Brewer, A. D. & Davis, R. A. (1978). US Patent 4097580.
Brewer, A. D., Neidermeyer, R. W. & McIntyre, W. S. (1975). US Patent 3920438.
Brewer, A. D., Neidermeyer, R. W. & McIntyre, W. S. (1976). US Patent 3997323.
Howell, P. A., Curtis, R. M. & Lipscomb, W. N. (1954). *Acta Cryst.* 7, 498–503.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kobayashi, K. & Iwasaki, F. (1984). *Chem. Lett.* pp. 575–578.
McIntyre, W. S., Lambert, B. & Brewer, A. D. (1977). Proc. Plant Growth Regulator Working Group, Vol. 4, p. 202.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Acta Cryst. (1990). C**46**, 1287–1289

Structure of 2,3-Dihydro-5-phenyl-1,4-dithiin 1,1,4,4-Tetroxide

By George Ferguson* and Alan J. Lough

*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N*1*G* 2*W*1

and A. David Brewer

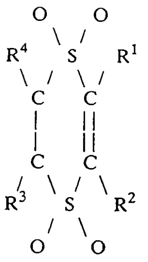
*Uniroyal Chemical Ltd, Guelph, Ontairo, Canada N*1*H* 6*N*3

(*Received* 19 *June* 1989; *accepted* 12 *September* 1989)

Abstract. $C_{10}H_{10}O_4S_2$, M_r = 258·3, orthorhombic, $P2_12_12_1$, a = 10·429 (4), b = 18·463 (7), c = 5·536 (3) Å, V = 1066·0 (10) Å^3, Z = 4, D_x = 1·61 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 4·7 cm^{-1}, $F(000)$ = 536, T = 294 K, R = 0·0318 for 1243 observed reflections. The dithiin ring has a half-chair conformation with the two C atoms of the double bond and the two S atoms defining a plane which is almost normal to the phenyl-ring plane (interplanar angle 93·2°). The bond lengths and angles of the molecule are similar to those in related structures.

Introduction. Dihydro-1,4-dithiin tetroxides are a class of compounds with varied and powerful biological activities which are specifically related to substitution patterns around the dithiin ring. In those cases where R^1 and R^2 are both alkyl groups, or are joined together in a chain of methylene groups, the compounds have powerful herbicidal and plant growth regulant activities (Brewer, Neidermeyer & McIntyre, 1975, 1976; Neidermeyer, Brewer & Judge, 1974; Murphy, 1975). Where R^1 is an alkyl group and R^2 is an H atom or when both R^1 and R^2 are H atoms, the compounds are potent bactericides, whereas those examples where R^1 is an aryl group and R^2 is an H atom are fungicides and viricides (Brewer & Davis, 1977, 1978). Cases where both R^1 and R^2 are both aryl, or where one is aryl and one is alkyl, are inactive (Brewer, 1985). The substitution pattern on the saturated side of the ring (R^3 and R^4) affects the intensity of the biological activity but not its nature (Brewer, 1985).

We report here the first X-ray analysis of a fungicidal aryl dithiin tetroxide (I). Previous X-ray studies have been carried out on alkyl substituted examples (II) (Arora, Bates, Kriek & Brewer, 1978), (III) (Bates, Kriek & Brewer, 1980) and of an unoxidized and biologically inactive aryl dihydrodithiin (Ferguson, Kaitner & Brewer, 1989).



(I) $R^1 = C_6H_5$, $R^2 = R^3 = R^4 = H$

(II) $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$

(III) $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$

Experimental. The reaction of ethane-1,2-dithiol and α-chloroacetophenone in benzene (with a catalytic quantity of p-toluenesulfonic acid) gave 2,3-dihydro-5-phenyl-1,4-dithiin which was then oxidized (with caution) in glacial acetic acid using hydrogen peroxide to yield 2-3-dihydro-5-phenyl-1,4-dithiin 1,1,4,4-tetroxide (71% yield; m.p. 478·5–479·5 K) (Brewer & Davis, 1977, 1978). Colourless

---

* E-mail address: CHMFERG@VM.UOGUELPH.CA

0108-2701/90/071287-03$03.00

needle-like crystals suitable for X-ray analysis were grown from glacial acetic acid.

Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $9 < \theta < 16°$. Crystal dimensions $0·42 \times 0·16 \times 0·14$ mm; intensities of reflections with indices h0 to 13, k0 to 23, l 0 to 7, with $2 < 2\theta < 54°$ measured; ω–2θ scans, ω-scan width $(0·6 + 0·35\tan\theta)°$; graphite-monochromated Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 1434 reflections measured, 1370 unique, 1243 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement. Data corrected for Lorentz, polarization and absorption effects (min. and max. transmission coefficients 0·908 and 0·950). Space group $P2_12_12_1$ was determined uniquely by systematic absences (h00 absent if $h = 2n + 1$; 0k0 absent if $k = 2n + 1$; 00l absent if $l = 2n + 1$). The structure was solved with the aid of *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement was by full-matrix least-squares calculations on F, initially with isotropic and then with anisotropic thermal parameters. A difference map showed maxima in positions consistent with the expected locations of the H atoms. In the final rounds of calculations, the H atoms were positioned on geometrical grounds (C—H 0·95 Å) and included (as riding atoms) in the structure-factor calculations with an overall $B_{\rm iso}$ of 3·5 Å^2. As the space group is chiral, we changed the enantiomorph to the opposite hand and ran two parallel refinements. One hand converged with $R = 0·0328$, $wR = 0·0530$, and the other with $R = 0·0318$ and $wR = 0·0521$; in all the tables that follow, the results from the refinement with $R = 0·0318$ are given. There were no significant differences in the molecular geometry of the two enantiomorphs. The final cycle of refinement included 146 variable parameters, goodness of fit 2·12, $w = 1/[\sigma^2(F_o) + 0·04(F_o)^2]$. Max. shift/e.s.d. in final refinement cycle < 0·005; density in final difference map ± 0·32 e Å^{-3}; there were no chemically significant features. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11-73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1983). Atomic coordinates* and details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of

Table 1. *Postional and thermal parameters with e.s.d.'s in parentheses*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$B_{\rm eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B(Å^2)
S1	−0·30493 (8)	0·40312 (4)	−0·4340 (2)	2·47 (1)
S4	−0·11672 (8)	0·29302 (4)	−0·0929 (2)	2·31 (1)
O11	−0·3156 (3)	0·4165 (2)	−0·6900 (5)	3·73 (6)
O12	−0·3857 (3)	0·4436 (1)	−0·2743 (6)	3·81 (6)
O41	−0·0591 (2)	0·2379 (1)	−0·2416 (6)	3·38 (5)
O42	−0·0834 (3)	0·2937 (2)	0·1571 (5)	3·54 (5)
C2	−0·3248 (3)	0·3094 (2)	−0·3801 (7)	2·53 (6)
C3	−0·2852 (3)	0·2908 (2)	−0·1266 (7)	2·62 (6)
C5	−0·0695 (3)	0·3771 (2)	−0·2223 (6)	2·05 (6)
C6	−0·1434 (3)	0·4192 (2)	−0·3559 (7)	2·41 (6)
C11	0·0688 (3)	0·3912 (2)	−0·1743 (7)	2·18 (6)
C12	0·1595 (3)	0·3664 (2)	−0·3410 (7)	2·69 (6)
C13	0·2880 (4)	0·3742 (2)	−0·2919 (8)	3·46 (8)
C14	0·3302 (3)	0·4061 (2)	−0·0751 (9)	3·55 (8)
C15	0·2390 (4)	0·4321 (2)	0·0889 (8)	3·19 (7)
C16	0·1097 (4)	0·4241 (2)	0·0396 (7)	2·84 (7)

Table 2. *Bond lengths* (Å) *and angles* (°)

S1—O11	1·443 (3)	C5—C6	1·321 (5)
S1—O12	1·431 (3)	C5—C11	1·489 (4)
S1—C2	1·767 (3)	C11—C12	1·399 (5)
S1—C6	1·764 (3)	C11—C16	1·398 (5)
S4—O41	1·440 (3)	C12—C13	1·375 (5)
S4—O42	1·427 (3)	C13—C14	1·407 (6)
S4—C3	1·768 (3)	C14—C15	1·400 (6)
S4—C5	1·779 (3)	C15—C16	1·384 (5)
C2—C3	1·503 (5)		

O11—S1—O12	118·2 (2)	S4—C3—C2	111·5 (2)
O11—S1—C2	108·9 (2)	S4—C5—C6	125·3 (3)
O11—S1—C6	106·6 (2)	S4—C5—C11	110·4 (2)
O12—S1—C2	109·7 (2)	C6—C5—C11	124·2 (3)
O12—S1—C6	108·8 (2)	S1—C6—C5	126·5 (3)
C2—S1—C6	103·6 (2)	C5—C11—C12	118·7 (3)
O41—S4—O42	117·3 (2)	C5—C11—C16	121·5 (3)
O41—S4—C3	109·8 (2)	C12—C11—C16	119·6 (3)
O41—S4—C5	105·7 (2)	C11—C12—C13	119·7 (4)
O42—S4—C3	110·2 (2)	C12—C13—C14	121·1 (4)
O42—S4—C5	108·4 (2)	C13—C14—C15	119·0 (3)
C3—S4—C5	104·7 (2)	C14—C15—C16	119·8 (4)
S1—C2—C3	110·5 (2)	C11—C16—C15	120·8 (4)

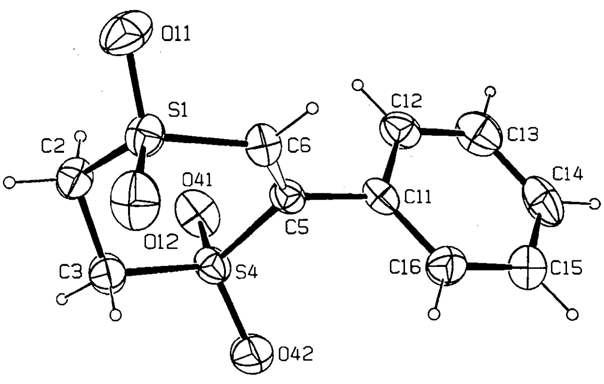


Fig. 1. A view of the molecule with the atomic numbering scheme. Ellipsoids are at the 50% probability level.

---

* Lists of structure factors, thermal parameters, calculated H-atom coordinates, mean planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52649 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the molecule prepared using *ORTEP*II (Johnson 1976).

Discussion. The analysis shows that the dithiin ring adopts a half-chair conformation. Atoms C5, C6, S1 and S4 define a plane (plane 1; maximum deviation 0·004 Å) with C2 and C3 0·519 (4) and −0·351 (4) Å from the plane, respectively. The phenyl-ring plane is almost normal (interplanar angle 93·2°) to plane 1. Relief from steric strain to which the *cis* H—C6═C5—C11 configuration might have given rise is achieved by significant bond angle distortion {C11—C5—C6 is 124·2 (3)°, greater than C11—C5—S4 [110·4 (2)°]} and by out-of-plane bending of C5 from the phenyl-ring plane [C5 is 0·121 (4) Å off the phenyl plane in a direction consistent with the phenyl plane being bent away from the hydrogen at C6].

The C5═C6 double bond [1·321 (5) Å] does not vary significantly from the corresponding values in 2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetroxide (II) [1·320 (4) Å] and 2,3-dihydro-5-methyl-1,4-dithiin 1,1,4,4-tetroxide (III) [1·338 (8) Å]. The S—C(sp^2) bond lengths [1·764 (3) and 1·779 (3) Å] are comparable with the corresponding distances in (II) [mean 1·779 (4) Å] and in (III) [mean 1·762 (6) Å]. The S—C(sp^3) distances [1·767 (3), 1·768 (3) Å] are also similar to those in (II) [mean 1·766 (3) Å] and (III) [mean 1·787 (7) Å]. The value quoted (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) for such bonds is 1·779 (20) Å for 94 samples, and with lower and upper quartile values of 1·764 and 1·790 Å respectively.

The average distance of an S═O bond in the molecule [1·435 (3) Å] is very close to the value listed [1·436 (10) Å from 316 samples] for bonds of this type (Allen *et al.*, 1987). The CH_2—CH_2 bond length [C2—C3 1·503 (5) Å] and other dimensions are also unexceptional; there are no untoward intermolecular contacts, the shortest being O11···C6 (at $-\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$) [3·199 (4) Å].

We thank NSERC Canada for financial support through the award of an Operating Grant.

References

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, G. A. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

ARORA, S. K., BATES, R. B., KRIEK, G. & BREWER, A. D. (1978). *Acta Cryst.* **B34**, 2918–2920.

B. A. FRENZ & ASSOCIATES INC. (1983). *SDP-Plus.* College Station, Texas 77840, USA, and Enraf–Nonius, Delft, The Netherlands.

BATES, R. B., KRIEK, G. R. & BREWER, A. D. (1980). *Acta Cryst.* **B36**, 736–738.

BREWER, A. D. (1985). 10th International Congress of Heterocyclic Chemistry, Waterloo, Ontario, Canada. Abstract S5–29.

BREWER, A. D. & DAVIS, R. A. (1977). US Patent 4004018.

BREWER, A. D. & DAVIS, R. A. (1978). US Patent 4097580.

BREWER, A. D., NEIDERMEYER, R. W. & MCINTYRE, W. S. (1975). US Patent 3920438.

BREWER, A. D., NEIDERMEYER, R. W. & MCINTYRE, W. S. (1976). US Patent 3997323.

FERGUSON, G., KAITNER, B. & BREWER, A. D. (1990). *Acta Cryst.* **C46**, 1284–1287.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

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

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MURPHY, H. J. (1975). *Proc. Northeast. Weed Sci. Soc.* **29**, 184–186.

NEIDERMEYER, R. W., BREWER, A. D. & JUDGE, F. D. (1974). *Proc. 12th Br. Weed Control Conf.* pp. 959–965.

Acta Cryst. (1990). **C46**, 1289–1293

Structure of 1,3-Cyclopentanedione

BY ANDRZEJ KATRUSIAK

Department of Crystal Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6,
60-780 *Poznań, Poland*

(*Received* 23 *January* 1989; *accepted* 29 *September* 1989)

Abstract. 1,3-Cyclopentanedione, $C_5H_6O_2$, M_r = 98·10, monoclinic, $C2/c$, a = 7·451 (2), b = 12·853 (3), c = 10·754 (2) Å, β = 111·90 (2)°, V = 956·2 (3) Å^3, Z = 8, D_x = 1·37 g cm^{-3}, m.p. 422–425 K, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·65 cm^{-1}, $F(000)$ = 416, T = 292 K, final R = 0·083 for 486 observed reflections. The molecules adopt the enol form and are connected head-to-tail by hydrogen bonds in

0108-2701/90/071289-05$03.00