C15—N2—C11	112.24 (15)	O1—C7—O2	124.23 (17)
C7—N1—C5	122.29 (15)	O1—C7—N1	118.19 (17)
C7—N1—C1	122.91 (14)	O2—C7—N1	117.58 (16)
C5—N1—C1	114.40 (14)		

C15—N2—C11—C12	55.8 (2)
N2—C11—C12—C13	−55.9 (2)
C11—C12—C13—C14	55.8 (2)
C11—C12—C13—C16	179.68 (16)
C12—C13—C14—C15	−55.9 (2)
C16—C13—C14—C15	−179.73 (16)
C11—N2—C15—C14	−55.9 (2)
C13—C14—C15—N2	56.5 (2)
C7—N1—C1—C2	−131.71 (17)
C5—N1—C1—C2	55.4 (2)
N1—C1—C2—C3	−53.1 (2)
C1—C2—C3—C4	52.1 (2)
C1—C2—C3—C6	176.33 (15)
C2—C3—C4—C5	−52.5 (2)
C6—C3—C4—C5	−176.44 (16)
C7—N1—C5—C4	131.01 (17)
C1—N1—C5—C4	−56.0 (2)
C3—C4—C5—N1	54.3 (2)
C5—N1—C7—O1	−4.3 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1*W*···O2	0.94 (2)	1.79 (2)	2.718 (2)	172 (2)
O3—H2*W*···O1^{i}	0.92 (2)	1.79 (2)	2.712 (2)	177 (2)
N2—H1···O2^{ii}	1.06 (2)	1.63 (2)	2.681 (2)	167 (2)
N2—H2···O3	0.97 (2)	1.84 (2)	2.796 (2)	172 (2)
C15—H15*A*···O3^{iii}	0.99	2.58	3.442 (2)	146
C12—H12*A*···O1^{iv}	0.99	2.58	3.303 (2)	129

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x-\frac{1}{2}, y, \frac{1}{2}-z$; (iv) $x, 1+y, z$.

For (1), NH atoms were refined freely, the OH atom was treated as a rigid group (initial position from difference synthesis, allowed to rotate but not tip) and the remaining H atoms were treated as riding. The largest features of residual electron density (0.5 e Å^{-3}) are 0.8 Å from the I atom. A rigid-body libration correction (Schomaker & Trueblood, 1968) gave R_{lib} = 0.039 and corrected bond lengths (Å) of N—C1 = 1.507, C1—C2 = 1.522, C2—C3 = 1.528, C3—C4 = 1.528, C4—C5 = 1.525, C5—N = 1.503 and C3—O = 1.435. For (2), the NH and OH atoms were refined freely, methyl group H atoms were refined as rigid groups (as for OH above) and the remaining H atoms were treated as riding. The freely refined N—H bonds are longer than expected (for fixed N—H of this type, the program system sets a distance of 0.91 Å), but attempts to idealize the N—H bond lengths with refinement restraints were unsuccessful (the program indicated that there were 'disagreeable restraints'). Clearly, if the N—H bonds are for any reason systematically too long, then the H···*A* hydrogen-bonding contacts will be too short. It is unlikely that X-ray methods alone can resolve this problem. A rigid-body libration correction (Schomaker & Trueblood, 1968) for the cation gave R_{lib} = 0.056 and corrected bond lengths (Å) of N2—C11 = 1.499, C11—C12 = 1.519, C12—C13 = 1.529, C13—C14 = 1.531, C14—C15 = 1.530 and C15—N2 = 1.492. The anion was not amenable to correction, presumably because of rotation about the exocyclic N—C bond.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *XP* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*97.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1355). Services for accessing these data are described at the back of the journal.

References

Ahrens, B., Jones, P. G. & Fischer, A. K. (1999). *Eur. J. Inorg. Chem.* pp. 1103–1110.
Brown, C. J. & Gray, L. R. (1982). *Acta Cryst.* B**38**, 2307–2308.
Czugler, M., Bombicz, P., Csoregh, I. & Gallardo, O. (1995). *Z. Kristallogr.* **210**, 368.
Dreele, R. B. von, Bradshaw, R. L. & Burke, W. J. (1983). *Acta Cryst.* C**39**, 253–255.
Fait, J. (1991). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Freytag, M. & Jones, P. G. (1999). *Acta Cryst.* C**55**, 1682–1685.
Jones, P. G. & Ahrens, B. (1998). *Eur. J. Org. Chem.* pp. 1678–1688.
Knorr, L. (1898). *Ann. Chem.* **301**, 1–10.
Mascal, M. (1997). *J. Chem. Soc. Perkin Trans.* 2, pp. 1999–2001.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
Schroth, W., Schädler, H.-D. & Andersch, J. (1989). *Z. Chem.* **29**, 129–135.
Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994*a*). *XEMP. Empirical Absorption Correction Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994*b*). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Steiner, T. (1998). *Acta Cryst.* B**54**, 456–463.

Acta Cryst. (1999). C**55**, 1877–1881

A rhodanine derivative and its cycloadduct with diphenyl nitrile imine

ANTHONY LINDEN, ENAS M. A. H. AWAD AND HEINZ HEIMGARTNER

Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland. E-mail: alinden@oci.unizh.ch

(Received 1 June 1999; accepted 30 June 1999)

Abstract

The phenylmethylene substituent at the C5 position of 5-benzylidene-3-phenyl-2-thioxo-1,3-thiazolidin-4-one, $C_{16}H_{11}NOS_2$, (I), is virtually coplanar with the planar five-membered ring, whereas the phenyl group at N3 is almost orthogonal to this plane. The crystals of the

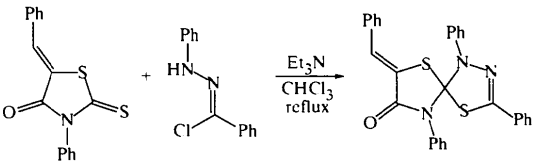
chiral cycloadduct, 7-benzylidene-2,4,9-triphenyl-1,6-dithia-3,4,9-triazaspiro[4.4]non-2-en-8-one, $C_{29}H_{21}N_3OS_2$, (III), are racemic. Both five-membered rings have an envelope conformation with the spiro-C atom as the envelope flap, although this envelope is quite flattened for the 1,3-thiazolidine ring. In both compounds, short intramolecular C—H···S contacts cause visible steric strain. The known starting material, (I), has been prepared by condensation of 3-phenyl-2-thioxothiazolidin-4-one and benzaldehyde. Its reaction with *N*-phenylbenzohydrazonoyl chloride, (II), in the presence of triethylamine yielded (III) *via* 1,3-dipolar cycloaddition of the intermediate nitrile imine.

Comment

Nitrile imines are well known 1,3-dipoles which undergo 1,3-dipolar cycloadditions with different kinds of double and triple bonds (Caramella & Grünanger, 1984; Claus, 1990; Shawali, 1993). Nowadays, these cycloadditions are commonly used in syntheses of five-membered N-heterocycles. The mechanistic aspects of the reaction have been investigated thoroughly and reviewed comprehensively by Huisgen and his group (Huisgen, 1984). In addition to the regio- and stereoselectivity, the chemoselectivity (site selectivity) of 1,3-dipolar cycloadditions of nitrile imines with multifunctional substrates (for example, the dipolarophilicity of different π-systems) is an interesting aspect. Because of the synthetic suitability of these reactions it is a worthwhile task to study this competition (Shawali, 1993; Grubert *et al.*, 1994).

In general, non-enolizable C=S groups are the most reactive dipolarophiles and, therefore, thioketones are called 'superdipolarophiles' (Huisgen & Langhals, 1989; Huisgen, Fišera *et al.*, 1995; Huisgen, Sicking & Sustmann, 1995; Fišera *et al.*, 1996). Several 1,3-dipolar cycloadditions of nitrile imines with C=S groups of thioketones, thioamides, thiocarbamates and carbon disulfide have been reported to give 1,3,4-thiadiazole derivatives (Huisgen *et al.*, 1962; Dickoré & Wegler, 1966; Wolkoff & Hammerum, 1976; Friedrich & Zamkanei, 1979; Bonini *et al.*, 1981; Fliege *et al.*, 1984; Grubert *et al.*, 1994; Dunstan *et al.*, 1998). In the case of isothiocyanates, addition occurred to the C=S and/or C=N bond (Huisgen *et al.*, 1962; Perronnet & Girault, 1973; Elmoghayar *et al.*, 1977). Especially interesting substrates, with respect to competition studies, are those containing C=C, C=N, C=O and C=S groups; for example, heterocyclic thiones. Several reactions with exclusive or strongly preferred additions to the C=S group have been reported (Huisgen *et al.*, 1962; Poirier, 1968; Büchel *et al.*, 1984; Greig *et al.*, 1985; Dunstan *et al.*, 1998). On the other hand, nitrile imines added to the C=C bond of 1-benzopyrane-2(2*H*)-thione (Baruah *et al.*, 1986), and with 1-benzopyrane-4(4*H*)-thione, both types of adducts have been obtained (Baruah *et al.*, 1988; Redhouse, 1990; *cf.* also Fišera *et al.*, 1995). Recently, a series of cycloadditions of various nitrile imines, generated *in situ* by treatment of hydrazonoyl halides with triethylamine, with 5-(arylidene)-3-phenyl-2-thioxo-1,3-thiazolidin-4-ones of type (I) has been reported (Hassaneen *et al.*, 1996). The results revealed that the reaction proceeded site selectively with the C=S group because only spirocyclic adducts of type (III) have been formed. Therefore, the C=S group shows the highest dipolarophilicity.

Following the described protocol (Hassaneen *et al.*, 1996), we reacted the 5-benzylidene-3-phenyl derivative of rhodanine, (I) (Andreasch & Zipser, 1903), with *N*-phenylbenzohydrazonoyl chloride, (II), in chloroform and triethylamine to yield the racemic spirocyclic adduct, (III). As part of the full characterization of compounds (I) and (III), their low-temperature crystal structures have been determined.



(I) (II) (III)

There are 34 entries for rhodanine derivatives in the Cambridge Structural Database (Allen & Kennard, 1993; April 1999 release), of which reliable atomic coordinates are available for 15. The rhodanine moiety in compound (I) has a geometry (Table 1) which is consistent with those of these 15 related structures. The bond lengths involving S1 indicate significant delocalization of the π-electrons of S1 with the adjacent C2=S2 and C5=C12 systems. The five-membered ring in compound (I) is planar and the r.m.s. deviation from the plane of the five constituent atoms is 0.007 Å. The maximum deviation from this plane of the peripheral atoms, S2, O4, C6 and C12 (not included in the plane calculation itself), is 0.060 (4) Å for C6. The plane of the phenyl ring of the phenylmethylene substituent makes an angle of only 4.19 (18)° with the plane of the five-membered ring, the twist being principally about the C12—C13 bond. This coplanarity permits significant π-electron delocalization across the C12—C13 bond, which is clearly evident in the length of this bond. Conversely, the plane of the *N*-phenyl substituent is nearly orthogonal to that of the five-membered ring, the interplanar angle being 78.36 (10)°. The two coplanar rings result in a short intramolecular contact of 2.56 Å between the H atom at C18 and S1 [C18···S1 = 3.289 (5) Å]. The steric strain caused by this close approach is evident in the significantly enlarged bond angles for S1—C5—C12 and C5—C12—C13, and to a lesser extent for C12—C13—C18.

There are no known reports of structures having the same spirocyclic heterocyclic ring core as compound

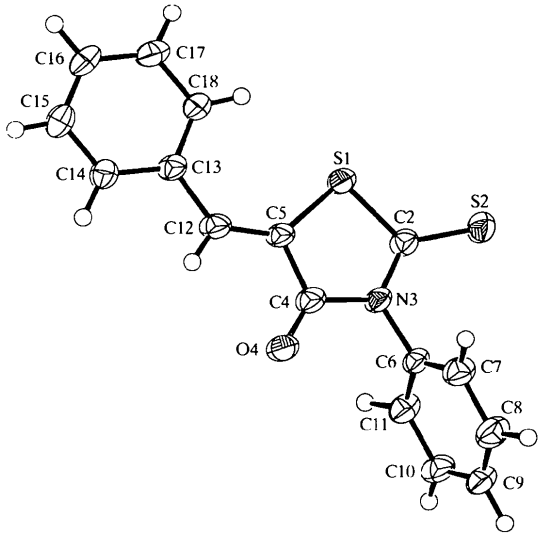


Fig. 1. View of the molecule of compound (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

(III). The bond lengths and angles in compound (III) are normal for spirocyclic compounds involving similar thiazolidine rings. The S—C bonds involving the spiro-C atom are significantly longer than the other S—C bonds (Table 2), because the former cannot take part in π-electron delocalization with an adjacent double-bonded group. This pattern has been observed before in similar spirocyclic thiazolidine ring systems (Kägi *et al.*, 1996; Mlostoń *et al.*, 1997). Both five-membered rings have the envelope conformation with the spiro-C atom, C2, acting as the envelope flap in each case. However, the 1,3-thiazolidine ring is a very flattened envelope with C2 lying only 0.132 (3) Å from the plane defined by S1, N3, C4 and C5. A half-chair conformation can be excluded because the r.m.s. deviation of these four atoms from their plane is 0.013 Å with a maximum deviation of 0.0169 (12) Å for C4. By contrast, the 1,3,4-thiazolidine ring is a much more strongly delineated envelope with C2 lying 0.415 (3) Å from the plane defined by S6, C7, N8 and N9. The r.m.s. deviation of these latter atoms from their plane is 0.006 Å.

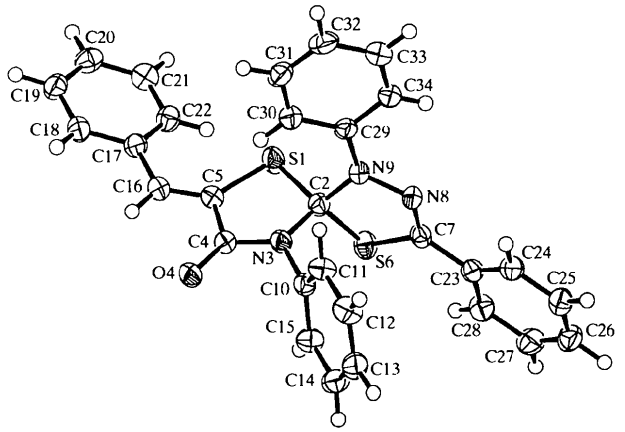


Fig. 2. View of the molecule of compound (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

The plane of the phenyl ring of the phenylmethylene substituent makes an angle of 26.88 (7)° with the above-defined four-atom plane of the 1,3-thiazolidine ring, the twist being principally about the C16—C17 bond. Nonetheless, significant π-electron delocalization across the C12—C13 bond is still evident from the length of this bond. As in compound (I), the plane of the *N*-phenyl substituent of the 1,3-thiazolidine ring lies nearly orthogonal to the four-atom plane of the parent five-membered ring, the interplanar angle being 74.42 (8)°. The planes of the phenyl and *N*-phenyl substituents on the 1,3,4-thiazolidine ring make angles of 8.13 (5) and 29.79 (9)°, respectively, with the plane defined by S6, C7, N8 and N9 of the parent ring. As with compound (I), the nearly coplanar alignments between some of the phenyl rings and their parent five-membered rings result in some short intramolecular C—H···S contacts where C22···S1 = 3.241 (2), H22···S1 = 2.62, C28···S6 = 3.124 (3) and H28···S6 = 2.70 Å. The strain caused by the contact involving S1 leads to an enlargement of the S1—C5—C16, C5—C16—C17 and C16—C17—C22 bond angles similar to that observed in the structure of (I), but no discernible geometrical distortions are apparent as a result of the contact involving S6.

Experimental

Compound (I) was obtained in 80.8% yield by the reaction of 3-phenyl-2-thioxo-1,3-thiazolidin-4-one (10.45 g, 50 mmol) and benzaldehyde (5.31 g, 50 mmol) in glacial acetic acid (50 ml) and sodium acetate (12 g, 146.3 mmol) following a known protocol (Andreasch & Zipser, 1903). Filtration of the precipitated product and crystallization from acetic acid gave yellow needles (m.p. 467 K). Triethylamine (0.7 ml, 5.0 mmol) was added at room temperature to a solution of (I) (1.48 g, 5.0 mmol) and *N*-phenylbenzohydrazonoyl chloride, (II) (1.15 g, 5.0 mmol), in chloroform (40 ml). The mixture was refluxed for 11 h, the solvent was evaporated, the residue was treated with methanol, and recrystallized from glacial acetic acid to give the spirocyclic adduct (III) in 53.2% yield as yellow prisms (m.p. 453 K). Suitable single crystals of (I) and (III) were obtained by recrystallization from glacial acetic acid.

Compound (I)

Crystal data

$C_{16}H_{11}NOS_2$ Mo $K\alpha$ radiation
M_r = 297.39 λ = 0.71069 Å

Monoclinic
$C2/c$
$a = 21.097\ (5)$ Å
$b = 5.356\ (7)$ Å
$c = 26.090\ (4)$ Å
$\beta = 107.173\ (13)°$
$V = 2817\ (3)$ Å^3
$Z = 8$
$D_x = 1.402$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 17.0–20.0°$
$\mu = 0.371$ mm^{-1}
$T = 173\ (1)$ K
Needle
$0.50 \times 0.20 \times 0.15$ mm
Yellow

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.849$, $T_{max} = 0.946$
3656 measured reflections
3212 independent reflections

2397 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 6$
$l = -33 \rightarrow 32$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.158$
$S = 1.032$
3212 reflections
192 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.105P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

S1—C2	1.751 (2)	N3—C4	1.413 (3)
S1—C5	1.757 (3)	C4—C5	1.486 (3)
S2—C2	1.637 (3)	C5—C12	1.343 (3)
N3—C2	1.371 (3)	C12—C13	1.464 (3)
C2—S1—C5	93.02 (11)	N3—C4—C5	110.19 (19)
C2—N3—C4	116.58 (18)	C12—C5—C4	119.0 (2)
C2—N3—C6	124.61 (18)	C12—C5—S1	131.61 (17)
C4—N3—C6	118.81 (18)	C4—C5—S1	109.38 (16)
N3—C2—S2	126.96 (17)	C5—C12—C13	130.6 (2)
N3—C2—S1	110.80 (17)	C18—C13—C12	123.7 (2)
S2—C2—S1	122.24 (14)	C14—C13—C12	117.8 (2)
C4—C5—C12—C13	−179.2 (2)	C5—C12—C13—C14	177.0 (3)

Compound (III)

Crystal data

$C_{29}H_{21}N_3OS_2$
$M_r = 491.62$
Monoclinic
$P2_1/n$
$a = 9.910\ (3)$ Å
$b = 16.737\ (3)$ Å
$c = 14.412\ (2)$ Å
$\beta = 93.571\ (17)°$
$V = 2385.8\ (8)$ Å^3
$Z = 4$
$D_x = 1.369$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 17.5–20.0°$
$\mu = 0.252$ mm^{-1}
$T = 173\ (1)$ K
Prism
$0.40 \times 0.32 \times 0.25$ mm
Yellow

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
5982 measured reflections
5470 independent reflections
3994 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 21$
$l = -18 \rightarrow 18$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.115$
$S = 1.035$
5470 reflections
337 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.871P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (III)*

S1—C5	1.757 (2)	N8—C7	1.289 (3)
S1—C2	1.834 (2)	N8—N9	1.391 (2)
S6—C7	1.762 (2)	N9—C29	1.415 (3)
S6—C2	1.835 (2)	N9—C2	1.457 (3)
N3—C4	1.370 (3)	C4—C5	1.495 (3)
N3—C10	1.443 (2)	C5—C16	1.341 (3)
N3—C2	1.468 (2)	C16—C17	1.461 (3)
C5—S1—C2	93.21 (9)	N3—C4—C5	111.06 (17)
C7—S6—C2	89.33 (10)	C16—C5—C4	119.78 (18)
C4—N3—C2	118.16 (16)	C16—C5—S1	129.19 (16)
C7—N8—N9	111.89 (17)	C4—C5—S1	110.99 (14)
N8—N9—C2	115.51 (15)	N8—C7—C23	123.05 (18)
N9—C2—N3	113.75 (16)	N8—C7—S6	115.08 (15)
N9—C2—S1	114.61 (14)	C23—C7—S6	121.86 (15)
N3—C2—S1	105.78 (13)	C5—C16—C17	129.18 (19)
N9—C2—S6	102.17 (13)	C18—C17—C16	118.31 (19)
N3—C2—S6	112.31 (14)	C22—C17—C16	123.42 (19)
S1—C2—S6	108.25 (11)		
C4—C5—C16—C17	177.90 (19)	C5—C16—C17—C18	−154.9 (2)

An absorption correction was not applied for compound (III) because the ψ scans indicated a flat absorption profile. Each H atom was placed in a geometrically idealized position and constrained to ride on its parent C atom while its U_{iso} was refined.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

The Swiss National Science Foundation and F. Hoffmann–La Roche AG, Basel, are thanked for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1307). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Andreasch, R. & Zipser, A. (1903). *Monatsh. Chem.* **24**, 499–518.

Baruah, A. K., Prajapati, D. & Sandhu, J. S. (1986). *Heterocycles*, **24**, 1527–1530.

Baruah, A. K., Prajapati, D. & Sandhu, J. S. (1988). *Tetrahedron*, **44**, 6137–6142.

Bonini, B. F., Mazzanti, G., Sarti, S., Zanirato, P. & Maccagnani, R. (1981). *J. Chem. Soc. Chem. Commun.* pp. 822–823.

Büchel, T., Prewo, R., Bieri, J. H. & Heimgartner, H. (1984). *Helv. Chim. Acta*, **67**, 534–549.

Caramella, P. & Grünanger, P. (1984). *1,3-Dipolar Cycloaddition Chemistry*, Vol. 1, edited by A. Padwa, pp. 291–392. New York: Wiley.

Claus, P. K. (1990). *Methoden der organischen Chemie* (Houben-Weyl), Vol. E14b, edited by D. Klamann & H. Hagemann, pp. 33–73. Stuttgart: Thieme Verlag.

Dickoré, K. & Wegler, R. (1966). *Angew. Chem. Int. Ed. Engl.* **5**, 970.

Dunstan, J. B. F., Elsey, G. M., Russell, R. A., Savage, G. P., Simpson, G. W. & Tiekink, E. R. T. (1998). *Aust. J. Chem.* **51**, 499–509.

Elmoghayar, M. R. H., Elnagdi, M. H., Ibrahim, M. K. A. & Sallam, M. M. M. (1977). *Helv. Chim. Acta*, **60**, 2171–2176.

Fišera, L., Huisgen, R., Kalwinsch, I., Langhals, E., Li, X., Mlostoń, G., Polborn, K., Rapp, J., Sicking, W. & Sustmann, R. (1996). *Pure Appl. Chem.* **68**, 789–798.

Fišera, L., Jarošková, L., Matejková, I. & Heimgartner, H. (1995). *Heterocycles*, **40**, 271–278.

Fliege, W., Grashey, R. & Huisgen, R. (1984). *Chem. Ber.* **117**, 1194–1214.

Friedrich, K. & Zamkanei, M. (1979). *Chem. Ber.* **112**, 1873–1878.

Greig, D. J., McPherson, M., Paton, R. M. & Crosby, J. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 1205–1208.

Grubert, L., Pätzel, M., Jugelt, W., Riemer, B. & Liebscher, J. (1994). *Liebigs Ann. Chem.* pp. 1005–1011.

Hassaneen, M. H., Shawali, A. S., Farag, D. S. & Awad, E. M. A. H. (1996). *Phosphorus Sulfur Silicon*, **113**, 53–58.

Huisgen, R. (1984). *1,3-Dipolar Cycloaddition Chemistry*, Vol. 1, edited by A. Padwa, pp. 1–176. New York: Wiley.

Huisgen, R., Fišera, L., Giera, H. & Sustmann, R. (1995). *J. Am. Chem. Soc.* **117**, 9671–9678.

Huisgen, R., Grashey, R., Seidel, M., Knupfer, H. & Schmidt, R. (1962). *Liebigs Ann. Chem.* **658**, 169–180.

Huisgen, R. & Langhals, E. (1989). *Tetrahedron Lett.* **30**, 5369–5372.

Huisgen, R., Sicking, W. & Sustmann, R. (1995). *J. Am. Chem. Soc.* **117**, 9679–9685.

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

Kägi, M., Linden, A., Mlostoń, G. & Heimgartner, H. (1996). *Helv. Chim. Acta*, **79**, 855–874.

Mlostoń, G., Linden, A. & Heimgartner, H. (1997). *Polish J. Chem.* **71**, 32–39.

Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1997). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.8. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Perronnet, J. & Girault, P. (1973). *Bull. Soc. Chim. Fr.* pp. 2843–2847.

Poirier, Y. (1968). *Bull. Soc. Chim. Fr.* pp. 1203–1204.

Redhouse, A. D. (1990). *Acta Cryst.* C**46**, 1572–1573.

Shawali, A. S. (1993). *Chem. Rev.* **93**, 2731–2777.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Wolkoff, P. & Hammerum, S. (1976). *Acta Chem. Scand. Ser. B*, **30**, 837–842.

Acta Cryst. (1999). C**55**, 1881–1882

An unexpected oxidation product of α-santonin

R. B. Bates,[a] B. L. Malik,[b] S. K. Paknikar,[b] K. J. McClure[a] and M. D. Carducci[a]

[a]*Department of Chemistry, University of Arizona, 1306 E. University, Tucson, AZ 85721-0041, USA, and* [b]*Department of Chemistry, Goa University, PO University 403202, Goa, India. E-mail: batesr@u.arizona.edu*

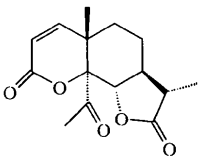
(*Received 1 April 1999; accepted 29 July 1999*)

Abstract

The structure proposed previously for this unexpected oxidation product of α-santonin was verified by X-ray diffraction to be [3*S*-(3a,3aα,5aβ,9aα,9bβ)]-9a-acetyl-3a,4,5,5a,9a,9b-hexahydro-3,5a-dimethyl-2*H*-furo[3,2-*h*]-[1]benzopyran-2,8(3*H*)-dione, $C_{15}H_{18}O_5$.

Comment

α-Santonin, an anthelmintic sesquiterpene isolated from many *Artemisia* species on oxidation with permanganate or lead tetraacetate, was expected to give a $C_{15}H_{18}O_5$ triketone (Paknikar *et al.*, 1994). A product with this molecular formula was obtained, but from its NMR spectra it was postulated to have the ketolactone structure (I) instead. The X-ray study reported herein verifies the proposed structure except for the absolute configuration, which is defined by its synthesis from natural α-santonin, whose absolute configuration is well established (Cocker & McMurry, 1960).



(I)

An interesting feature of the NMR spectrum was the unusually far downfield location of the absorption for H-5α at δ 2.77, suggesting deshielding by the ketone carbonyl group. The X-ray study shows that in the solid phase, H-5α is indeed in a position to be strongly deshielded by the ketone carbonyl group. In fact, the asymmetric unit contains two molecules (1 and 2) which share this conformation, making it likely that this conformation is an energy minimum which would predominate in solution as well, as suggested by the above NMR evidence.

There are no unusually short intermolecular distances. The molecules stack along the *a* axis with lactone interactions involving γ-lactones with γ-lactones, γ-lactones