in the range of 20–65°. The space group, Pna2₁ or Pnam, was deduced from systematic absences (0kl absent with k + l odd, h0l absent with h odd). The intensity data were collected on a Syntex P2₁, automatic diffractometer with a crystal approximately 0.54 x 0.18 x 0.11 mm. The crystal was mounted with the a axis approximately along the φ axis of the diffractometer. A 0/2θ scanning mode with graphite-monochromated Cu Kα radiation was used to measure 1128 independent reflections with 2θ values below 130°; of these, 1006 reflections were considered as observed by the criterion I > 3.0σ(I), where σ(I) 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 program MULTAN (Germain, Main & Woolfson, 1971). The correct space group was proved to be Pnam by the structure determination, and the normalized structure factors were also shown to have centrosymmetric distributions. The ratios between 〈E〉, 〈E²〉, and 〈E²−1〉 are 0.815, 1.000, and 0.922, respectively. The E map showed the positions of all non-hydrogen atoms. The refinement was carried out by the full-matrix least-squares method (Busing, Martin
& Levy, 1962) with isotropic temperature factors and by the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. Most of the H 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 H atoms in the refinement.

The weight of the reflection was assigned as $1/\sigma(F)^2$, where $\sigma(F)$ was calculated from counting statistics.

The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. The final R index ($\sum |F_o| - |F_c|)/\sum |F_o|$) was 0.063 and the weighted disagreement index, $R_w$, was 0.067. Two low-order strong reflections (200, 110), whose calculated structure amplitudes were much higher than the observed values, were given zero weight in the least-squares refinement and were excluded from the calculation of the disagreement index. The magnitude of $[\sum w(F_o - F_c)^2/(m - n)]^{1/2}$, where $m$ is the number of reflections and $n$ is the number of parameters refined, was approximately unity.

The atomic scattering factors used for C, O and S atoms were those from International Tables for X-ray Crystallography (1962). For H, the values given by Stewart, Davidson & Simpson (1965) were used. The final positional parameters are given in Table 1.

Discussion. cis-9-Ethyl-9-methylthioxanthene 10-oxide is one of a series of tricyclic compounds under study in this laboratory. It has been shown by NMR and X-ray crystal structure studies that in the cis isomer of 9-alkylthioxanthene 10-oxide, the 10-oxide group prefers the 'boat-equatorial' conformation and that the 10-oxide group governs the stereochemistry of these isomers when the size of the 9-alkyl substituent is small (Ternay & Evans, 1974; Jackobs & Sundaralingam, 1969; Ternay, Chasar & Sax, 1967). The NMR data have indicated that the 'boat-axial' conformation of both the 9-alkyl and 10-oxide groups becomes significant when the 9-alkyl substituent is an ethyl group. Furthermore, cis-9-isopropylthioxanthene 10-oxide appears to be conformationally homogeneous in solution with both groups in the 'boat-axial' conformation (Evans, 1970; Evans & Ternay, 1975), and this conformation has been confirmed by the crystal structure determination in the solid state (Chu, 1975). The objectives of the present study are (1) to determine the conformation of the title compound, (2) to determine whether the 9-ethyl or 9-methyl group has the cis relation with the 10-oxide, (1a) or (1b), and (3) to determine whether the 9-alkyl or 10-oxide group governs the stereochemistry of this isomer in the solid state (A or B).

Table 1. Fractional atomic coordinates ($x \times 10^4$) for non-hydrogen atoms and fractional coordinates ($x \times 10^3$) and thermal parameters for hydrogen atoms

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<th></th>
<th>x</th>
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<th>z</th>
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The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

Fig. 1. ORTEP drawing (Johnson, 1965) of one molecule of the title compound with torsion angles (°) around the central ring.
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Fig. 2. Bond lengths (Å) and bond angles (°) of the title compound with e.s.d.'s in parentheses. Note that the two halves of the molecule are related by a mirror plane.

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

The bond lengths and bond angles with their standard deviations are shown in Fig. 2. The C–S and S–O bond lengths and the C–S–C and C–S–O bond angles have values similar to those found in other thioxanthene 10-oxides (Chu, 1975). The C atoms of both the methyl and ethyl groups lie on the mirror plane. The torsion angle C(11)–C(9)–C(16)–C(17) is 62 ± 1°. The packing of the molecules in the crystal is shown in Fig. 3. The closest intermolecular contact is 2.68 Å between O and H(2). There are no intermolecular contacts less than the van der Waals distances.

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References