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 c. 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 $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ [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.

References

BRUNSKILL, J. S. A., DE, A. & EWING, D. F. (1978). J. Chem. Soc. Perkin Trans. 1, pp. 629–633.

CHIANG, J. F. & BAUER, S. H. (1969). J. Am. Chem. Soc. 91, 1898–1901.

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.

EINSTEIN, F. W. B., SUTTON, D. & VOGEL, P. L. (1978). Can. J. Chem. 56, 891–895.

JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

ROBERTS, P. & SHELDRICK, G. M. (1976). XANADU. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). SHELX. Program for crystal structure determination. Univ. of Cambridge, England.

SMITH, D. L. & BARRETT, E. K. (1971). Acta Cryst. B27, 2043–2057.

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

TALBERG, H. J. (1977). Acta. Chem. Scand. Ser. A, 31, 743–751.

WELCH, A. J. (1974). PhD Thesis, p. 192. Univ. of London.

ZABICKY, J. (1961). J. Chem. Soc. pp. 683–687.

3a,6a-Dimethyl-2,3,3a,5,6,6a-hexahydrofuro[3,2-b]furan-2,5-dione, $C_8H_{10}O_4$

By Mino R. Caira

University of Port Elizabeth, Port Elizabeth, South Africa

William H. Watson*

FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

and Jacques Kagan and Shiv P. Singh

University of Illinois at Chicago, Chicago, Illinois 60680, USA

Abstract. $M_r = 170·2$, orthorhombic, Fdd2, $a = 13·055$ (2), $b = 20·759$ (2), $c = 6·080$ (1) Å, $U = 1647·6$ Å^3, $Z = 8$, $D_x = 1·372$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·95$ mm^{-1}, $F(000) = 720$, $T = 293$ K. Final $R = 0·034$ for 296 independent observed reflexions. The molecule consists of two cis-fused γ-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.

* To whom correspondence should be addressed.

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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).
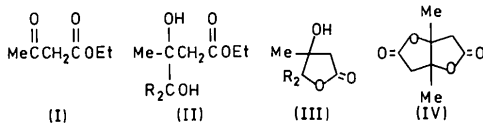
Experimental. Rectangular block $0.17 \times 0.23 \times 0.33$ mm cleaved from a large crystal and mounted on a Syntex $P2_1$ four-circle diffractometer. Lattice parameters obtained by least-squares refinement of angular data for 15 reflexions with $16 < 2\theta < 28.4°$. Space group $Fdd2$ (No. 43) deduced from systematic absences. With Cu $K\alpha$ radiation and $\theta:2\theta$ scan technique (variable scan speed, $3.91–29.30°$ min^{-1}), intensities of 341 unique reflexions measured $[(\sin\theta/\lambda)_{max} = 0.546$ Å^{-1} and $(h,k,l)_{max} = 14,22,6]$. Check reflexion (220) showed no systematic intensity variation. After removal of 31 systematically absent reflexions and data reduction (Lorentz–polarization corrections only, absorption ignored), 296 of remaining 310 reflexions had $I > 3\sigma(I)$ and were included in final refinement. Six independent non-H atoms located in an E map phased by $MULTAN78$ (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement followed with C and O atoms vibrating anisotropically and $f'' = 0.0$ for all atoms. Four of the five H atoms revealed in difference syntheses and all included at constrained, idealized positions (C–H 1.08 Å) with fixed isotropic temperature factors equal to those of their parent atoms $(0.050–0.063$ Å^2). Function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$ (derived from counting statistics). $(\Delta/\sigma)_{av}$ in final cycle 0.01, $(\Delta/\sigma)_{max}$ 0.03. At convergence, $R = 0.034$, $R_w = 0.043$, $S = 2.602$. No peaks higher than 0.13 e Å^{-3} in final difference synthesis.

A referee suggested that the effects of polar dispersion error (Ueki, Zalkin & Templeton, 1966; Cruickshank & McDonald, 1967) due to neglect of f'' corrections and the use of an incomplete $(l \geq 0)$ data set should be assessed. Refinements were carried out with the restricted data set for both polarities with $f'' = 0.1$ for oxygen. The weighted R factors were 0.044 and 0.043 indicating that the polarity of the $f'' = 0$ model, (1), can be rejected at the 0.5% level (Hamilton, 1965). However, comparison of the z coordinates in Table 1 for model (1) and the best $f'' = 0.1$ model, (2), shows a

maximum difference of 0.0015 for C(5), which is twice the corresponding reported e.s.d. in z. Bond lengths affected most are O(1)–C(2) and O(3)–C(4), for which increases of 0.005 and 0.006 Å are indicated (Table 2). Although the e.s.d.'s for the z coordinates in model (1) are slightly underestimated, bond-length differences are of the same order as the e.s.d.'s reported.

All calculations performed with $XRAY76$ (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors for C and O those of Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965).

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 γ-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^i) bond. *cis*-fusion of a γ-lactone with another five-membered ring is energetically more favorable than *trans*-fusion. In *cis*-fused systems, the γ-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 17σ] has considerable π-character and results in the lactone group being planar [torsion angle C(4)–O(3)–C(2)–C(5) 1.3 (4)°]. The lactone rings thus adopt envelope conformations with the bridgehead atoms as flaps. Atom C(4^i) deviates by 0.43 Å from the plane of the lactone group (for which $\sigma_{plane} = 0.006$ Å). The C(2)–C(5), O(3)–C(4) ring torsion angles are -17.9 (4), 15.6 (4)° respectively while the largest, C(5)–C(4^i), C(4)–C(4^i), involving the flap atom, are 26.4 (4), -25.6 (4)° respectively. In this arrangement, steric repulsion between the methyl groups is partly relieved [C(6)$\cdots$C(6^i) 3.048 (6) Å, C(6)–C(4)–C(4^i)–C(6^i) $-37.4°$]. The closest approach of two methyl H atoms is 2.12 Å. 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 nonbonded distances less than 3.0 Å, *e.g.* O(3)$\cdots$C(2^i) 2.949 (4), O(3)$\cdots$O(3^i) 2.925 (3) Å.

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

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *of the non-*H *atoms for models* (1) *and* (2) *and equivalent isotropic thermal parameters* ($\mathring{A}^2 \times 10^3$) *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 $\frac{1}{4} - x, \frac{1}{4} + y, \frac{1}{4} - z$ to $\frac{1}{4} + x, \frac{1}{4} + y, \frac{3}{4} + z$, etc.

	x	y	z (1)	z (2)	$|\Delta z|/\sigma_z(1)$	U_{eq}*
O(1)	3027 (2)	5012 (2)	0	0	—	80 (2)
C(2)	3673 (2)	5031 (2)	−1416 (7)	1429 (7)	1·9	49 (2)
O(3)	4209 (2)	4501 (1)	−1948 (7)	1946 (7)	0·3	49 (1)
C(4)	4967 (2)	4633 (2)	−3662 (6)	3674 (6)	2·0	40 (2)
C(5)	4009 (2)	5582 (1)	−2787 (8)	2802 (8)	1·9	49 (2)
C(6)	4606 (3)	4309 (2)	−5760 (9)	5774 (9)	1·6	65 (2)

$* \ U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha + 2U_{12}aba^*b^*\cos\gamma].$

Table 2. *Bond distances* ($\mathring{A}$) *and valence angles* (°) *with e.s.d.'s in parentheses for models* (1) *and* (2)

	(1)	(2)	$\Delta l/[(\sigma_{l_1})^2 + (\sigma_{l_2})^2]^{1/2}$
O(1)—C(2)	1·206 (4)	1·211 (4)	0·88
C(2)—O(3)	1·343 (4)	1·343 (4)	0·00
O(3)—C(4)	1·463 (5)	1·469 (5)	0·15
C(4)—C(4^i)	1·526 (6)	1·527 (5)	0·13
C(4^i)—C(5)	1·506 (4)	1·507 (4)	0·18
C(5)—C(2)	1·482 (5)	1·482 (5)	0·00
C(4)—C(6)	1·517 (6)	1·518 (6)	0·12
O(1)—C(2)—O(3)	120·6 (4)	120·2 (3)	
O(1)—C(2)—C(5)	129·3 (4)	129·5 (3)	
O(3)—C(2)—C(5)	110·0 (3)	110·3 (3)	
C(2)—O(3)—C(4)	111·7 (3)	111·4 (3)	
O(3)—C(4)—C(4^i)	103·0 (3)	103·0 (2)	
O(3)—C(4)—C(5^i)	107·1 (3)	106·9 (3)	
O(3)—C(4)—C(6)	107·8 (3)	108·1 (2)	
C(6)—C(4)—C(4^i)	117·4 (3)	117·4 (3)	
C(6)—C(4)—C(5^i)	116·2 (3)	116·1 (3)	
C(4)—C(4^i)—C(5)	104·2 (2)	104·1 (2)	
C(4^i)—C(5)—C(2)	103·5 (2)	103·5 (2)	

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

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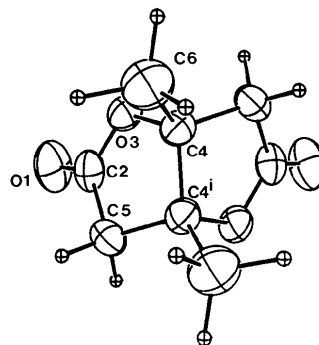

Fig. 1. Perspective view of the molecule along [001]. Thermal ellipsoids of the non-H atoms are drawn at the 50% probability level with *ORTEP*II (Johnson, 1971).

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
CRUICKSHANK, D. W. J. & MCDONALD, W. S. (1967). *Acta Cryst.* **23**, 9–11.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
HUDSON, D. W. & MILLS, O. S. (1972). *J. Chem. Soc. Chem. Commun.* pp. 647–648.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
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.
SINGH, S. P. & KAGAN, J. (1969). *J. Chem. Soc. Chem. Commun.* p. 1121.
STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
UEKI, T., ZALKIN, A. & TEMPLETON, D. H. (1966). *Acta Cryst.* **20**, 836–841.

3,3',5,5'-Tetrabromophenolsulfonphthalein (Bromphenol Blue),* $C_{19}H_{10}Br_4O_5S$

BY B. VEERAPANDIAN, D. M. SALUNKE AND M. VIJAYAN

Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560 012, India

Abstract. $M_r = 670\cdot02$, monoclinic, $C2/c$, $a = 31\cdot003$ (4), $b = 11\cdot037$ (2), $c = 21\cdot183$ (3) Å, $\beta = 143\cdot7$ (1)°, $V = 4291\cdot2$ Å^3, $D_m = 2\cdot06$, $D_x = 2\cdot07$ Mg m^{-3}, $Z = 8$, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 7\cdot45$ mm^{-1}, $F(000) = 2560$, $T = 293$ K, $R = 0\cdot061$ for 1697 observed reflections. The bromphenol blue molecule consists essentially of three planar groupings: the sulfonphthalein ring system and two dibromophenol rings attached to the tetrahedral C atom of the five-membered ring of the sulfonphthalein system. The dibromophenol rings are inclined with respect to each

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* 4,4'-(3*H*-2,1-Benzoxathiol-3-ylidene)bis[2,6-dibromophenol]
S,*S*-dioxide.