

The dithiolene ligand and tetrathiafulvalene precursor molecules 4,5-bis(bromomethyl)-1,3-dithiol-2-one and 4,5-bis[(dihydroxyphosphoryl)methyl]-1,3-dithiol-2-one

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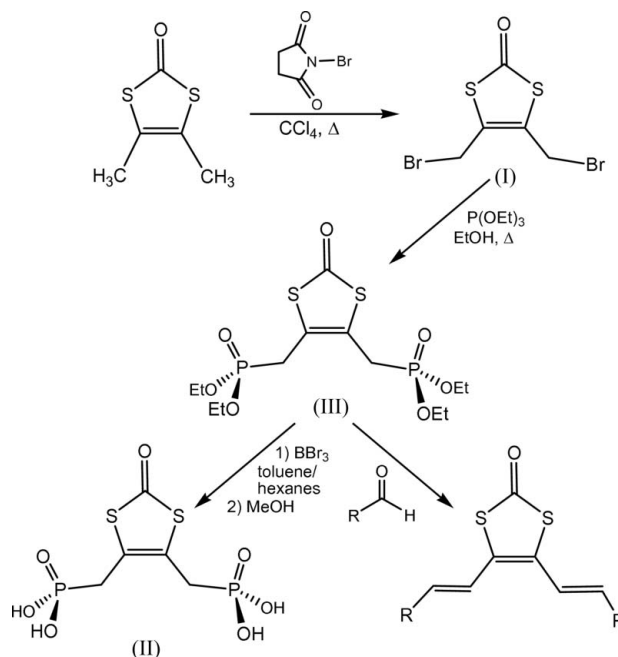
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The crystal structures of 4,5-bis(bromomethyl)-1,3-dithiol-2-one, $C_5H_4Br_2OS_2$, (I), and 4,5-bis[(dihydroxyphosphoryl)methyl]-1,3-dithiol-2-one, $C_5H_8O_7P_2S_2$, (II), occur with similar unit cells in the same monoclinic space group. Both molecules reside on a twofold symmetry axis coincident with the C=O bond, so that the substituents in the 4- and 5-positions project above and below the plane of the 1,3-dithiol-2-one ring. In both structures, the molecules align themselves in a head-to-tail fashion along the *b* axis, and these rows of molecules then stack, with alternating directionality, along the *c* axis. For (II), an extensive network of intermolecular hydrogen bonds occurs between molecules within the same stack and between adjacent stacks. Each $-CH_2P(O)(OH)_2$ group participates in four hydrogen bonds, twice as donor and twice as acceptor.

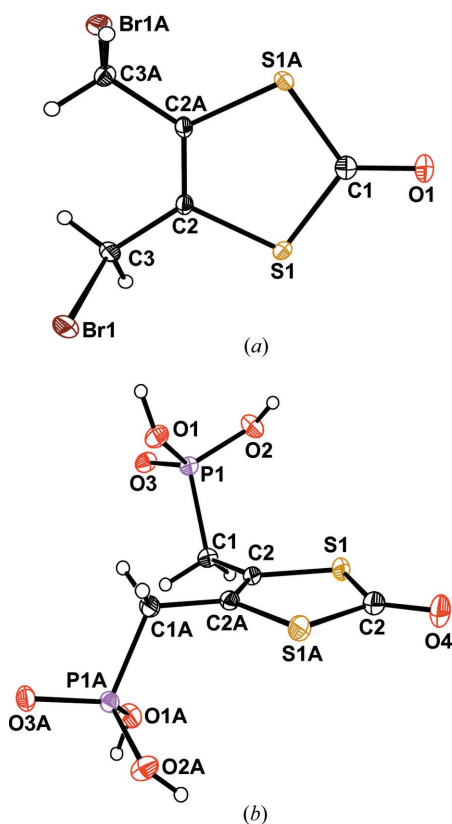
Comment

Molecules including the 1,3-dithiol-2-one moiety are useful both as protected forms of dithiolene ligands (Rauchfuss, 2004; Rowe *et al.*, 1985) and as precursors to tetrathiafulvalene-type compounds, which are of interest for their potential applications as superconducting (Dressel & Drichko, 2004; El-Wareth & Sarhan, 2005) or magnetic materials (El-Wareth & Sarhan, 2005), sensors (El-Wareth & Sarhan, 2005; Moonen *et al.*, 2005), light-harvesting materials (Martín *et al.*, 2007) and other electronic devices (Rovira, 2004) designed from a bottom-up approach. We recently described an improved synthesis (Chandrasekaran & Donahue, 2009) and crystal structure (Chandrasekaran *et al.*, 2009) of 4,5-dimethyl-1,3-dithiol-2-one, one of the simplest molecules of this type. An underappreciated aspect of this particular compound is the facility with which it is converted to variants that are more richly functionalized. Following a literature protocol (Crivil-

lers *et al.*, 2007), 4,5-dimethyl-1,3-dithiol-2-one is readily transformed into 4,5-bis(bromomethyl)-1,3-dithiol-2-one, (I), a molecule from which a panorama of synthetic options then unfolds. For example, a straightforward Michaelis–Arbuzov reaction (Gorgues *et al.*, 2004; Gautier *et al.*, 2004) with triethyl phosphite yields 4,5-bis[(diethoxyphosphoryl)methyl]-1,3-dithiol-2-one, (III) (see Scheme). In turn, classical Wittig chemistry provides a means by which this molecule can be elaborated, with the appropriate carbonyl compound, to include any of a broad variety of substituents linked to the 1,3-dithiol-2-one *via* an olefinic bond (see Scheme) (Gautier *et al.*, 2004). Alternatively, dealkylation with BBR_3 (Gauvry & Mortier, 2001) affords the corresponding 4,5-bis[(dihydroxyphosphoryl)methyl]-1,3-dithiol-2-one, (II), a molecule which is of some interest for its utility as precursor to a robust water-soluble dithiolene ligand whose metal complexes should be similarly water soluble. We report here the structures of (I) and its derivative (II) as part of an ongoing effort aimed at creating facile synthetic access to new types of dithiolene ligands.



Compound (I) (Fig. 1*a*) crystallizes in the monoclinic space group $C2/c$ on a twofold symmetry axis coincident with the C=O bond. The Br atoms of the bromomethyl groups thus project themselves above and below the plane defined by the 1,3-dithiol-2-one ring, thereby maximizing their separation. Molecules of (I) arrange themselves in a head-to-tail fashion into one-dimensional rows in the direction of the *b* axis (Fig. 2*a*). These rows then stack along the *c* axis, with alternating directionality of the head-to-tail alignment of the molecules in the row. Although intermolecular hydrogen bonding is not present within this crystal packing pattern, relatively short intermolecular $Br1 \cdots H3A^i$ [symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$] and $Br1 \cdots S1^{ii}$ [symmetry code: (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$] contacts of 3.06 Å (Fig. 2*b*) and

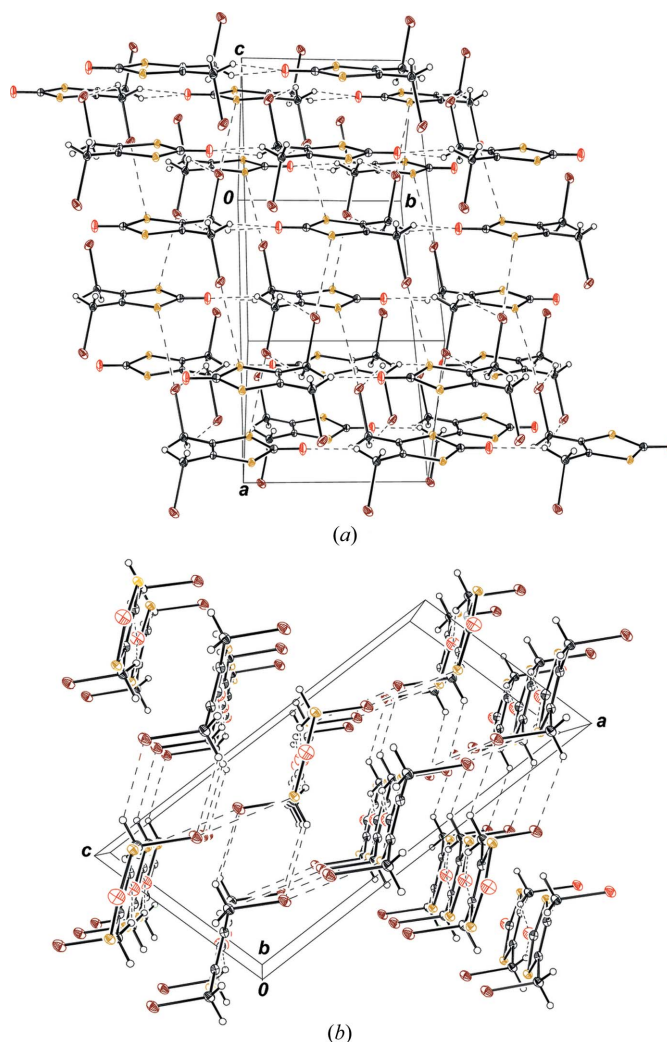
**Figure 1**

The molecular structures of (a) (I) and (b) (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level.

3.6266 (5) Å (Fig. 2a), respectively, are made between adjacent rows of molecules. Within a row along the *b* axis, short nonbonding O1···H3Bⁱⁱⁱ [symmetry code: (iii) *x*, *y* − 1, *z*] distances of 2.40 Å are observed between neighboring molecules (Fig. 2a).

The crystal structure of (II) is similar to that of bromomethyl compound (I) in that it crystallizes on a twofold axis in the space group *C2/c* with an up and down (*C*₂) disposition of the (dihydroxyphosphoryl)methyl substituents (Fig. 1b). A further similarity is the head-to-tail alignment of the molecules into rows parallel to the *b* axis, stacked along the *c* axis and alternating in the orientation of the molecules between rows by 180° (Fig. 3a). The principal difference between the two structures arises from a dense network of intermolecular hydrogen bonding in (II). Each phosphoryl group is a participant in four P—OH···O=P hydrogen bonds, two as donor and two as acceptor. The two lone pairs on the terminal O atom of each —CH₂P(O)(OH)₂ group enable it to act twice as a hydrogen-bond acceptor. The intermolecular hydrogen bonding occurs both between molecules within the same stack and between molecules in adjacent *c* axis stacks (Figs. 3a and 3b).

Structurally characterized molecules having the 1,3-dithiol-2-one moiety are not uncommon, although it is noteworthy that the majority of such examples incorporate this fragment as part of a tetrathioethylene group, the opposing side of which is either chelated to a transition metal (Yang *et al.*, 1991;

**Figure 2**

(a) A packing diagram for (I), with the *b* axis coincident with the horizontal axis. (b) A packing diagram with the *b* axis orthogonal to the plane of paper. The stacking of molecules is coincident with the *c* axis. Short intermolecular contacts are shown as dashed lines. (In the electronic version of the paper, Br atoms are illustrated in maroon, S atoms in gold–yellow and O atoms in red.)

Kobayashi *et al.*, 1992; Fourmigué *et al.*, 1998; Keefer *et al.*, 1998; Smucker *et al.*, 2003; Llusar *et al.*, 2005; Faulmann *et al.*, 2006; Rabaça *et al.*, 2006; Nomura & Fourmigué, 2007; Llusar *et al.*, 2008) or a heavy main group element (Chohan *et al.*, 1999; Avarvari & Fourmigué, 2003), or is alkylated (Simonsen *et al.*, 1990; Xue *et al.*, 2003; Nomura *et al.*, 2009) or arylated (Yu *et al.* 1995). Of the crystallographically identified molecules that might be compared with (I) and (II), the nearest and best comparison is given by 4,5-dicarbamoyl-1,3-dithiol-2-one, (IV) (Baudron *et al.*, 2003). Like both (I) and (II), it is a molecule that is symmetrically substituted in the 4- and 5-positions with a functional group that allows for further synthetic modification and which confers both water solubility and the opportunity for extensive hydrogen bonding in its corresponding metal complexes (Oku *et al.*, 1997; Baudron *et al.*, 2005). Like (II), (IV) engages in multiple hydrogen bonds with neighboring molecules, but it does so strictly within a

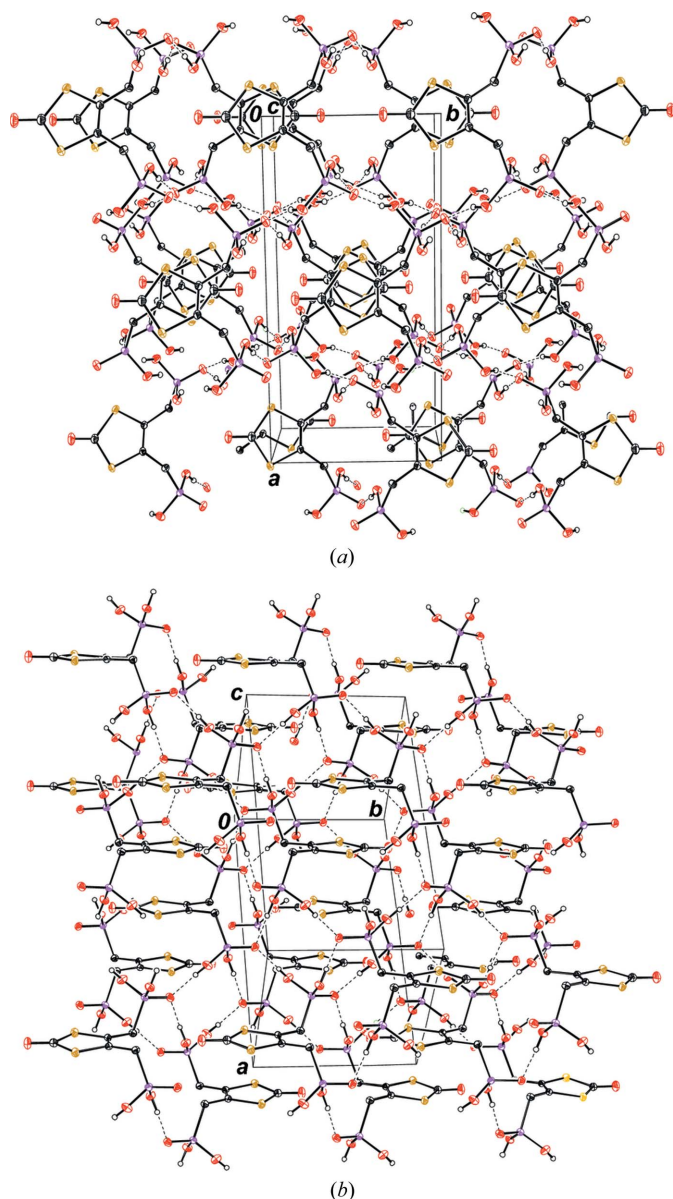


Figure 3

(a) A packing diagram for (II), viewed down the c axis. The alternating disposition of the one-dimensional rows of molecules along the (horizontal) b axis is seen. (b) A packing diagram showing the intermolecular hydrogen bonding between (dihydroxyphosphoryl)methyl groups in different rows of (II). The b axis is coincident with the horizontal axis. Hydrogen bonds are shown as dashed lines. (In the electronic version of the paper, S atoms are illustrated in gold–yellow, P atoms in purple and O atoms in red.)

two-dimensional sheet network. Compound (II) enables a rather different pattern of hydrogen bonding that involves molecules above, below and to either side of the plane of the 1,3-dithiol-2-one (Figs. 3*a* and 3*b*) to create a three-dimensional network. It is likely that a pattern of intermolecular hydrogen bonding similar to that observed for (II) will be asserted in the crystal structures of simple metal complexes with the unmasked -ene-1,2-dithiolate form of this molecule, such as square-planar bis(dithiolene) complexes of the group 10 metals.

Experimental

Compound (I) was prepared according to the method of Crivillers *et al.* (2007). Colorless plates were grown by slow evaporation of a dichloromethane solution at ambient temperature. Compound (II) was prepared by dealkylation of the corresponding diethyl methylphosphonate (0.50 g), according to the procedure of Gauvry & Mortier (2001). Pale-yellow plates were obtained by diffusion of diisopropyl ether vapor into a methanol solution (yield 0.079 g, 22%; m.p. 528 K). ^1H NMR (CD_3OD): δ 3.24 (*m*, $-\text{CH}_2-$). ^{31}P NMR (CD_3OD): δ 21.01. Analysis calculated for $\text{C}_5\text{H}_8\text{O}_7\text{P}_2\text{S}_2$: C 19.61, H 2.63%; found: C 20.70, H 2.99%.

Compound (I)

Crystal data

$\text{C}_5\text{H}_4\text{Br}_2\text{OS}_2$	$V = 840.20 (14) \text{ \AA}^3$
$M_r = 304.02$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.9026 (15) \text{ \AA}$	$\mu = 10.07 \text{ mm}^{-1}$
$b = 7.8804 (8) \text{ \AA}$	$T = 100 \text{ K}$
$c = 7.4012 (7) \text{ \AA}$	$0.16 \times 0.13 \times 0.09 \text{ mm}$
$\beta = 104.836 (1)^\circ$	

Data collection

Bruker APEXII CCD area-detector diffractometer	7166 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008 <i>b</i>)	1062 independent reflections
$T_{\min} = 0.307$, $T_{\max} = 0.464$	1005 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	47 parameters
$wR(F^2) = 0.044$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
1062 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

$\text{C}_5\text{H}_8\text{O}_7\text{P}_2\text{S}_2$	$V = 1017.4 (3) \text{ \AA}^3$
$M_r = 306.17$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 15.078 (3) \text{ \AA}$	$\mu = 0.86 \text{ mm}^{-1}$
$b = 8.1736 (14) \text{ \AA}$	$T = 100 \text{ K}$
$c = 8.3628 (15) \text{ \AA}$	$0.23 \times 0.22 \times 0.06 \text{ mm}$
$\beta = 99.188 (2)^\circ$	

Data collection

Bruker APEX CCD area-detector diffractometer	8625 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick 2008 <i>b</i>)	1269 independent reflections
$T_{\min} = 0.829$, $T_{\max} = 0.955$	1196 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	74 parameters
$wR(F^2) = 0.069$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
1269 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

For both compounds, the methylene H atoms were placed in calculated positions ($\text{C}-\text{H} = 0.99 \text{ \AA}$) and included as riding contributions, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. In (II), H atoms attached to O atoms were placed in locations derived from a difference map

Table 1

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1O\cdots O3^i$	0.86	1.70	2.5538 (16)	170
$O2-H2O\cdots O3^{ii}$	0.84	1.68	2.4959 (16)	161

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

($O-H = 0.84-0.86$ Å) and included as riding contributions, with $U_{iso}(H) = 1.2U_{eq}(O)$.

For both compounds, data collection: *APEX2* (Bruker, 2008). Cell refinement: *SAINT-Plus* (Bruker, 2006) for (I); *SAINT* (Bruker, 2008) for (II). Data reduction: *SAINT-Plus* for (I); *SAINT* for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008a); molecular graphics: *SHELXTL* (Sheldrick, 2008a). Software used to prepare material for publication: *SHELXL97* for (I); *SHELXTL* for (II).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3090). Services for accessing these data are described at the back of the journal.

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