

seems to be induced by the O atoms of the water molecules, which are relatively close to the TMP molecules. For molecule *A* (Fig. 1) O(1) is closer to C(1) and C(2) than to C(3) and C(4), resulting in an extra attraction between O(1) and C(2). For C(1) the environment of O atoms is such that the resulting attractive C...O force is approximately zero. For molecule *B* O(2) is relatively close to C(7); in this case there is no cancelling of C(8)...O attractions, but a net resulting force approximately in the C(8)...O(2) direction. These C...O forces give a tentative explanation for the observed variations in molecular geometry if it is assumed that the molecules do not respond to these forces by rigid-body translations or rotations.

The computations were carried out on a Cyber 74/18 computer at the Computation Center of the University of Groningen.

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1,5-Dithiacyclooctane-3,7-dione Bis(ethylene acetal)

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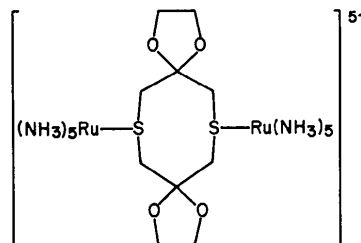
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Abstract. $C_{10}H_{16}O_4S_2$, monoclinic, $P2_1/c$, $a = 5.489(2)$, $b = 10.821(4)$, $c = 10.190(4)$ Å, $\beta = 105.87(3)^\circ$, $Z = 2$, $D_c(140\text{ K}) = 1.51$, $D_x(298\text{ K}) = 1.47$ Mg m⁻³. The structure refined to $R = 0.024$ for 674 reflections with $I > 3\sigma(I)$. A rather long S...S' distance of 3.576(1) Å spans the neutral eight-membered ring.

Introduction. The crystal structure determination of the title compound was undertaken primarily to determine the non-bonded S...S distance across a neutral, dithioether eight-membered ring. Although of interest in its own right, the title compound was chosen because it was easily synthesized (Stein, 1978) and because its melting point of 472 K made it more tractable than 1,5-dithiacyclooctane, which is a liquid at room temperature. Interest in the S...S distance stems from several observations, primarily based on studies of 1,5-dithiacyclooctane. The photoelectron spectrum of this compound shows a splitting of the low-energy peak into a doublet, suggesting that the lone

pairs on the two S atoms interact to give bonding and antibonding combinations (Stein, 1978). In addition, oxidation by NOBF₄ in acetonitrile gives rise to a long-lived cation radical and a dication, both of which contain S—S bonds (Musker & Wolford, 1976). Preliminary studies (Hirschon, 1979) on the title compound indicate that it does not form a radical cation under similar conditions. Nevertheless, a through-space interaction between the two S atoms has been implicated when it bridges two Ru atoms (Stein, 1978) by the observation of an intervalence transition in the visible spectrum of the mixed-valence complex.



The spectrum of the analogous complex with 1,5-dithiacyclooctane as a bridging group exhibits this band with approximately twice the intensity. These crystal structure results are necessary to test the correlation between S—S bond distances and through-space interaction, as well as to provide bond parameters for theoretical calculations.

Colorless needles were obtained from acetone. The crystal selected for data collection was a long needle 0.37×0.075 mm thick that was cut to a length of 0.37 mm. Two previous crystals had been rejected because of twinning. The initial cell constants found were $a = 5.489$ (2), $b = 10.821$ (4), $c = 19.603$ (9) Å, $\beta = 90.25$ (3)°. This orientation yielded systematic absences hkl , $h + l = 2n + 1$; $0k0$, $k = 2n + 1$; $hk0$, no conditions. This B lattice was transformed into a P lattice of dimensions $a = 5.489$ (2), $b = 10.821$ (4), $c = 10.190$ (4) Å, $\beta = 105.87$ (3)° with $h' = h$, $k' = k$ and $l' = (-h + l)/2$. The successful solution of the structure confirms the choice of $P2_1/c$ for the space group.

Intensity data were collected at 140 K on a Syntex $P2_1$ diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Data were collected by an ω -scan technique with $2\theta < 45^\circ$. Of the 749 unique reflections, 674 had $I > 3\sigma(I)$. Neutral-atom scattering factors were those of Cromer & Waber (1974) for S, O and C and those of Stewart, Davidson & Simpson (1965) for H. The real and imaginary anomalous-scattering corrections given by Cromer & Liberman (1970) were used for S. The S atom was located from a Patterson map and was used to compute a Fourier map which allowed the remaining non-hydrogen atoms to be located. Full-matrix least-squares refinement of these atoms, using anisotropic thermal parameters, brought $R = \sum(|F_o| - |F_c|) / \sum |F_o|$ to 0.062. The eight H atoms

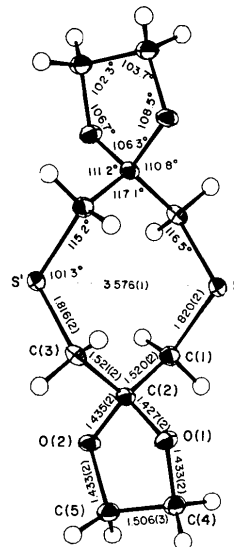


Fig. 1. An ORTEP (Johnson, 1970) drawing of the $C_{10}H_{16}O_4S_2$ molecule showing 50% thermal ellipsoids. The isotropic temperature factors of the H atoms are set to $B = 1.0$ Å². Bond lengths (Å) and their e.s.d.'s are given. The angles have e.s.d.'s of 0.1–0.2°.

were added at calculated positions and included in the refinement, yielding a final R of 0.024. The function minimized was $\sum w(|kF_o| - |F_c|)^2$, with the weighting factor, w , determined by a Hughes (1941) weighting scheme. The last shift in any parameter in the final cycle of refinement was less than a tenth of its e.s.d. All calculations were performed on a Data General Eclipse computer using a program library developed in this laboratory. Table 1 gives the final atomic coordinates.* Bond lengths and bond angles are shown in Fig. 1.

Discussion. Since there are two molecules per unit cell, the title compound must lie on a center of inversion. Molecular models show that there are many dissimilar conformations for this molecule that preserve the center of symmetry and allow the S...S distance to range from a bonding distance to *ca* 5 Å. From solution of the structure the two S atoms are separated by 3.576 (1) Å and the six C atoms in the eight-membered ring lie almost in a plane with one S atom above and the other below that plane. The 1,3-dioxolane rings are well separated from each other and there are no significant intermolecular contacts.

The S...S distance is even greater than that found in complexes of 1,5-dithiacyclooctane where the molecule functions as a bridging ligand. In $[Ni(1,5-dithiacyclooctane)_2Cl_2]$ the transannular S...S distance is

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35635 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic fractional coordinates

	x	y	z	B_{eq} or B_{iso} (Å ²)*
S	0.03577 (8)	0.49496 (4)	0.17969 (4)	1.30 (3)
O(1)	0.1113 (2)	0.2130 (1)	0.0729 (1)	1.41 (6)
O(2)	0.4063 (2)	0.2835 (1)	-0.0304 (1)	1.40 (7)
C(1)	0.2810 (3)	0.4211 (2)	0.1179 (2)	1.39 (7)
C(2)	0.1883 (3)	0.3198 (2)	0.0127 (2)	1.16 (7)
C(3)	-0.0325 (3)	0.3510 (2)	-0.1095 (2)	1.33 (7)
C(4)	0.3302 (3)	0.1354 (2)	0.1171 (2)	1.57 (8)
C(5)	0.4645 (4)	0.1573 (2)	0.0086 (2)	1.46 (8)
H(1)	0.395 (4)	0.385 (2)	0.195 (2)	1.7 (4)
H(2)	0.368 (4)	0.486 (2)	0.080 (2)	1.7 (4)
H(3)	-0.027 (4)	0.295 (2)	-0.179 (2)	1.3 (4)
H(4)	-0.176 (4)	0.342 (2)	-0.086 (2)	1.0 (4)
H(5)	0.275 (4)	0.054 (2)	0.120 (2)	1.8 (4)
H(6)	0.434 (4)	0.162 (2)	0.207 (2)	1.9 (4)
H(7)	0.643 (4)	0.149 (2)	0.040 (2)	1.7 (4)
H(8)	0.396 (4)	0.102 (2)	-0.072 (2)	1.8 (4)

* B_{eq} , the equivalent value of the anisotropic temperature factor, is listed for the non-hydrogen atoms (Willis & Pryor, 1975).

3.335 (3) Å (Hill & Hope, 1974), while in the 1,5-dithiacyclooctane–diiodine adduct, the distance is 3.44 (1) Å (Nichols, 1978). A possible explanation for this apparent anomaly may be attributed to an increased C–C–C angle found in the diacetal. The presence of the five-membered 1,3-dioxolane ring requires the O–C–O angle to be smaller than tetrahedral. This forces the C–C–C angle to increase with a corresponding increase in the transannular S...S distance. These results suggest that there is little if any sulfur–sulfur interaction in the neutral eight-membered-ring dithioether. If the structure is not altered appreciably in the mixed-valence ruthenium complex, the interaction that produces the intervalence transition must occur over a distance of ~3.6 Å. This is the frontier of the van der Waals radii of two S atoms (3.7 Å).

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17-Methoxy-16,17-seco-8 α ,13 α -androsta-4,9(11)-diene-3,15,17-trione

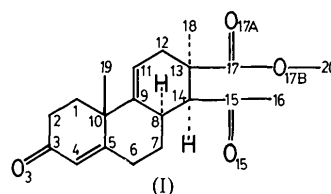
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Abstract. C₂₀H₂₆O₄, $M_r = 330.4$, orthorhombic, *Pbca*, $a = 22.968$ (18), $b = 12.807$ (4), $c = 12.017$ (5) Å, $V = 3535$ Å³, $Z = 8$, $\rho_x = 1.24$ Mg m⁻³, $T \sim 298$ K, $F(000) = 1424$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å. Intensities for 2307 unique reflections were collected on a diffractometer. A block-diagonal least-squares refinement gave a final R of 0.051 for 1435 observed [$I \geq 3\sigma(I)$] reflections. The title compound exists as a racemic mixture.

Introduction. The title compound (I) was prepared in good yield by an SnCl₄-catalysed addition of methyl (*Z*)-2-methyl-4-oxo-2-pentenoate to 9-methyl-1-vinyl-3,4,6,7,8,9-hexahydro-6-naphthalenone (Das, 1978). The establishment of the structure and stereochemistry of adduct (I) revealed the geometric and electronic requirements of this complex Diels–Alder reaction and made it possible to develop short total syntheses of androstane-type steroids (Kakushima, Allain, Dickinson, White & Valenta, 1979; Kakushima, Das, Reid, White & Valenta, 1979).



Crystallographic data were measured on a specimen crystal of approximate dimensions 0.83 × 0.20 × 0.13 mm using a Picker FACS-I diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Preliminary photographic work had shown the crystal to be orthorhombic, and the space group (*Pbca*) was uniquely determined by the systematic absences $0kl: k$ odd, $h0l: l$ odd and $hk0: h$ odd. The lattice parameters were refined by a least-squares fit of cell dimensions and an orientation matrix to the centred diffractometer settings for 12 Friedel pairs of reflections in the interval $33^\circ \leq 2\theta \leq 37^\circ$. Of the 2307 independent reflections measured in the range $2\theta \leq 45^\circ$, 872 (37.8%) were

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