Fig. 4. The crystal structure of (2b).

Table 10 (deposited) also provides details of the H bonding. H(311) is H-bonded to O(98) of the ethanol solvent molecule, whilst H(61) makes a contact of 2.66 Å with S(31) of the thiapyran molecule at x, y, 1 + z, this ‘head-to-tail’ linkage generating infinite chains of (2b) parallel to e. Fig. 4 is a view of the crystal packing arrangement, and clearly shows a graphitic-like interaction between C(21)-C(26) rings related across ½, ½, ½ [these rings occupy (parallel) planes 3.505 Å apart, and the centroid-centroid distance is 4.555 Å] that cross-link pairs of the parallel chains described above.

We are grateful to Dr M. B. Hursthouse of Queen Mary College, London, for diffractometer facilities [compound (1a)]. AJW also thanks Enraf–Nonius Ltd, Delft, for their recent kind hospitality and use of diffractometer [compound (2b)].

References


3a,6a-Dimethyl-2,3,3a,5,6,6a-hexahydrofuro[3,2-b]furan-2,5-dione, C₈H₁₀O₄

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(Received 15 August 1983; accepted 8 November 1983)

Abstract. Mᵦ = 170.2, orthorhombic, Fdd2, a = 13.055 (2), b = 20.759 (2), c = 6.080 (1) Å, U = 1647.6 Å³, Z = 8, Dₓ = 1.372 Mg m⁻³, λ(Cu Kα) = 1.5418 Å, μ = 0.95 mm⁻¹, F(000) = 720, T = 293 K. Final R = 0.034 for 296 independent observed reflections. The molecule consists of two cis-fused ɣ-lactone rings with methyl groups attached to the bridgehead atoms. A crystallographic twofold axis passes through the midpoint of the bridgehead bond. The ring C–O distances are 1.343 (5) and 1.463 (5) Å and the lactone groups are planar. Each five-membered ring thus adopts an envelope form with the flap at the bridgehead atom. This conformation alleviates steric repulsion between the methyl groups.

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Introduction. Ethyl acetoacetate (I) irradiated in primary or secondary alcohols yields glycols (II) which lactonize under further irradiation to (III) (Singh & Kagan, 1969). Silica-gel column chromatography of the products from the reaction using methanol yielded a small quantity of crystalline solid. The mass spectrum indicated a molecular weight of 170 with the major peak at 85 mass units. Although simple, the $^1$H and $^{13}$C NMR spectra could not be assigned unambiguously. X-ray analysis revealed the structure to be (IV).

Experimental. Rectangular block 0.17 x 0.23 x 0.33 mm cleaved from a large crystal and mounted on a Syntex $P_2_1$ four-circle diffractometer. Lattice parameters obtained by least-squares refinement of angular data for 15 reflexions with $16 < 2	heta < 28.4^\circ$. Space group $Fdd2$ (No. 43) deduced from systematic absences. With Cu $K\alpha$ radiation and $\theta$-2$\theta$ scan technique (variable scan speed, 3.91-29.30 $^\circ$ min$^{-1}$), intensities of (220) showed no systematic intensity variation. After removal of 31 systematically absent reflexions and data reduction (Lorentz–polarization corrections only, ab-)

...M. R. CAIRA, W. H. WATSON, J. KAGAN AND S. P. SINGH 499

...fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1, bond lengths and angles in Table 2. The molecule is illustrated in Fig. 1. It consists of two cis-fused $\gamma$-lactone rings with a methyl substituent on each of the bridgehead C atoms. The two asymmetric portions of the molecule are related by a crystallographic twofold axis which passes through the midpoint of the C(4)$-\$C(4') bond. cis-fusion of a $\gamma$-lactone with another five-membered ring is energetically more favorable than trans-fusion. In cis-fused systems, the $\gamma$-lactone ring usually adopts an envelope conformation (Hudson & Mills, 1972). In the title molecule, the C(2)$-O(3)$ bond [shorter than C(4)$-O(3)$ by 17$\sigma$] has considerable $\pi$-character and results in the lactone group being planar [torsion angle C(4)$-O(3)$-C(2)$-C(5) 1.3 (4)$^\circ$]. The lactone rings thus adopt envelope conformations with the bridgehead atoms as flaps. Atom C(4') deviates by 0.43 $\AA$ from the plane of the lactone group (for which $\sigma$plane $= 0.006$ $\AA$). The C(2)$-C(5)$, O(3)$-C(4)$ ring torsion angles are $-17.9$ (4), 15.6 (4)$^\circ$ respectively while the largest, C(5)$-C(4')$, C(4)$-C(4')$, involving the flap atom, are 26.4 (4), $-25.6$ (4)$^\circ$ respectively. In this arrangement, steric repulsion between the methyl groups is partly relieved [C(6)$-C(6') 3.048 (6) \AA$, C(6)$-C(6')-C(4')-C(6') -37.4^\circ$]. The closest approach of two methyl H atoms is 2.12 $\AA$. The combination of cis-fusion and ring pucker causes the two planar carbonyl groups to be nearly orthogonal to each other and there are several intramolecular non-bonded distances less than 3.0 $\AA$, e.g. O(3)$-C(2') 2.949 (4), O(3)$-O(3') 2.925 (3) $\AA$.

The molecules are held together by van der Waals forces. The shortest O$\cdots$O intermolecular distance is 3.337 (2) $\AA$ for O(1)$\cdots$O(1') [(ii) $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$].

Discussion. Fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1, bond lengths and angles in Table 2. The molecule is illustrated in Fig. 1. It consists of two cis-fused $\gamma$-lactone rings with a methyl substituent on each of the bridgehead C atoms. The two asymmetric portions of the molecule are related by a crystallographic twofold axis which passes through the midpoint of the C(4)$-\$C(4') bond. cis-fusion of a $\gamma$-lactone with another five-membered ring is energetically more favorable than trans-fusion. In cis-fused systems, the $\gamma$-lactone ring usually adopts an envelope conformation (Hudson & Mills, 1972). In the title molecule, the C(2)$-O(3)$ bond [shorter than C(4)$-O(3)$ by 17$\sigma$] has considerable $\pi$-character and results in the lactone group being planar [torsion angle C(4)$-O(3)$-C(2)$-C(5) 1.3 (4)$^\circ$]. The lactone rings thus adopt envelope conformations with the bridgehead atoms as flaps. Atom C(4') deviates by 0.43 $\AA$ from the plane of the lactone group (for which $\sigma$plane $= 0.006$ $\AA$). The C(2)$-C(5)$, O(3)$-C(4)$ ring torsion angles are $-17.9$ (4), 15.6 (4)$^\circ$ respectively while the largest, C(5)$-C(4')$, C(4)$-C(4')$, involving the flap atom, are 26.4 (4), $-25.6$ (4)$^\circ$ respectively. In this arrangement, steric repulsion between the methyl groups is partly relieved [C(6)$-C(6') 3.048 (6) \AA$, C(6)$-C(6')-C(4')-C(6') -37.4^\circ$]. The closest approach of two methyl H atoms is 2.12 $\AA$. The combination of cis-fusion and ring pucker causes the two planar carbonyl groups to be nearly orthogonal to each other and there are several intramolecular non-bonded distances less than 3.0 $\AA$, e.g. O(3)$-C(2') 2.949 (4), O(3)$-O(3') 2.925 (3) $\AA$.

The molecules are held together by van der Waals forces. The shortest O$\cdots$O intermolecular distance is 3.337 (2) $\AA$ for O(1)$\cdots$O(1') [(ii) $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$].

* Lists of H-atom coordinates, anisotropic thermal parameters, dihedral angles, equations of least-squares planes and structure factors for model (1) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39013 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
Table 1. Fractional atomic coordinates \((10^4)\) of the non-H atoms for models (1) and (2) and equivalent isotropic thermal parameters \((\text{Å}^2 \times 10^3)\) for model (1) with e.s.d.'s in parentheses

Model (1) coordinates correspond to equivalent positions as listed in International Tables for X-ray Crystallography (1952); for model (2) one must change \(\frac{1}{5}-x, \frac{1}{5}+y, \frac{1}{5}-z\) to \(\frac{1}{5}+x, \frac{1}{5}+y, \frac{1}{5}+z\), etc.

<table>
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<th>(y)</th>
<th>(z)</th>
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<td>4309(2)</td>
<td>-5760(9)</td>
<td>5774(9)</td>
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</table>

* \(U_{eq} = \frac{1}{3}[U_{11}(aa^*) + U_{22}(bb^*) + U_{33}(cc^*) + 2U_{12}(ab^*) \cos \gamma + 2U_{23}(bc^*) \cos \alpha + 2U_{13}(ca^*) \cos \beta] \)

Table 2. Bond distances (Å) and valence angles (°) with e.s.d.'s in parentheses for models (1) and (2)

<table>
<thead>
<tr>
<th>(1)</th>
<th>(2)</th>
<th>(\Delta \theta / \sigma_\theta (1))</th>
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<td>1.211(4)</td>
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<tr>
<td>C(3)--C(4)</td>
<td>1.465(3)</td>
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<tr>
<td>C(4)--C(5)</td>
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<tr>
<td>O(3)--C(4)</td>
<td>1.482(5)</td>
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</tr>
</tbody>
</table>

Symmetry code: (i) \(-x, 1-y, z\).

We thank the Robert A. Welch Foundation (P-074), the TCU Research Foundation, the CSIR (Pretoria), and the University of Port Elizabeth for their financial support. This is FASTBIOS contribution number 113.

References

Oak Ridge National Laboratory, Tennessee.


3,3',5,5'-Tetabromophenolsulphonphthalein (Bromphenol Blue)* C19H10Br4O5S

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Abstract. \(M_r = 670.02\), monoclinic, \(C2/c\), \(a = 31.003(4)\), \(b = 11.037(2)\), \(c = 21.183(3)\) Å, \(\beta = 143.7(1)^\circ\), \(V = 4291.2\) \(\text{Å}^3\), \(D_m = 2.06\), \(D_x = 2.07\) \(\text{Mg m}^{-3}\), \(Z = 8\), \(Mo \text{Ka}\), \(\lambda = 0.7107\) Å, \(\mu = 7.45\) mm\(^{-1}\), \(F(000) = 2560\), \(T = 293\) K, \(R = 0.061\) for 1697 observed reflections. The bromphenol blue molecule consists essentially of three planar groupings: the sulphonphthalein ring system and two dibromophenol rings attached to the tetrahedral C atom of the five-membered ring of the sulphonphthalein system. The dibromophenol rings are inclined with respect to each other by \(4,4'-(3H-2,1-Benzoxathiol-3-ylidene)bis[2,6-dibromophenol]S,S-dioxide.\)

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