exist between the two groups. In the 2-formyl-3,4-dihydronaphthalene group, the six-membered aromatic ring C(5)—C(10) is planar within experimental error, but the ring formed by C(1) to C(5) and C(10) is not. The torsion angles in Table 2 suggest an approximate twofold axis bisecting the C(3)—C(4) and C(1)—C(10) bonds. Therefore, the ring is best described as a 1,3-diplanar form or twist-chair-boat conformation. The formyl group is twisted by 20·8° from the C(1)—C(2)—C(5)—C(10) plane.

This report is the first confirmation by X-ray diffraction of the intermediate proposed by Meth-Cohn & Taljaard (1983) and Meth-Cohn (1987). The side chain is particularly interesting since this is the site of the positive charge. The delocalization of the positive charge in the side chain accounts for the stability of the allyl cation which allows this intermediate to be isolated from an aqueous solution. The C(1)—C(12) bond of 1·501 (6) Å is typical of a $C(sp^2)$—$C(sp^2)$ single bond which is in agreement with the assumption of no interaction between the ring and side chain. The side chain atoms N(1)—C(13)—C(12)—C(16)—N(2) are planar and coplanar. However, there are significant deviations of the angles from 120° which appear to be related to steric interactions. All the angles which face the dihydronaphthalene group are larger than 120° (the range is 123·2 to 132·9°), reducing steric interactions.

References

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KATRITZKY, A. R. & MARSON, C. M. (1987). *J. Org. Chem.* **52**, 2726–2730.

METH-COHN, O. (1987). *S. Afr. J. Chem.* **40**, 189–190.

METH-COHN, O. & TALJAARD, H. C. (1983). *Tetrahedron Lett.* **24**, 4607–4610.

MUNDY, B. P. & ELLERD, M. G. (1988). *Name Reactions and Reagents in Organic Synthesis*, pp. 214–215. New York: John Wiley.

ROGERS, D. (1981). *Acta Cryst.* A**37**, 734–741.

SHELDRICK, G. M. (1986). Desktop *SHELXTL*. Nicolet XRD Corporation, Madison, Wisconsin 53711–0508, USA.

Acta Cryst. (1990). C**46**, 1284–1287

Structure of 2,3-Dihydro-5-nitro-6-phenyl-1,4-dithiin

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Abstract. $C_{10}H_9NO_2S_2$, $M_r = 239·3$, monoclinic, $P2_1/c$, $a = 5·822$ (1), $b = 15·367$ (3), $c = 12·137$ (2) Å, $\beta = 103·5$ (2)°, $V = 1056·0$ (6) Å^3, $Z = 4$, $D_x = 1·51$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 4·6$ cm^{-1}, $F(000) = 496$, $T = 294$ K, $R = 0·0408$ for 1764 observed reflections. Because one C atom is disordered over two sites, the six-membered dithiin ring adopts two different conformations in the crystal structure, one a twisted half boat and the other a cyclohexene half chair. The nitro- and phenyl-group planes are inclined at 22·2 and 68·5° respectively to the plane of the S—C═C—S moiety.

Introduction. 2,3-Dihydro-1,4-dithiin tetroxides are a class of compounds with varied and powerful biological activities. Depending on the type and positions of substitution, members of this class may have strong herbicidal (Brewer, Neidermeyer & McIntyre, 1975), plant growth regulant (Brewer, Neidermeyer & McIntyre, 1976; McIntyre, Lambert & Brewer, 1977), fungicidal (Brewer & Davis, 1977), or viricidal (Brewer & Davis, 1978) activity. Two crystallographic studies of dihydrodithiin tetroxides have been published previously (Arora, Bates, Kriek & Brewer, 1978; Bates, Kriek & Brewer, 1980).

By contrast, the unoxidized dihydrodithiins are essentially devoid of biological activity (Brewer, 1985). Very few simple 1,4-dithiins have been studied by X-ray methods (Howell, Curtis & Lipscomb, 1954; Kobayashi & Iwasaki, 1984) and the most simple compounds in this area are liquids at room temperature. We now report the results of our X-ray

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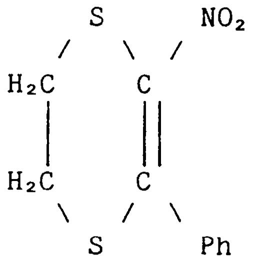
analysis of the title compound (1) which is a yellow crystalline solid at room temperature.


(1)

Experimental. 2,3-Dihydro-5-phenyl-1,4-dithiin (10 g) was dissolved in acetic anhydride (30 ml) and a mixture of equal parts of acetic acid and concentrated nitric acid (9·5 g) was added dropwise with stirring and strong cooling. The reaction is strongly exothermic and the reaction mixture (which became yellow orange) was allowed to stand in an ice–water bath for a further two hours before being poured onto crushed ice. The yellow solid which was obtained was washed with water, dried and recrystallized from absolute ethanol to give yellow prisms.

Table 1. *Positional 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:

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

Atoms C3 and C3*A* had occupancies 0·60 (1) and 0·40 (1) respectively.

	x	y	z	B(Å^2)
S1	0·88632 (11)	0·03700 (4)	0·33971 (5)	4·54 (1)
S4	0·39904 (11)	0·06521 (4)	0·12011 (5)	4·66 (1)
O1	0·3432 (4)	−0·1687 (1)	0·2035 (2)	6·07 (5)
O2	0·0975 (3)	−0·0715 (1)	0·1229 (2)	6·87 (5)
N	0·2936 (3)	−0·0937 (1)	0·1773 (2)	4·14 (4)
C2	0·8471 (5)	0·1181 (2)	0·2300 (3)	6·03 (7)
C3	0·6980 (7)	0·0957 (3)	0·1234 (3)	4·20 (8)
C3*A*	0·6166 (12)	0·1439 (4)	0·1810 (5)	4·9 (1)
C5	0·4708 (4)	−0·0256 (1)	0·2084 (2)	3·38 (4)
C6	0·6569 (4)	−0·0370 (1)	0·2973 (2)	3·17 (4)
C11	0·6857 (4)	−0·1097 (1)	0·3803 (2)	3·04 (4)
C12	0·8716 (4)	−0·1681 (2)	0·3929 (2)	3·79 (4)
C13	0·9009 (4)	−0·2322 (2)	0·4743 (2)	4·39 (5)
C14	0·7487 (5)	−0·2381 (2)	0·5452 (2)	4·68 (5)
C15	0·5657 (5)	−0·1800 (2)	0·5341 (2)	4·79 (5)
C16	0·5335 (4)	−0·1157 (2)	0·4520 (2)	3·98 (5)

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

S1—C2	1·799 (3)	C5—C6	1·351 (3)
S1—C6	1·738 (2)	C6—C11	1·487 (3)
S4—C3	1·794 (4)	C11—C12	1·387 (3)
S4—C3*A*	1·782 (6)	C11—C16	1·382 (3)
S4—C5	1·749 (2)	C12—C13	1·377 (3)
O1—N	1·211 (3)	C13—C14	1·374 (4)
O2—N	1·227 (3)	C14—C15	1·373 (4)
N—C5	1·457 (3)	C15—C16	1·385 (3)
C2—C3	1·422 (4)	O1···C3*A**	3·188 (6)
C2—C3*A*	1·393 (7)		
C2—S1—C6	106·1 (1)	N—C5—C6	120·1 (2)
C3—S4—C3*A*	38·9 (3)	S1—C6—C5	124·7 (2)
C3—S4—C5	95·9 (2)	S1—C6—C11	109·4 (1)
C3*A*—S4—C5	104·0 (2)	C5—C6—C11	125·6 (2)
O1—N—O2	122·7 (2)	C6—C11—C12	121·5 (2)
O1—N—C5	120·3 (2)	C6—C11—C16	119·3 (2)
O2—N—C5	117·0 (2)	C12—C11—C16	119·1 (2)
S1—C2—C3	116·8 (2)	C11—C12—C13	120·4 (2)
S1—C2—C3*A*	117·2 (4)	C12—C13—C14	120·4 (2)
S4—C3—C2	117·8 (3)	C13—C14—C15	119·6 (2)
S4—C3*A*—C2	120·3 (4)	C14—C15—C16	120·5 (3)
S4—C5—N	111·2 (1)	C11—C16—C15	120·1 (2)
S4—C5—C6	128·7 (2)		

* Atom at equivalent position 1 − x, −0·5 + y, 0·5 − z.

Accurate cell dimensions and the crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 24 reflections in the range $10 < \theta < 15°$. Crystal dimensions 0·55 × 0·45 × 0·30 mm; intensities of reflections with indices h −7 to 7, k 0 to 19, l 0 to 15, 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. 2584 reflections measured, 2297 unique ($R_{\rm int}$ 0·017), 1764 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement. Data corrected for Lorentz and polarization effects; no correction for absorption. Space group $P2_1/c$ was determined uniquely by the systematic absences ($h0l$ absent if $l = 2n + 1$; $0k0$ absent if $k = 2n + 1$). The structure was solved with the aid of *MULTAN* (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 that one of the atoms in the dithiin ring (C3) was disordered over two sites (C3, C3*A*; 0·60/0·40) and this was allowed for by appropriate occupancy-factor refinement; also visible in the difference map were maxima in positions consistent with the expected locations of most of the H atoms. In the final rounds of calculations, the occupancies for the disordered atoms were fixed at the values obtained from isotropic refinement; 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 5·0 Å^2. The final cycle of refinement included 145 variable parameters, $R = 0·0408$, $wR = 0·0604$, goodness of fit 2·31, $w = 1/[\sigma^2(F_o) + 0·04(F_o)^2]$. Max. shift/e.s.d. in final refinement cycle 0·002; density in final difference map ±0·40 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 the molecule prepared using *ORTEP*II (Johnson, 1976).

Discussion. The analysis shows that the dithiin ring adopts two different conformations in the crystal structure. The major conformer has a twist-boat conformation with C2 0·366 (3) and C3 0·922 (4) Å from the plane through S1, C6, C5, S4 (plane 1); the minor conformer adopts approximately a cyclohexene half-chair form [with C3*A* −0·229 (7) Å from plane 1]. Twist from coplanarity about the double bond C5═C6 is revealed by the S1—C6—C5—S4 torsion angle of −4·5 (3)°. The nitro-group plane is rotated by 22·2 (3)°, and the phenyl-ring plane by 68·5 (4)° from plane 1. Relief from steric strain which this conformation might have imposed is achieved by significant bond-angle bending; thus C11—C6—C5 [125·6 (2)°] is greater than C11—C6—S1 [109·4 (1)°], N—C5—C6 [120·1 (2)°] is greater than N—C5—S4 [111·2 (1)°], and C5—N—O1 [120·3 (2)°] is greater than C5—N—O2 [117·0 (2)°]. In the parent 1,4-dithiin (Howell *et al.*, 1954), a boat conformation is found with a 137° fold angle. 2,5-Diphenyl-1,4-dithiin has a boat conformation in its crystal structure and a slightly twisted boat form in its 1:1 complex with 2,4-diphenylthiophene (Kobayashi & Iwasaki, 1984).

It is possible that the C5═C6 double bond is also affected by overcrowding; its length [1·351 (3) Å] is longer than the upper quartile value quoted by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) for 106 *cis* C—C═C—C systems [mean value 1·317 (13), lower quartile 1·310, upper quartile 1·323 Å]. This bond is also longer than the corresponding value in 2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetroxide (Arora *et al.*, 1978) [1·320 (4) Å]; in 2,3-dihydro-5-methyl-1,4-dithiin 1,1,4,4-tetroxide (Bates *et al.*, 1980) the C═C bond length is also shorter [1·338 (8) Å], but because of the higher e.s.d. value, the difference may not be significant.

The S—C(sp^2) bond lengths [1·738 (2) and 1·749 (2) Å] are close to the values reported by Allen *et al.* (1987) [mean value 1·751 (9), lower quartile 1·740, upper quartile 1·764 Å], for such bonds. The values found in the present analysis are shorter than the corresponding distances in 2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetroxide (Arora *et al.*, 1978) [1·779 (4) and 1·778 (3) Å]; in the less crowded 2,3-dihydro-5-methyl-1,4-dithiin 1,1,4,4-tetroxide (Bates *et al.*, 1980), the corresponding distances are 1·768 (5) and 1·755 (6) Å. The S—C(sp^3) distances [1·799 (3), 1·794 (4), 1·782 (6) Å (to C3*A*)] are slightly lower than the values reported for such bonds by Allen *et al.* (1987) [mean 1·817 (13), lower quartile 1·808, upper quartile 1·824 Å]. The apparently short CH_2—CH_2 bond lengths [C2—C3 1·422 (4), C2—C3*A* 1·393 (7) Å] are probably an artefact of the disorder at C3 (which could be resolved) and possibly at C2 (which has U_{ii} values almost twice those of the other ring atoms but which could not be resolved into two discrete sites). Other dimensions are unexceptional; there are no untoward intermolecular contacts, the shortest being 3·188 (6) Å between a nitro oxygen and C3*A* of an adjacent molecule.

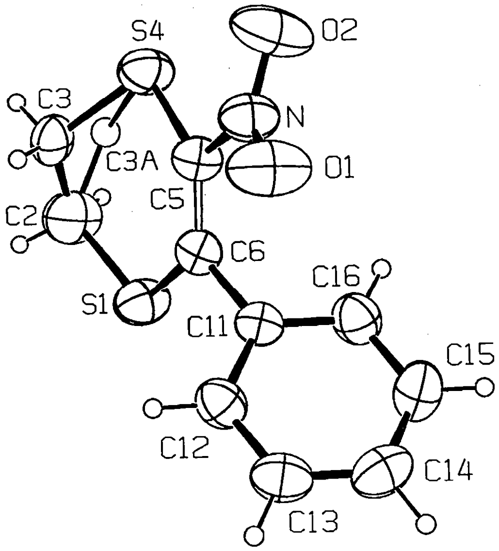


Fig. 1. A view of the molecule with the numbering scheme. Ellipsoids are at the 50% probability level except for atom C3*A* which is shown for clarity by a sphere of arbitrary size.

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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.

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* 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 52646 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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.

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

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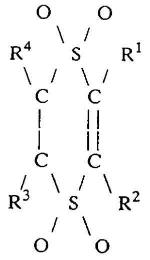
Abstract. $C_{10}H_{10}O_4S_2$, $M_r = 258{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}429\,(4)$, $b = 18{\cdot}463\,(7)$, $c = 5{\cdot}536\,(3)$ Å, $V = 1066{\cdot}0\,(10)$ Å^3, $Z = 4$, $D_x = 1{\cdot}61$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 4{\cdot}7$ cm^{-1}, $F(000) = 536$, $T = 294$ K, $R = 0{\cdot}0318$ 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

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