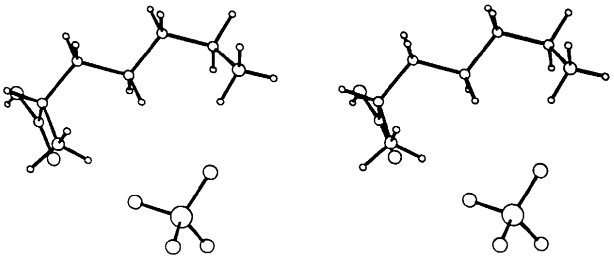

Fig. 2. Stereoscopic view of L-lysine sulphate.

of L-lysine–$PtCl_6$, a favourable interaction of the ε-NH_3^+ group with the Cl atoms of the $PtCl_6^{2-}$ octahedron is achieved through a similar value of the dihedral angle χ_4.

Crystal packing and hydrogen bonds. The crystal structure is stabilized by ionic interactions and hydrogen bonds which are given in Table 4. There are seven hydrogen bonds in the asymmetric unit of the crystal structure, one involving each H atom covalently bonded to N or O. The three H atoms of the α-amino group are donated to O(1) and to two O(2) of three different sulphate ions. A similar situation occurs for the ε-NH_3^+ group. The strongest hydrogen bond connects the carboxylic –OH group to O(3). The only potential acceptor atom not participating in hydrogen bonding is O(6).

This work was partially supported by a grant from the Consiglio Nazionale delle Ricerche, Italy.

Table 4. *Hydrogen bonds*

D is the donor and *A* is the acceptor atom. The following superscripts distinguish atoms related, by symmetry operations, to those in Table 1: none, x,y,z; (i) $1+x,y,z$; (ii) $\frac{1}{2}+x,\frac{3}{2}-y,1-z$; (iii) $-x,-\frac{1}{2}+y,\frac{3}{2}-z$; (iv) $1-x,-\frac{1}{2}+y,\frac{3}{2}-z$; (v) $\frac{1}{2}-x,1-y,\frac{1}{2}+z$.

C–*D*···*A*	*D*···*A*	C–*D*···*A*
C*A*–N···O(1^{i})	2·774 (5) Å	114·4 (5)°
C*A*–N···O(2)	2·764 (5)	121·4 (5)
C*A*–N···O(2^{ii})	2·835 (5)	105·1 (5)
C*E*–NZ···O(1^{iii})	2·894 (6)	87·1 (5)
C*E*–NZ···O(3)	2·909 (6)	116·2 (5)
C*E*–NZ···O(4^{iv})	2·777 (7)	92·3 (5)
C–O(5)···O(3^{v})	2·634 (5)	116·4 (6)

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Dithiin Tautomers: Dimethyl 2,4-Diphenyl-2*H*,4*H*-1,3-dithiin-5,6-dicarboxylate(I), $C_{20}H_{18}O_4S_2$, and Dimethyl 2,6-Diphenyl-2*H*,4*H*-1,3-dithiin-4,5-dicarboxylate (II), $C_{20}H_{18}O_4S_2$

By Isabella L. Karle and Jerome Karle

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, *USA*

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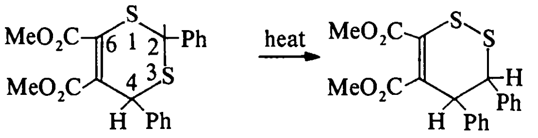
Abstract. (I) $M_r = 386{\cdot}46$, triclinic, $P\bar{1}$, $a = 10{\cdot}886$ (2), $b = 11{\cdot}392$ (2), $c = 16{\cdot}475$ (3) Å, $\alpha = 106{\cdot}09$ (1), $\beta = 82{\cdot}70$ (1), $\gamma = 101{\cdot}69$ (1), $V = 1916{\cdot}8$ (12) Å^3, $Z = 4$, $D_c = 1{\cdot}340$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 26{\cdot}2$ cm^{-1}, $F(000) = 808$, $R = 6{\cdot}1\%$ for 5007 unique reflections. (II) $M_r = 386{\cdot}46$, triclinic, $P\bar{1}$, $a = 9{\cdot}528$ (3), $b = 9{\cdot}834$ (3), $c = 11{\cdot}303$ (4) Å, $\alpha = 94{\cdot}80$ (3), $\beta = 86{\cdot}57$ (3), $\gamma = 114{\cdot}74$ (2)°, $V = 958{\cdot}1$ (10) Å^3, $Z = 2$, $D_c = 1{\cdot}341$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 26{\cdot}2$ cm^{-1}, $F(000) = 404$, $R = 5{\cdot}3\%$ for 2501 unique reflections. Crystal structure analyses have established that dimethyl 2,4-diphenyl-2*H*,4*H*-1,3-dithiin-5,6-dicarboxylate (I) undergoes tautomerization in a basic solution with a migration of a proton and a double bond in the dithiin ring to produce dimethyl 2,6-diphenyl-2*H*,4*H*-1,3-dithiin-4,5-dicarbox-

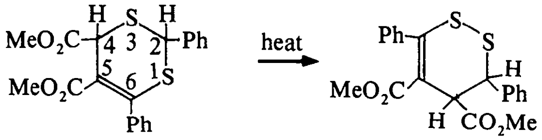
ylate (II). An interesting consequence of the tautomerization is that identical ring conformations result in I and II if one of the $-COOCH_3$ side chains in II is interchanged with one of the phenyl substituents. Compound I crystallizes in space group $P\bar{1}$ with two molecules per asymmetric unit having identical conformations.

Introduction. *m*-Dithiins have been synthesized from acetylenic esters, aromatic aldehydes plus hydrogen sulfide (Eisner & Krishnamurthy, 1971). Upon brief heating at 458 K, thermal rearrangement occurs in the *m*-dithiins and results in isomeric *o*-dithiins in quantitative yield (Eisner & Spreadbury, private communication):



(I) (colorless)

base



(II) (yellow)

The initial objective of this crystal structure analysis was to establish the stereoconfiguration of I at C(2) and C(4). A crystal in the original sample was shown to have structure II instead of I. A crystal in a subsequent sample proved to have structure I. The relationship between I and II is one of tautomerization and is caused by a change in pH. The chemical change involves the migration of a proton from C(4) to C(6) and the relocation of the double bond from C(5)—C(6) to C(4)—C(5) (with numbering as in I). The structure and stereoconfigurations of I and II will be described and compared.

Experimental. Crystals of I and II were provided by Dr Ulli Eisner and Mr Alan Spreadbury from Trent Polytechnic (Nottingham). I: white opaque chunks, exhibiting twinning, crystal used for data collection – clear colorless plate, 0·40 × 0·20 × 0·07 mm; II: crystal used – cloudy yellow prism, 0·40 × 0·60 × 0·60 mm. I and II: Nicolet P3F diffractometer, graphite monochromator, Cu $K\alpha$, $\theta/2\theta$ scan, $2\theta_{max} = 112°$, hkl, $\bar{h}kl$, $h\bar{k}l$ and $\bar{h}\bar{k}l$, standard reflections (006, 030, 600 for I, 006, 050, 200 for II) monitored every 60 measurements, intensity variations 3% for I, 1·5% for II, 14 centered reflections for measuring lattice parameters, correction for Lorentz and polarization effects, not for absorption.

Each structure was solved by direct phase determination using the symbolic addition procedure (Karle & Karle, 1963). The positions of all the hydrogen atoms were obtained from difference maps. Compound II was refined by full-matrix least-squares refinement using $|F|$ values on the 26 non-hydrogen atoms only while the parameters for the hydrogen atoms were kept constant. The conventional R factor was 5·3% for all the data, including those reflections with measured zero intensities;* $R_w = 6{\cdot}0\%$, $S = 1{\cdot}5$, weights given by Gilardi (1973), scattering factors from *International Tables for X-ray Crystallography* (1974), and the ratio of maximum LS shift to error was 0·5.

Initial refinement for compound I containing 52 non-hydrogen atoms and 36 hydrogen atoms per asymmetric unit was performed with restrained least squares using a sparse matrix. This procedure has been quite successful in protein refinements (Konnert & Hendrickson, 1980) and is now being applied to smaller molecules that contain a large number of atoms (Flippen-Anderson, Konnert & Gilardi, 1982; Karle & Karle, 1981). The restraints are applied to distances between bonded atoms (*e.g.* for C—C, 1·52 Å with an average restraint of ±0·04 Å; for C=C, 1·33 ± 0·04 Å, *etc.*), and to distances between next-nearest neighbors (*e.g.* for C—C—C, 2·48 ± 0·06 Å), which are equivalent to restraints on the bond angles. The advantages of the restrained procedure are the simultaneous refinement of all the bond lengths and angles for 88 atoms, including H atoms, and the great saving in computer time, especially on systems with parallel processors. A refinement with restraints, from a trial structure to a final structure with an acceptable R value, uses about 15% of the time required for a similar refinement with full-matrix least squares.

Restrained refinement for I resulted in an R factor of 7·9% for all the data. Subsequent full-matrix refinement on the parameters derived from the restrained refinement lowered the R factor to 6·1% for all the data; $R_w = 5{\cdot}4\%$, $S = 3{\cdot}4$. The values for the coordinates remained the same, within one e.s.d., in both refinement procedures. The only changes were some adjustments to the anisotropic thermal parameters. The coordinates and B_{eq} values reported in Tables 1 and 2 for both crystals are from the full-matrix least-squares refinements.* The computer programs used were *ORFLS* (Busing, Martin & Levy, 1962), *ORTEP* (Johnson, 1965) and in-house programs, including *CONLSQ*.

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* A list of observed and calculated structure factors, anisotropic thermal parameters, and coordinates for hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38187 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and* B_{eq} (Å^2) *values for dimethyl* 2,4-*diphenyl*-2*H*,4*H*-1,3-*dithiin*-5,6-*dicarboxylate, tautomer* I

The values in parentheses are the estimated standard deviations.

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S(1)*A*	0·6876 (1)	0·9685 (1)	0·4302 (1)	3·0
C(2)*A*	0·6954 (4)	1·1197 (4)	0·5091 (3)	2·8
S(3)*A*	0·8437 (1)	1·1626 (1)	0·5578 (1)	3·0
C(4)*A*	0·8233 (4)	1·0384 (4)	0·6103 (3)	3·0
C(5)*A*	0·8152 (4)	0·9106 (4)	0·5477 (3)	2·9
C(6)*A*	0·7643 (4)	0·8802 (4)	0·4722 (3)	3·0
C(7)*A*	0·7127 (4)	1·0454 (4)	0·6788 (3)	2·9
C(8)*A*	0·6002 (4)	0·9649 (4)	0·6679 (3)	3·6
C(9)*A*	0·5019 (4)	0·9769 (5)	0·7308 (3)	4·3
C(10)*A*	0·5160 (4)	1·0687 (5)	0·8043 (3)	4·0
C(11)*A*	0·6278 (5)	1·1491 (5)	0·8162 (3)	4·6
C(12)*A*	0·7273 (4)	1·1389 (4)	0·7540 (3)	4·0
C(13)*A*	0·6810 (4)	1·2123 (4)	0·4644 (3)	2·8
C(14)*A*	0·5757 (4)	1·2719 (4)	0·4886 (3)	3·7
C(15)*A*	0·5560 (5)	1·3548 (5)	0·4461 (3)	4·9
C(16)*A*	0·6409 (6)	1·3810 (5)	0·3805 (4)	5·6
C(17)*A*	0·7447 (5)	1·3232 (5)	0·3572 (3)	5·1
C(18)*A*	0·7647 (4)	1·2396 (4)	0·3985 (3)	3·8
C(19)*A*	0·7693 (4)	0·7584 (4)	0·4054 (3)	3·1
C(20)*A*	0·9055 (5)	0·6377 (4)	0·3095 (3)	4·7
C(21)*A*	0·8623 (4)	0·8201 (5)	0·5790 (3)	3·5
C(22)*A*	0·8676 (5)	0·6079 (5)	0·5636 (4)	6·2
O(1)*A*	0·6782 (3)	0·6860 (3)	0·3793 (2)	3·9
O(2)*A*	0·8881 (3)	0·7508 (3)	0·3751 (2)	3·4
O(3)*A*	0·9279 (3)	0·8487 (3)	0·6373 (2)	4·8
O(4)*A*	0·8212 (3)	0·7022 (3)	0·5385 (2)	4·4
S(1)*B*	0·8198 (1)	0·4293 (1)	−0·0523 (1)	3·1
C(2)*B*	0·8043 (4)	0·4609 (4)	0·0642 (3)	3·1
S(3)*B*	0·6601 (1)	0·5184 (1)	0·1080 (1)	3·2
C(4)*B*	0·6876 (4)	0·6580 (4)	0·0715 (3)	3·2
C(5)*B*	0·6956 (4)	0·6307 (4)	−0·0251 (3)	3·1
C(6)*B*	0·7461 (4)	0·5351 (4)	−0·0777 (3)	3·2
C(7)*B*	0·8007 (4)	0·7543 (4)	0·1100 (3)	3·0
C(8)*B*	0·9139 (5)	0·7750 (5)	0·0639 (3)	4·5
C(9)*B*	1·0136 (5)	0·8622 (5)	0·1007 (3)	5·3
C(10)*B*	1·0002 (5)	0·9297 (5)	0·1836 (3)	4·3
C(11)*B*	0·8883 (5)	0·9104 (5)	0·2302 (3)	3·9
C(12)*B*	0·7877 (4)	0·8218 (4)	0·1941 (3)	3·7
C(13)*B*	0·8045 (4)	0·3415 (4)	0·0852 (3)	3·1
C(14)*B*	0·9001 (5)	0·3316 (5)	0·1295 (3)	4·0
C(15)*B*	0·9022 (5)	0·2179 (6)	0·1464 (3)	5·3
C(16)*B*	0·8096 (6)	0·1181 (5)	0·1187 (4)	6·0
C(17)*B*	0·7138 (5)	0·1281 (5)	0·0762 (4)	5·4
C(18)*B*	0·7107 (5)	0·2389 (5)	0·0590 (3)	4·0
C(19)*B*	0·7422 (5)	0·4995 (4)	−0·1736 (3)	3·6
C(20)*B*	0·6058 (5)	0·4099 (5)	−0·2843 (3)	6·4
C(21)*B*	0·6492 (5)	0·7224 (5)	−0·0556 (3)	3·9
C(22)*B*	0·6397 (6)	0·8030 (6)	−0·1727 (4)	7·6
O(1)*B*	0·8314 (3)	0·5035 (4)	−0·2224 (2)	5·0
O(2)*B*	0·6239 (3)	0·4516 (3)	−0·1934 (2)	4·5
O(3)*B*	0·5891 (3)	0·7970 (3)	−0·0113 (2)	5·0
O(4)*B*	0·6845 (4)	0·7179 (4)	−0·1364 (2)	5·9

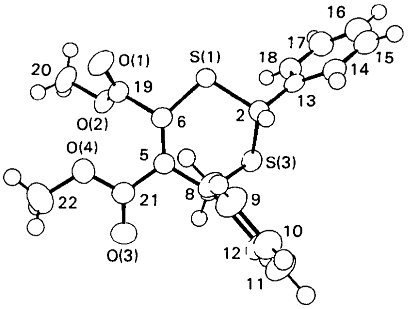

Fig. 1. Computer drawing of molecule I*A*. Atoms C(4) and C(7) lie behind atoms C(8) and C(9), respectively. Thermal ellipsoids are drawn at the 50% probability level, except for the hydrogen atoms that are represented by small spheres. Molecule I*B* is almost identical to molecule I*A*.

Table 2. *Fractional coordinates and* B_{eq}(Å^2) *values for dimethyl* 2,6-*diphenyl*-2*H*,4*H*-1,3-*dithiin*-4,5-*dicarboxylate, tautomer* II

The values in parentheses are the estimated standard deviations.

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S(1)	0·2019 (1)	0·5550 (1)	0·2415 (1)	2·9
C(2)	0·3731 (5)	0·6877 (5)	0·1657 (4)	2·7
S(3)	0·5282 (1)	0·7733 (1)	0·2698 (1)	2·7
C(4)	0·5614 (5)	0·6092 (5)	0·2941 (4)	2·5
C(5)	0·4189 (5)	0·4717 (5)	0·3286 (4)	2·5
C(6)	0·2706 (5)	0·4464 (5)	0·3152 (4)	2·6
C(7)	0·1324 (5)	0·3182 (5)	0·3643 (4)	2·7
C(8)	0·0398 (5)	0·2004 (5)	0·2867 (5)	3·4
C(9)	−0·0854 (6)	0·0783 (5)	0·3318 (5)	4·4
C(10)	−0·1184 (6)	0·0805 (6)	0·4533 (5)	4·8
C(11)	−0·0290 (6)	0·2010 (6)	0·5306 (5)	4·6
C(12)	0·0972 (5)	0·3199 (5)	0·4847 (4)	3·6
C(13)	0·3325 (5)	0·8059 (5)	0·1188 (4)	2·8
C(14)	0·3104 (6)	0·9139 (5)	0·1973 (5)	3·9
C(15)	0·2761 (6)	1·0222 (6)	0·1507 (6)	5·2
C(16)	0·2630 (6)	1·0228 (6)	0·0284 (6)	5·4
C(17)	0·2842 (6)	0·9133 (6)	−0·0490 (5)	4·7
C(18)	0·3198 (5)	0·8058 (5)	−0·0026 (4)	3·5
C(19)	0·6453 (5)	0·5755 (5)	0·1830 (4)	3·1
C(20)	0·8882 (6)	0·6519 (7)	0·0825 (5)	6·5
C(21)	0·4550 (5)	0·3534 (5)	0·3757 (4)	3·0
C(22)	0·6582 (6)	0·2766 (6)	0·3950 (5)	4·8
O(1)	0·5844 (4)	0·4834 (4)	0·1051 (3)	4·2
O(2)	0·7957 (3)	0·6676 (4)	0·1874 (3)	4·5
O(3)	0·3678 (4)	0·2424 (4)	0·4204 (3)	4·7
O(4)	0·6067 (3)	0·3863 (4)	0·3605 (3)	3·7

Table 3. *Bond lengths in the m-dithiin tautomers* I *and* II, $C_{20}H_{18}O_4S_2$ (Å)

The e.s.d.'s for the bond lengths are near 0·005 Å for C—S bonds, near 0·007 Å for C—C bonds, and near 0·006 Å for C—O bonds.

	I*A*	I*B*	II
Dithiin ring			
S(1)—C(2)	1·842	1·844	1·826
C(2)—S(3)	1·811	1·812	1·811
S(3)—C(4)	1·817	1·809	1·813
C(4)—C(5)	1·526	1·529	1·521
C(5)—C(6)	1·355	1·356	1·344
C(6)—S(1)	1·750	1·740	1·750
Ring side groups			
C(2)—C(13)	1·485	1·494	1·512
C(4)—C(7)	1·540	1·545	
C(4)—C(19)			1·535
C(5)—C(21)	1·471	1·474	1·489
C(6)—C(7)			1·507
C(6)—C(19)	1·519	1·522	
Phenyl			
C(7)—C(8)	1·372	1·375	1·399
C(8)—C(9)	1·392	1·390	1·398
C(9)—C(10)	1·365	1·374	1·391
C(10)—C(11)	1·367	1·366	1·401
C(11)—C(12)	1·393	1·399	1·390
C(12)—C(7)	1·395	1·392	1·382
C(13)—C(14)	1·409	1·384	1·402
C(14)—C(15)	1·384	1·403	1·388
C(15)—C(16)	1·387	1·372	1·396
C(16)—C(17)	1·381	1·367	1·403
C(17)—C(18)	1·377	1·376	1·386
C(18)—C(13)	1·389	1·393	1·385
CO_2Me			
C(19)—O(1)	1·195	1·182	1·192
C(19)—O(2)	1·337	1·336	1·339
O(2)—C(20)	1·462	1·467	1·471
C(21)—O(3)	1·202	1·202	1·191
C(21)—O(4)	1·336	1·328	1·346
O(4)—C(22)	1·449	1·456	1·448

Discussion. *Crystal* I. The two independent molecules in the asymmetric unit are almost identical in every respect. Molecule *A* is shown in Fig. 1. The dithiin ring has a half-chair conformation with C(2) and S(3) on opposite sides of the average plane of the other four atoms. The relative stereoconfiguration has been established at C(2) with the proton axial and directed upward while the phenyl group is equatorial and at C(4) the phenyl group is directed upward and axial while the proton is directed downward.

Bond lengths, bond angles and torsional angles listed in Tables 3, 4 and 5 show the great similarity in values between molecules *A* and *B* in crystal I.

Crystal II. Upon the treatment of I with a base, the proton on C(4) migrates to C(6) and the double bond is reformed between C(4) and C(5). Furthermore, in the resulting tautomer II, a rearrangement of the conformation of the dithiin ring occurs so that it resembles the original conformation of I. In Figs. 2 and 3, molecule II has been rotated and renumbered so that its confor-

Table 4. *Bond angles in the m-dithiin tautomers* I *and* II, $C_{20}H_{18}O_4S_2$ (°)

The e.s.d.'s for the bond angles are near 0·6°.

	I*A*	I*B*	II
Dithiin ring			
C(6)S(1)C(2)	105·4	106·7	104·3
S(1)C(2)S(3)	110·4	111·1	109·2
C(2)S(3)C(4)	98·4	99·5	98·8
S(3)C(4)C(5)	112·5	112·6	115·6
C(4)C(5)C(6)	123·8	123·5	126·8
C(5)C(6)S(1)	129·0	128·8	127·1
Ring side groups			
S(1)C(2)C(13)	107·4	107·2	108·3
S(3)C(2)C(13)	110·9	110·2	110·3
S(3)C(4)C(7)	112·0	113·2	
C(5)C(4)C(7)	112·6	112·1	
S(3)C(4)C(19)			107·9
C(5)C(4)C(19)			112·0
C(4)C(5)C(21)	113·6	113·5	113·7
C(6)C(5)C(21)	122·5	122·9	119·3
C(5)C(6)C(19)	124·0	123·7	
S(1)C(6)C(19)	106·9	107·5	
C(5)C(6)C(7)			125·2
S(1)C(6)C(7)			107·6
Phenyl			
C(2)C(13)C(14)	118·3	119·8	120·2
C(13)C(14)C(15)	120·1	119·5	118·5
C(14)C(15)C(16)	120·1	119·6	120·6
C(15)C(16)C(17)	119·8	121·1	120·2
C(16)C(17)C(18)	120·6	119·9	119·2
C(17)C(18)C(13)	120·6	120·3	120·2
C(18)C(13)C(14)	118·8	119·6	121·2
C(18)C(13)C(2)	122·9	120·7	118·5
C(4)C(7)C(8)	122·6	122·1	
C(6)C(7)C(8)			119·3
C(7)C(8)C(9)	120·5	120·5	119·8
C(8)C(9)C(10)	120·5	120·4	118·6
C(9)C(10)C(11)	119·7	119·8	121·6
C(10)C(11)C(12)	120·7	120·3	119·0
C(11)C(12)C(7)	119·6	119·9	119·9
C(12)C(7)C(8)	119·0	119·1	120·9
C(12)C(7)C(4)	118·4	118·8	
C(12)C(7)C(6)			119·7
CO_2Me			
C(5)C(21)O(3)	123·6	123·6	127·8
C(5)C(21)O(4)	113·6	113·4	110·3
O(3)C(21)O(4)	122·8	123·0	121·8
C(21)O(4)C(22)	116·7	117·0	116·9
C(6)C(19)O(1)	123·9	124·9	
C(4)C(19)O(1)			124·9
C(6)C(19)O(2)	110·2	109·1	
C(4)C(19)O(2)			109·0
O(1)C(19)O(2)	125·6	125·7	126·1
C(19)O(2)C(20)	115·6	115·4	114·4

Table 5. *Torsional angles in tautomers* I *and* II (°)

The e.s.d.'s for torsional angles are near 1·0°.

	I*A*	I*B*	II*
Dithiin ring			
C(6)S(1)C(2)S(3)	+36	+31	+49
S(1)C(2)S(3)C(4)	−65	−61	−67
C(2)S(3)C(4)C(5)	+64	+64	+52
S(3)C(4)C(5)C(6)	−32	−35	−17
C(4)C(5)C(6)S(1)	−5	−4	−7
C(5)C(6)S(1)C(2)	+2	+5	−10
Ring side groups			
S(1)C(2)C(13)C(14)			72
S(1)C(2)C(13)C(18)	−61	−62	
S(3)C(4)C(19)O(1)			+99
S(3)C(4)C(7)C(8)	+106	+106	
C(4)C(5)C(21)O(3)	−17	−14	−171
S(1)C(6)C(19)O(1)	−61	−66	
S(1)C(6)C(7)C(8)			−73

* Mirror image of the molecule represented by the coordinates in Table 2.

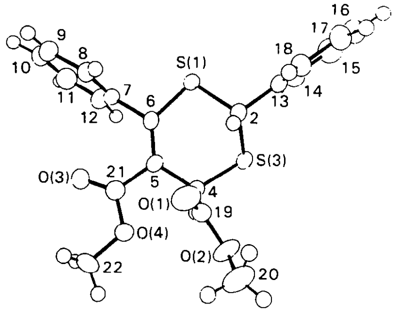

Fig. 2. Computer drawing of molecule II.

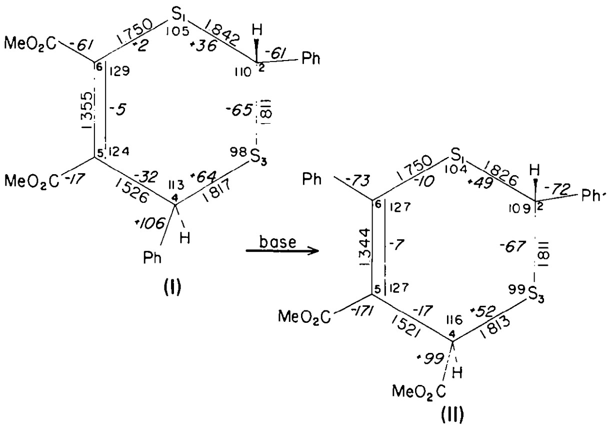

Fig. 3. Comparison of geometric parameters (Å and deg) in the tautomers I and II.

mation and configuration resemble those of molecule I most closely. In this orientation, it appears in II as if the phenyl group and the methoxycarbonyl group have interchanged positions between C(4) and C(6) as compared to I.

Fig. 3 shows the close resemblance between the values of the bond lengths, bond angles and torsional angles associated with the dithiin rings in I and II. The only major difference is at C(5) where the methoxycarbonyl side group flips over by nearly 160°. The remaining bond lengths and angles for molecule II, listed in Tables 3 and 4, are also very nearly equal to those observed in molecules I*A* and I*B*.

These are the first 1,3-dithiins whose structure have been determined, although the structures of a number of 1,4-dithiins have appeared in the literature (see *e.g.* Levi & Doedens, 1980). In the three molecules in this paper, the C—S bond adjacent to the double bond has an average value of 1·747 (5) Å as compared to an average of 1·820 (5) Å for the nine single C—S bonds. The CSC angle adjacent to C=C has an average value of 105·5 (6)° while the CSC angle surrounded by saturated carbon atoms has an average value of 98·9 (6)°.

In the packing in crystals I and II there are only van der Waals contacts between molecules. In both crystals the nearest approaches are between molecules related by centers of symmetry. In crystal I the nearest approaches between non-hydrogen atoms are S(3)*A*···O(2)′*A* at 3·12 (1), S(3)*B*···O(2)′*B* at 3·27 (1), O(1)*A*···C(14)′*A* at 3·32 (1) and O(1)*B*···C(14)′*B* at 3·42 (1) Å. In crystal II the closest contact is between O(1)···O(1)′ at 3·06 (1) Å. All other distances between non-hydrogen atoms have considerably greater values.

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Methyl (±)-5α-Acetoxymethyl-4β-methoxy-1-oxo-1,2,3,4,4aβ,5,6,7,8,8aα-decahydronaphthalene-4aβ-carboxylate, $C_{16}H_{24}O_6$

By Byron Rubin, Jay Epstein and Laura Brooks

Emory University, Department of Chemistry, Atlanta, Georgia 30322, *USA*

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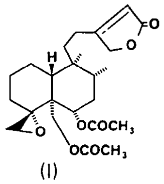
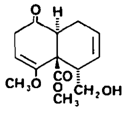
Abstract. $M_r = 312·4$, monoclinic, $P2_1/c$, $a = 8·479$ (6), $b = 17·225$ (10), $c = 11·411$ (8) Å, $\beta = 102·64$ (5)°, $V = 1626$ (2) Å^3, $Z = 4$, $D_x = 1·27$, $D_m = 1·25$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·059$ mm^{-1}, $T = 296$ K. The structure, which was refined to $R = 0·068$ using 2263 observed reflections, has a *cis* relationship between the methoxy and ring-junction ester function.

Introduction. Ajugarin I, (I), isolated from *Ajuga remota* (Labiatae) (Kubo, Lee, Balogh-Nair, Nakanishi & Chapya, 1976), shows significant antifeeding activity against African army worms, *Spodotera exempta,* and has been well characterized (Hosazawa, Kato, Munakato & Chen, 1974).



(I)



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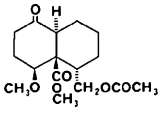

(III)

In designing the *de novo* synthesis of this natural product, it was essential to establish the stereochemistry of several intermediates along the synthetic pathway. The structure reported here is one of these intermediates.

The title compound, (III), whose synthesis is described elsewhere (Goldsmith & Thottathil, 1982)

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