Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Department of Chemistry, Univ. of Glasgow, Scotland.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Reasearch Forest Drive, The Woodlands, TX 77381, USA.
Nemoto, T., Ono, T., Uchida, A., Ohashi, Y. & Yamamoto, G. (1994). *Acta Cryst.* **C50**, 297–300.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Yamamoto, G., Nemoto, T. & Ohashi, Y. (1992). *Bull. Chem. Soc. Jpn*, **65**, 1957–1966.

Acta Cryst. (1996). **C52**, 720–722

Redetermination of 4,5-Di(benzoylthio)-4,5-didehydro-1,3-dithiolane-2-thione at 120 K

Philip J. Cox[a]* and Solange M. S. V. Doidge-Harrison[b]

[a]*School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen AB9 1FR, Scotland, and* [b]*School of Applied Sciences, The Robert Gordon University, St Andrews Street, Aberdeen AB1 1HG, Scotland. E-mail: paspjc@pharmacy.rgu.ac.uk*

(*Received 10 October 1995; accepted 6 November 1995*)

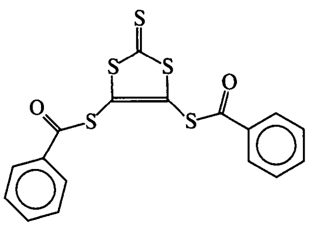
Abstract

The disorder present in the crystal structure of the title thiocarboxylic acid ester [2-oxo-1,3-dithiol-4,5-diyl bis(thiobenzoate), $C_{17}H_{10}O_2S_5$] at 288 K is absent at 120 K.

Comment

Disorder may occur in solvent molecules, methyl groups and spherical anions such as BF_4^-, PF_6^- or SO_4^{2-} by a process of free rotation (dynamic disorder) or by the occurrence of more than one position of similar energy (static disorder). Even where disorder persists on cooling, confirming the presence of static disorder, the reduction in thermal motion, possibly containing elements of dynamic disorder, can make it much easier to model the static disorder.

The 4,5-dimercapto-1,3-dithiole-2-thione (dmit) ligand has been widely used in the synthesis of metal complexes, including molecular inorganic superconductors derived from transition metal dmit complexes (Cassoux & Valade, 1992). The rather unstable dmit ligand can be stabilized by preparation of the title compound, (dmit[COPh]$_2$; Steimecke, 1979), (I). Any variation in molecular conformation of this compound with temperature would be particularly relevant to conductivity studies. At 288 K, a single oxygen (O7) in the compound is reported to be disordered equally over three positions (Solans, Font-Bardía, Font-Altaba, Vicente & Seguí, 1987). The current low-temperature study shows a single position for this atom but confirms it is the most thermally active atom in the molecule; the chemically equivalent O15 atom is the second most thermally active site. At 120 K, the C7—O7 bond length of 1.202 (6) Å is normal, while at 288 K three bond lengths of 1.241 (20), 1.268 (52) and 1.299 (30) Å correspond to the three disordered O-atom positions. There are no significant differences between other bond lengths at 120 and 288 K, and the different values for some chemically equivalent bonds and angles are reproduced in this study.



(I)

At 120 K, valence angles about C7 are similar to those about C15. As expected, there is a small decrease in cell volume [from 1796 (1) to 1738 (2) Å^3] on lowering the temperature and a corresponding increase in

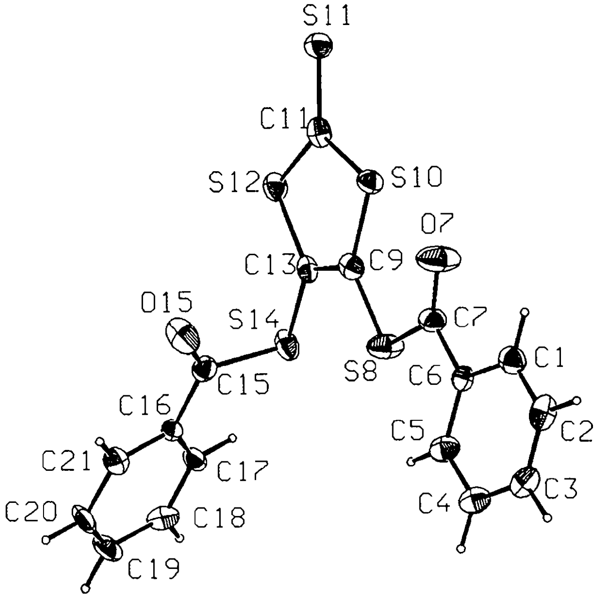


Fig. 1. The atomic arrangement in the title molecule. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

calculated density [from 1.50 to 1.554 Mg m^{-3}]. The conformational differences for the molecules in the two studies are small and at both temperatures the five-membered ring is planar with the largest endocyclic deviation [0.008 (5) Å] for the S12 atom. Exocyclic deviations from this ring at 288 K [S8 0.026 (5), S14 −0.059 (4) and S11 −0.178 (5) Å] are a little different from those at 120 K [S8 −0.019 (6), S14 −0.183 (6) and S11 −0.081 (6) Å]. Intermolecular separations are very similar [*e.g.* S11···S11($-x-1$, $-y$, $-z$) 3.531 (4) Å at 120 K and 3.623 (3) Å at 288 K; S11···S14($-x$, $-y$, $-z$) 3.619 (3) Å at 120 K and 3.623 (3) Å at 288 K].

The overall molecular conformation at 120 K may be described by the orientation of the rings; the phenyl rings are inclined at an angle of 80.9 (1)° with respect to one another and the five-membered ring is inclined at 11.3 (1)° with respect to one phenyl ring (C1–C6) and at 83.1 (1)° with respect to the other (C16–C21). Calculations based on the structure determination at 288 K yield almost identical orientation angles of 80.9 (1), 11.8 (1) and 83.2 (1)°, respectively.

Experimental

Crystal data

$C_{17}H_{10}O_2S_5$
$M_r = 406.55$
Monoclinic
$P2_1/c$
$a = 9.627\ (8)$ Å
$b = 10.584\ (7)$ Å
$c = 17.084\ (9)$ Å
$\beta = 93.15\ (6)^\circ$
$V = 1738.1\ (21)$ Å^3
$Z = 4$
$D_x = 1.554$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2.12$–25.09°
$\mu = 0.674$ mm^{-1}
$T = 120\ (2)$ K
Parallelepiped
0.24 × 0.22 × 0.18 mm
Brown

Data collection

Delft Instruments FAST area-detector diffractometer
Measurement method: Darr, Drake, Hursthouse & Malik (1993)
Absorption correction: none
6782 measured reflections

2626 independent reflections
1414 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0892$
$\theta_{\rm max} = 25.09^\circ$
$h = -10 \rightarrow 10$
$k = -9 \rightarrow 11$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0434$
$wR(F^2) = 0.0921$
$S = 0.710$
2626 reflections
218 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.03$

$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.1094 (6)	0.5594 (4)	−0.1580 (3)	0.0301 (14)
C2	0.1845 (6)	0.6550 (4)	−0.1931 (3)	0.0330 (14)
C3	0.3181 (6)	0.6822 (4)	−0.1649 (3)	0.0315 (14)
C4	0.3768 (6)	0.6195 (4)	−0.1007 (3)	0.0309 (14)
C5	0.3041 (5)	0.5240 (4)	−0.0663 (3)	0.0274 (13)
C6	0.1694 (5)	0.4934 (4)	−0.0945 (3)	0.0213 (12)
C7	0.0842 (6)	0.3940 (4)	−0.0603 (3)	0.0280 (13)
O7	−0.0391 (4)	0.3845 (4)	−0.0742 (3)	0.0580 (13)
S8	0.17656 (14)	0.28829 (12)	0.00437 (9)	0.0368 (4)
C9	0.0455 (5)	0.1923 (4)	0.0395 (3)	0.0243 (13)
S10	−0.12874 (13)	0.19515 (11)	0.00683 (8)	0.0241 (4)
C11	−0.1857 (5)	0.0744 (4)	0.0672 (3)	0.0246 (13)
S11	−0.34789 (14)	0.02709 (11)	0.06017 (8)	0.0295 (4)
S12	−0.05451 (14)	0.01245 (11)	0.12858 (8)	0.0283 (4)
C13	0.0810 (5)	0.1059 (4)	0.0963 (3)	0.0230 (13)
S14	0.25006 (14)	0.07228 (12)	0.13188 (8)	0.0293 (4)
C15	0.2591 (6)	0.1650 (4)	0.2220 (3)	0.0263 (13)
O15	0.1641 (4)	0.2330 (3)	0.2375 (2)	0.0427 (11)
C16	0.3914 (5)	0.1509 (4)	0.2681 (3)	0.0182 (12)
C17	0.4881 (5)	0.0585 (4)	0.2527 (3)	0.0248 (13)
C18	0.6122 (5)	0.0505 (5)	0.2970 (3)	0.0301 (14)
C19	0.6385 (6)	0.1345 (5)	0.3576 (3)	0.0336 (14)
C20	0.5429 (6)	0.2267 (5)	0.3738 (3)	0.0322 (14)
C21	0.4206 (5)	0.2344 (4)	0.3293 (3)	0.0279 (14)

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

C6—C7	1.474 (6)	C11—S11	1.638 (5)
C7—O7	1.202 (6)	C11—S12	1.726 (5)
C7—S8	1.776 (5)	S12—C13	1.750 (5)
S8—C9	1.751 (5)	C13—S14	1.742 (5)
C9—C13	1.364 (6)	S14—C15	1.824 (5)
C9—S10	1.739 (5)	C15—O15	1.204 (5)
S10—C11	1.749 (5)	C15—C16	1.468 (7)
C1—C6—C7	116.9 (5)	S12—C11—S10	113.2 (3)
C5—C6—C7	123.7 (5)	C11—S12—C13	97.3 (2)
O7—C7—C6	123.1 (5)	C9—C13—S14	125.3 (4)
O7—C7—S8	121.7 (4)	C9—C13—S12	116.2 (4)
C6—C7—S8	115.2 (4)	S14—C13—S12	118.3 (3)
C9—S8—C7	103.5 (3)	C13—S14—C15	100.6 (2)
C13—C9—S10	116.1 (4)	O15—C15—C16	126.1 (5)
C13—C9—S8	118.4 (4)	O15—C15—S14	120.4 (4)
S10—C9—S8	125.5 (3)	C16—C15—S14	113.4 (4)
C9—S10—C11	97.3 (2)	C17—C16—C15	122.9 (5)
S11—C11—S12	126.2 (3)	C21—C16—C15	118.3 (4)
S11—C11—S10	120.6 (3)		
C9—C13—S14—C15	99.4 (4)	S12—C13—S14—C15	−86.8 (3)

Absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection which lasted about 8 h. Non-H atoms were refined with anisotropic displacement parameters and H atoms were allowed to ride on their attached C atoms with a common isotropic displacement parameter. The unit-cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989) and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993).

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994).

The use of the EPSRC X-ray crystallographic service at the University of Wales, Cardiff, Wales, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cassoux, P. & Valade, L. (1992). *Molecular Inorganic Superconductors* in *Inorganic Materials*, edited by D. W. Bruce, pp. 1–52. Chichester: Wiley.

Darr, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.

Karaulov, A. I. (1992). *ABSMAD. Program for FAST Data Processing.* University of Wales, Cardiff, Wales.

Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES.* Version of 11th September, 1989. Distributed by Delft Instruments, Delft, The Netherlands.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Solans, X., Font-Bardía, M., Font-Altaba, M., Vicente, R. & Seguí, A. (1987). *Acta Cryst.* C**43**, 1415–1417.

Steimecke, G. (1979). *Phosphorus Sulfur*, **7**, 49–55.

Zsolnai, L. (1994). *ZORTEP. An Interactive ORTEP Program.* University of Heidelberg, Germany.

Acta Cryst. (1996). C**52**, 722–724

1,3-Dicyclopropyl-2-(1,2,3-triphenylcyclopropen-3-yl)propane-1,3-dione: a Substituted Cyclopropene with a β-Dicarbonyl Fragment

JÜRGEN KOPF,[a] CORNELIA BRETZKE,[a] IVAN NIKITICH DOMNIN[b] AND VLADIMIR NIKOLAEVICH PLOTKIN[b]

[a]*Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany, and* [b]*Organic Chemistry Department, St. Petersburg University, 198904 St. Petersburg, Peterhof, Russia. E-mail: kopf@rz.informatik.uni-hamburg.d400.de*

(*Received 4 July 1995; accepted 18 September 1995*)

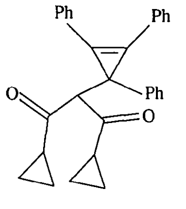
Abstract

The title compound, $C_{30}H_{26}O_2$, has a conformation in which one of the cyclopropanecarbonyl moieties bisects the plane of the cyclopropene ring. The bulky 1,2,3-triphenylcyclopropenyl substituent in the α-position of the β-diketone excludes the possibility of any enolization process. The asymmetry of the single-bond lengths in substituted cyclopropenes, reported previously [Allen (1982). *Tetrahedron*, **38**, 645–655], is not observed in the present compound.

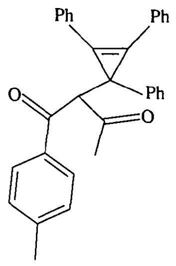
Comment

It is known that cyclopropenyl substituents possess pronounced electron-donating properties (Komendantov, Kostikov, Panasyuk & Domnin, 1987). At the same time, the 1,2,3-triphenylcyclopropenyl group is sterically bulky. Both these factors prevent an enolization process upon introduction of this group in the α-position of dicyclopropanoylmethane.

It has been reported that the presence of an acetyl group in a β-diketone fragment, connected to a 1,2,3-triphenylcyclopropenyl substituent, enables a thermocatalytic isomerization in corresponding substituted cyclopentadienols (Plotkin, Domnin, Dmitrieva & Komendantov, 1987). To the contrary, the title compound does not display such behaviour. Therefore, an X-ray structure determination of the title compound, (I), was undertaken and the results are compared with a crystal structure determination of 1-(4-methylphenyl)-2-(1,2,3-triphenylcyclopropen-3-yl)-butane-1,3-dione, (II) (Fundamenskiy, Starova, Plotkin, Domnin & Yufit, 1989).



(I)



(II)

In actual fact the structures (II) and the title compound, (I), are essentially the same. In both, the acetyl and one of the cyclopropanecarbonyl groups are in a bisected conformation towards the plane of the cyclopropene ring. In each, the phenyl ring at position 1 of the cyclopropene is also in a bisected conformation [the angle between the plane through the cyclopropene ring and that of the phenyl ring C11–C16 is 84.7 (2)° in (II) and 87.5 (5)° in (I)]. In (I), the bond lengths C4—C5 and C4—C6 [1.526 (2) and 1.528 (2) Å] are characteristic of the diketo form, whereas for the enol form the expected values are in the range 1.363–1.400 Å (Emsley, 1984). The bond lengths C5—O5 and C6—O6 are also typical of the diketo form [1.206 (2) and 1.210 (2) Å, respectively]. Moreover, the value of the dihedral angle O5—C5···C6—O6 of the two carbonyl groups is as high as