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3,3′-Dihydroxy-5,5,5′,5′-tetramethyl-2,2′-thiodicyclohex-2-en-1-one

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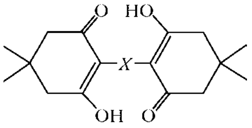
Molecules of the title compound, $C_{16}H_{22}O_4S$, have twofold crystallographic symmetry and are stabilized by strong intramolecular O—H···O hydrogen bonds and very weak intermolecular C—H···O hydrogen bonds, forming layers normal to the *c* axis. The molecular structure is compared with those of the Se- and CH_2-bridged analogues.

Comment

When two dimedone (5,5-dimethylcylohexane-1,3-dione) molecules are bridged at their 2-positions with *X* (where *X* = Se, S or CH_2), they are bound with strong intramolecular O—H···O hydrogen bonds in enol forms, (I*a*)–(I*c*). It is of interest to determine how their molecular structures and hydrogen bonds depend on the bridge *X* atoms.



(I*a*) *X*=Se
(I*b*) *X*=S
(I*c*) *X*=CH_2

The crystal structures of (I*a*) (Kivekäs & Laitalainen, 1983) and (I*c*) (Low *et al.*, 2003; Bolte & Scholtyssik, 1997) are reported to be similar to each other, even though the space group for (I*a*) is $P4_2bc$ with *Z* = 4 and that for (I*c*) is *Pccn* with *Z* = 8. The space group of the title compound, (I*b*) (Fig. 1 and Table 1), is found to be $P4_2bc$, with slightly smaller lattice constants *a* and *c* than those for (I*a*). Although the crystal structures of seven derivatives of structure (I*c*) substituted at the methylene bridge with *p*-substituted phenyl groups have been determined by Bolte *et al.* (1997, 2001), their molecular structures are not further mentioned here to ensure focus on the structural differences due to unsubstituted bridge *X* atoms. The mean values for the structure and ring puckering parameters (Cremer & Pople, 1975; Taylor, 1980) of (I*c*) are used here unless otherwise specified, since the structures of the two independent molecules in the crystal of (I*c*) are similar to each other.

The C—*X* bond length decreases from 1.916 (10) Å for (I*a*) to 1.763 (2) Å for (I*b*) to 1.515 (1) Å for (I*c*), while the C—*X*—C bond angle increases from 100.9 (4)° for (I*a*) to 104.8 (2)° for (I*b*) to 116.1 (1)° for (I*c*). The C—*X* bond lengths are approximately correlated with the covalent radii of *X* (1.22, 1.02 and 0.68 Å for *X* = Se, S and CH_2, respectively; Cambridge Crystallographic Data Center, 2006). The intramolecular O···O hydrogen-bond distance of 2.732 (2) Å for (I*b*) (Table 2) is also between the corresponding distances of 2.857 (12) Å for (I*a*) and 2.641 (1) Å for (I*c*).

The ring-puckering parameters [θ = 61.6 (3)° and φ_2 = −2.4 (4)°] for the C2—C1—C6—C5—C4—C3 sequence of the cyclohexenone ring in (I*b*) are indicative of conformations somewhere between half-boat and envelope for the cyclohexenone ring as observed for (I*a*) [θ = 60.9 (17)° and φ_2 = −3.6 (19)°] and (I*c*) [θ = 59.0 (3)° and φ_2 = 178.5 (4)°; θ = 119.8 (3)° and φ_2 = 0.9 (6)°]. It is interesting that the total puckering amplitude *Q* decreases slightly but significantly from (I*a*) to (I*c*) [*Q* = 0.490 (15), 0.476 (2) and 0.458 (2) Å for (I*a*)–(I*c*), respectively]. The average distance of atoms O1 and O2 from the mean plane of the cyclohexenone ring also decreases from 0.121 Å for (I*a*) to 0.099 Å for (I*b*) to 0.046 Å for (I*c*). The observed dependence of *Q* on the bridge *X* atoms could therefore be ascribed to the intramolecular O—H···O hydrogen bonds, which bring about deformation of the cyclohexenone ring by shrinking of the O1···O2′ (and

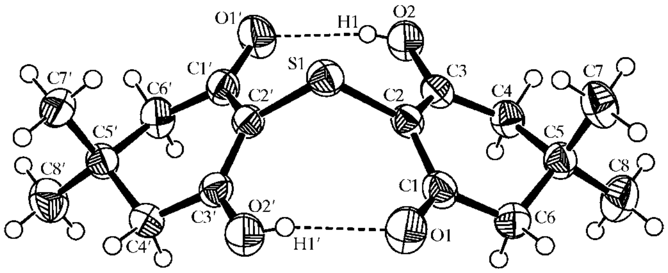


Figure 1
A perspective view of (I*b*), showing the non-H (and H1) atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Primed atoms are at the symmetry position (1 − *x*, −*y*, *z*).

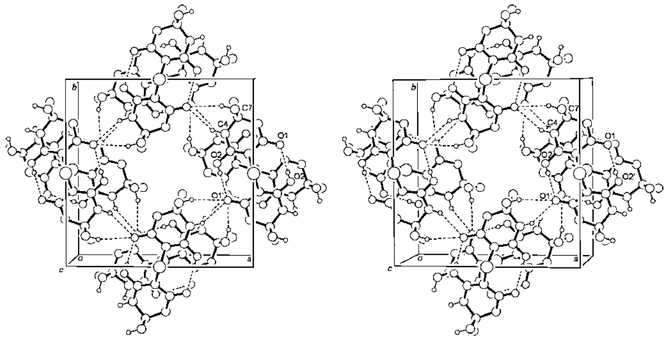


Figure 2
A stereoview of the molecular packing for (I*b*), with intra- and intermolecular hydrogen bonds shown as dashed lines (see Table 2). The non-H atoms of one molecule involved in the hydrogen bonding are labeled. Atoms are drawn as circles of arbitrary radii.

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O2···O1′) distances. The bond distances along the O1—C1—C2—C3—O2 sequence in (I*b*) suggest some π conjugation, as reported for (I*a*) and (I*c*), although the degrees of the bond alternation in (I*a*)–(I*c*) do not seem to be systematic.

In the crystal structures of (I*a*)–(I*c*), mirror-image molecules are stacked along the individual C_2 axes passing through the bridge atoms, forming column structures. The C—*X*—C planes of the upper and lower molecules in these columns relate by *ca* 60°, as displayed in Fig. 2 for (I*b*). There are very weak intermolecular C—H···O hydrogen bonds (Desiraju & Steiner, 1999) or contacts involving methyl H atoms between columns in the crystal structure of (I*b*) (Fig. 2 and Table 2), forming layers of molecules normal to *c*. Similar weak contacts could also be identified in the crystal structures of (I*a*) and (I*c*), although Low *et al.* (2003) doubted their structural significance.

Experimental

Compound (I*b*) was prepared from dimedone and sulfur chloride, according to the procedure of Gompper *et al.* (1964), and isolated through a silica gel column. Suitable crystals were obtained by evaporation of a benzene–methanol solution (m.p. 504–507 K).

Crystal data

$C_{16}H_{22}O_4S$
M_r = 310.41
Tetragonal, $P4_2bc$
a = 13.3426 (14) Å
c = 9.049 (2) Å
V = 1610.9 (4) Å^3
Z = 4
D_x = 1.280 Mg m^{-3}
Mo *Kα* radiation
μ = 0.21 mm^{-1}
T = 298 (2) K
Rectangular, colorless
1.00 × 0.40 × 0.20 mm

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.815, $T_{\max}$ = 0.959
1251 measured reflections
1251 independent reflections
1004 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 30.0°
3 standard reflections every 150 reflections intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.097
S = 1.07
1251 reflections
102 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.1022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.29 e Å^{-3}
$\Delta\rho_{\min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.014 (2)
Absolute structure: Flack (1983)
Flack parameter: −0.02 (17)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.763 (2)	C1—C2	1.425 (3)
O1—C1	1.253 (2)	C2—C3	1.381 (3)
O2—C3	1.300 (2)		
O1—C1—C2—C3	−167.6 (3)	C1—C2—C3—O2	168.6 (2)
O1—C1—C2—S1	10.6 (3)	S1—C2—C3—O2	−9.7 (3)

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···O1^{i}	0.72 (4)	2.04 (4)	2.732 (2)	163 (5)
C4—H2···O1^{ii}	0.97	2.62	3.521 (3)	154
C7—H8···O1^{ii}	0.96	2.65	3.524 (3)	152

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

All H atoms were located in a difference Fourier synthesis. C-bound H atoms were refined with restrained isotropic displacement parameters [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C$_{\rm methyl}$) or 1.2$U_{\rm eq}$(C$_{\rm methylene}$)] using a riding model, with C—H distances of 0.96 (methyl) or 0.97 Å (methylene). The hydroxy H atom was refined isotropically with a fixed displacement parameter [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O)].

Data collection: *MSC/AFC Diffractometer Control Software* (Rigaku/MSC & Rigaku, 2001); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku, 2001); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3008). Services for accessing these data are described at the back of the journal.

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