^{13}C NMR (D_2O, K_2CO_3): 3.22 (s, CH$_3$), 45.00 (d, CH$_2$—P), 47.00 (d, CH$_2$—P), 60.87 (d, CH—CH$_3$), 79.28 (s, CH—Ph), 125.98 (s, $^3C_{arom}$), 128.31 (s, $^4C_{arom}$), 128.93 (s, $^2C_{arom}$), 138.45 p.p.m. (s, $^1C_{arom}$); ^{31}P NMR (D_2O, K_2CO_3): 6.12 (s, P—cycle), 8.20 p.p.m. (s); IR (cm^{-1}, KBr): 3060 (s, OH), 2998 (w), 1332 (w), 1178 (vs, P=O), 1120 (s, P=O), 1082 (vs, P—O), 982 (s, P—O), 936 (m).

Crystal data

$C_{11}H_{17}NO_6P_2$	Mo $K\alpha$ radiation
$M_r = 321.21$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 24
$Pca2_1$	reflections
$a = 14.361$ (2) Å	$\theta = 10.9$–$11.9°$
$b = 13.711$ (2) Å	$\mu = 0.318$ mm^{-1}
$c = 7.475$ (2) Å	$T = 293$ K
$V = 1471.9$ (4) Å^3	Elongated prism
$Z = 4$	$0.31 \times 0.29 \times 0.26$ mm
$D_x = 1.449$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 29.93°$
ω–2θ scans	$h = 0 \rightarrow 18$
Absorption correction: none	$k = 0 \rightarrow 19$
2306 measured reflections	$l = 0 \rightarrow 10$
2306 independent reflections	2 standard reflections
1885 reflections with	every 120 reflections
$I > 2\sigma(I)$	intensity decay: 4.15%

Refinement

Refinement on F	$w = 1/[\sigma^2(F_o)$
$R = 0.026$	$+ 0.00016\|F_o\|^2]$
$wR = 0.033$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.836$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
1885 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}
180 parameters	Extinction correction: none
H-atom parameters not refined	Scattering factors from *International Tables for Crystallography* (Vol. C)

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

P1—O1	1.588 (1)	P2—O5	1.488 (2)
P1—O2	1.478 (1)	P2—O6	1.532 (2)
P1—O3	1.498 (1)	P2—C1	1.816 (2)
P1—C2	1.812 (2)	O1—C4	1.451 (2)
P2—O4	1.539 (2)	N—C2	1.502 (2)
O1—P1—O2	110.52 (7)	O5—P2—C1	107.95 (7)
O1—P1—O3	107.84 (7)	O6—P2—C1	108.88 (8)
O1—P1—C2	102.60 (7)	P1—O1—C4	113.7 (1)
O2—P1—O3	117.23 (8)	C2—N—C3	112.5 (1)
O2—P1—C2	109.56 (8)	P2—C1—N	114.1 (1)
O3—P1—C2	108.06 (8)	P1—C2—N	113.3 (1)
O4—P2—O5	116.93 (8)	N—C3—C11	112.5 (1)
O4—P2—O6	107.48 (8)	C4—C3—C11	114.2 (2)
O4—P2—C1	103.26 (8)	O1—C4—C3	108.6 (1)
O5—P2—O6	111.81 (9)	O1—C4—C5	110.6 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H16···O5^i	0.96	1.58	2.517 (2)	162
O6—H11···O3^{ii}	1.18	1.26	2.432 (2)	168
N—H17···O2^i	0.93	1.78	2.629 (2)	151

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

H atoms were located by difference Fourier syntheses.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

References

Altomare, A., Cascarano, M., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Engel, R. (1977). *Chem. Rev.* **77**, 349–367.
Engel, R. (1987). In *Synthesis of Carbon–Phosphorus Bonds*. Boca Raton, Florida: CRC Press.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fields, E. K. (1952). *J. Am. Chem. Soc.* **74**, 1528–1531.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Makaranets, B. I., Polynova, T. N., Porai-Koshits, M. A. & Il'ichev, S. A. (1987). *Zh. Strukt. Khim.* **27**, 117–124.
Moedritzer, K. & Irani, R. R. (1966). *J. Org. Chem.* **31**, 1603–1606.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Ortiz-Avila, C. Y., Bhardwaj, C. & Clearfield, A. (1994). *Inorg. Chem.* **33**, 2499–2500.
Schwarzenbach, G., Biedermann, W. & Bangerter, F. (1948). *Helv. Chim. Acta*, **32**, 1175–1186.
Villemin, D. & Martin, B. (1995). *Synth. Commun.* **25**, 2319–2326.
Villemin, D. & Sauvaget, F. (1994). *Synlett*, pp. 435–436.

1,3,4,6-Tetrathiapentalene-2,5-dione

Harald Müller[a] and Marie-Thérèse Averbuch[b]

[a]*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, CEDEX 9, France, and* [b]*LEDSS, UMR CNRS 5616, Université Joseph Fourier, BP 53, 38041 Grenoble, CEDEX 9, France. E-mail: mueller@esrf.fr*

Abstract

The title compound, [1,3]dithiolo[4,5-*d*][1,3]dithiole-2,5-dione, $C_4O_2S_4$, is a sulfur heterocyclic system formally composed of a tetrathioethylene unit (C_2S_4) and two carbonyl groups. The bicyclic molecule is essentially planar and exhibits D_{2h} symmetry, although

the exocyclic-O atoms lie slightly [± 0.128 (3) Å] out of the plane through the five-membered 1,3-dithiole (C_3S_2) ring.

Comment

In the course of our investigations into new conducting and superconducting organic materials, 1,3,4,6-tetrathia-pentalene-2,5-dione (or thiapendione for short) (Schumaker *et al.*, 1984) emerged as a key building block for the synthesis of sulfur heterocyclic systems (Müller & Ueba, 1993; Müller, Jouan & Salhi, 1997), supercon-ducting radical cations (Müller, Svensson *et al.*, 1997), metal complexes (Müller *et al.*, 1998) and coordina-tion polymers with sulfur-rich ligands (Xenikos *et al.*, 1997). Furthermore, owing to its bifunctional character, thiapendione has also been employed successfully as a precursor for novel conducting polymers (Müller, Salhi & Divisia-Blohorn, 1997). Common features of thia-pendione and the compounds mentioned above are the tetrathioethylene, the tetrathiapentalene (C_4S_4) and the carbonyl (C=O) moieties. Bond lengths in these struc-tural elements provide a sensitive measure of the degree of oxidation and charge distribution in these materials, and enable a correlation of structural and spectroscopic data to be made. A structure determination of the neu-tral parent compound thiapendione, (I), has not been performed until now.

O atom (O1), of the carbonyl group deviates slightly [0.128 (3) Å] from the plane of the 1,3-dithiole moiety. The S—C bond distances of the central tetrathioethylene unit are identical within experimental accuracy [C1—S1 = 1.731 (1) and C1^i—S2 = 1.730 (1) Å] and slightly shorter than the S1—C2 and S2—C2 bonds [1.779 (2) and 1.776 (2) Å, respectively] to the carbonylic atom C2. The C=C (C1=C1^i) and the carbonyl (C2=O1) dou-ble bonds are 1.343 (2) and 1.205 (2) Å, respectively, and correspond to expected values (Allen *et al.*, 1987).

The thiapendione molecules lie in planes approxi-mately perpendicular to the [10$\bar{2}$] direction and form pancake-like stacks along the *x* axis. The two shortest in-termolecular S···S distances observed are 3.5513 (5) Å (S1···S2^{ii}) within such a plane and 3.8381 (6) Å (S1···S2^{iii}) between two adjacent planes.

O=⟨S—S⟩=O
 ⟨S—S⟩
   (I)

The bicyclic title compound, (I), consists of two fused 1,3-dithiole rings, which share the central C=C double bond and each bear an exocyclic-O atom. The central double bond (C1=C1^i) in thiapendione is located about a centre of inversion, resulting in the crystallographi-cally equivalent five-membered (C_3S_2) rings. The mol-ecule (Fig. 1) is practically ideally planar; maximum de-viations from the plane through the five-membered 1,3-dithiole ring (C1=C1^i—S2—C2—S1) are 0.058 (3) for C2 and 0.033 (3) Å for C1^i. Interestingly, the exocyclic-

Experimental

The title compound was synthesized according to Schumaker *et al.* (1984) and recrystallized from acetonitrile.

Crystal data

$C_4O_2S_4$	Mo $K\alpha$ radiation
$M_r = 208.30$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 24
$P2_1/c$	reflections
$a = 3.9321$ (8) Å	$\theta = 9.85–14.00°$
$b = 10.886$ (2) Å	$\mu = 1.296$ mm^{-1}
$c = 8.3000$ (9) Å	$T = 293$ K
$\beta = 103.60$ (1)°	Elongated prism, diamond-
$V = 345.32$ (9) Å^3	like section
$Z = 2$	0.32 × 0.24 × 0.19 mm
$D_x = 2.007$ Mg m^{-3}	Translucent pale yellow
D_m not measured	

Data collection

Enraf–Nonius CAD-4	1079 reflections with
diffractometer	$I > 2\sigma(I)$
ω scans	$R_{int} = 0.012$
Absorption correction:	$\theta_{max} = 32.96°$
ψ scan (North *et al.*,	$h = -6 \to 5$
1968)	$k = 0 \to 16$
$T_{min} = 0.701$, $T_{max} = 0.786$	$l = 0 \to 12$
1388 measured reflections	2 standard reflections
1319 independent reflections	every 120 reflections
	intensity decay: -1.58%

Refinement

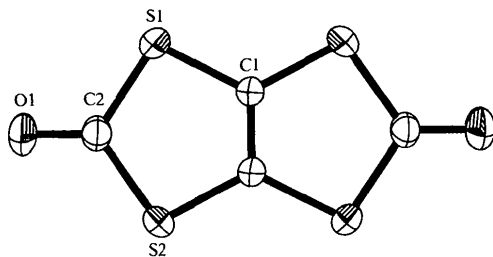|	
Refinement on F	$(\Delta/\sigma)_{max} = 0.003$
$R = 0.030$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$wR = 0.045$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
$S = 1.919$	Extinction correction: none
1079 reflections	Scattering factors from
46 parameters	*International Tables for*
$w = 1/[\sigma^2(F_o)$	*Crystallography* (Vol. C)
$+ 0.00029\|F_o\|^2]$	

Fig. 1. An *ORTEP*II (Johnson, 1976) representation of the title molecule showing 45% probability displacement ellipsoids.

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.3186 (1)	−0.17922 (3)	0.91892 (4)	0.03759 (8)
S2	0.2064 (1)	0.07052 (3)	0.76954 (4)	0.03828 (8)
O1	−0.1105 (4)	−0.1297 (1)	0.6310 (2)	0.0563 (3)
C1	0.5273 (3)	−0.0564 (1)	1.0334 (2)	0.0304 (3)
C2	0.0954 (4)	−0.0878 (1)	0.7492 (2)	0.0368 (3)

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

S1—Cl	1.731 (1)	S2—C2	1.776 (2)
S1—C2	1.779 (2)	O1—C2	1.205 (2)
S2—Cl^i	1.730 (1)	C1—Cl^i	1.343 (2)
Cl—S1—C2	94.82 (6)	S2^i—Cl—Cl^i	118.3 (1)
Cl^i—S2—C2	94.83 (6)	S1—C2—S2	113.78 (7)
S1—Cl—S2^i	123.61 (7)	S1—C2—O1	123.0 (1)
S1—Cl—Cl^i	118.1 (1)	S2—C2—O1	123.2 (1)
S1···S2^{ii}	3.5513 (5)	S1···S2^{iii}	3.8381 (6)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1320). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

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

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Müller, H., Jouan, C. & Salhi, F. (1997). *Synth. Met.* **85**, 1457–1458.

Müller, H., Puig-Molina, A., Narymbetov, B. Zh., Zorina, L. V., Khasanov, S. S. & Shibaeva, R. P. (1998). *Z. Anorg. Allg. Chem.* **624**, 1492–1496.

Müller, H., Salhi, F. & Divisia-Blohorn, B. (1997). *Tetrahedron Lett.* **38**, 3215–3218.

Müller, H., Svensson, S. O., Fitch, A. N., Lorenzen, M. & Xenikos, D. G. (1997). *Adv. Mater.* **9**, 896–900.

Müller, H. & Ueba, Y. (1993). *Synthesis*, pp. 853–854.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Schumaker, R. R., Lee, V. Y. & Engler, E. M. (1984). *J. Org. Chem.* **49**, 564–568.

Xenikos, D. G., Müller, H., Jouan, C., Sulpice, A. & Tholence, J. L. (1997). *Solid State Commun.* **102**, 681–685.

Redetermination of 2,3-dichloro-5,6-dicyano-1,4-dihydroxybenzene†

Gakuse Hoshina, Shigeru Ohba and Masanobu Tsuchimoto

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan. E-mail: ohba@chem.keio.ac.jp

Abstract

The crystal structure of the title compound, $C_8H_2Cl_2N_2O_2$, was reported recently [Reddy, Ovchinnikov, Shishkin, Struchkov & Desiraju (1996). *J. Am. Chem. Soc.* **118**, 4085–4089]. However, the space group has been corrected from $Pna2_1$ to $Pnma$ in the present study. The molecule lies on a mirror plane perpendicular to b.

Comment

Crystals of the title compound, 2,3-dichloro-5,6-dicyano-1,4-dihydroxybenzene (DDH), are orthorhombic and the systematic absences ($0kl$, $k+l$ odd, and $hk0$, h odd) indicate that the space group is $Pnma$ (No. 62) or $Pn2_1a$, the $a\bar{c}b$ setting of $Pna2_1$ (No. 33). Assuming the centrosymmetric space group $Pnma$, the structure solution was straightforward.
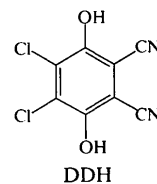
Reddy *et al.* (1996) reported the crystal structure of DDH in space group $Pna2_1$, with lattice constants $a = 16.503(2)$, $b = 8.542(1)$ and $c = 6.421(2)\,\text{Å}$ at 140 K. Their fractional coordinates of non-H atoms (x', y', z') are related to those obtained in the present paper (x, y, z) as $x' = 1 - x$, $y' = z + \frac{1}{2}$ and $z' = 0.365 = y + 0.115$. The crystal structure is essentially the same as that reported by Reddy *et al.* (1996). There are intramolecular O—H···Cl hydrogen bonds, which cause expansion of the O1—C3—C2 and O2—C6—C1 bond angles. Fig. 2 shows the intermolecular O—H···N≡C hydrogen-bond network in the $y = \frac{1}{4}$ plane, which is a crystallographic mirror plane.

† Alternative name: 4,5-dichloro-3,6-dihydroxyphthalonitrile.