SHORT COMMUNICATIONS

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2,5-Dimethyl[1,2]dithiolo[1,5-*b*][1,2]oxathiole.

By R. Bardi, A. M. Piazzesi and V. Busetti, *Istituto di Chimica Organica, Università di Padova, and Biopolymer Research Center, CNR,* 35100 *Padova, Italy*

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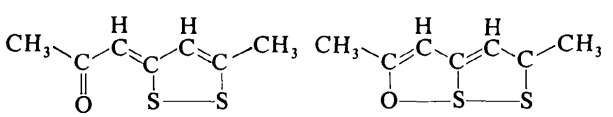
Abstract

$C_7H_8OS_2$, monoclinic, $P2_1/c$, $a = 4{\cdot}44$ (2), $b = 10{\cdot}78$ (2), $c = 17{\cdot}19$ (5) Å, $\beta = 97{\cdot}3$ (1)°, $D_m = 1{\cdot}4$, $D_c = 1{\cdot}40$ Mg m^{-3}, $Z = 4$, $V = 816{\cdot}8$ Å^3, $M_r = 172{\cdot}3$, $F(000) = 360$, μ(Cu $K\alpha$) = 5·30 mm^{-1}. The structure was solved both by direct methods and by Patterson synthesis. The least-squares refinement converged to $R = 0{\cdot}067$ for 1127 three-dimensional observations. The molecule is nearly planar and the electronic distribution is not completely described by a ketonic formula, as there is partial bonding between O and S atoms.

Introduction

Following the structure determination of thiothiophthene (Bezzi, Mammi & Garbuglio, 1958), many derivatives and isosteres have been studied (Busetti, Valle & Bardi, 1978; Sletten & Velsvik, 1973, and references therein) in order to correlate them with that aromatic system and to explain their peculiar properties.

The chemical behaviour (Traverso, 1958), dipolar-moment measurements (Sanesi, Traverso & Lazzarone, 1963), NMR (Hertz, Traverso & Walter, 1959) and IR (Pietra, Garbuglio & Mammi, 1964) data suggested that for this oxygen compound the carbonyl limit formula (I) should be predominant in a structure containing two condensed five-membered rings (II).



(I) (II)

Single-crystal X-ray diffraction data were collected by Ni-filtered Cu $K\alpha$ radiation using the multiple-film equi-inclination Weissenberg method for layers $0kl$ to $3kl$ up to $2\theta = 162{\cdot}5°$; the integrated intensities of 1127 reflections out of 1432 were measured by a flying-spot microdensitometer. For interlayer scaling, *hnl* reflections were recorded on precession photographs with Zr-filtered Mo $K\alpha$ radiation. The structure was solved both by direct methods and by Patterson synthesis and then refined by full-matrix isotropic least squares; the conventional R index was 0·14. Anisotropic refinement improved R to 0·075; the weighting scheme was $w = \{1 + [(k|F_o| - b)/a]^2\}^{-1}$, with $a = 8|F_{min}| = 16$, $b = 5|F_{min}| = 10$ and $k = 0{\cdot}8$. The positions of the H atoms were not revealed by difference Fourier synthesis. By including calculated H-atom coordinates the R index fell to 0·067. Fractional atomic coordinates are in Table 1. Bond

Table 1. *Fractional atomic coordinates* (×10^4, *for* H ×10^3) *with e.s.d.'s in parentheses*

	x	*y*	*z*
S(1)	1793 (3)	2019 (1)	2167 (1)
S(2)	209 (3)	2215 (1)	3260 (1)
O(1)	4020 (10)	1998 (3)	957 (2)
C(1)	887 (14)	4355 (5)	4164 (3)
C(2)	1479 (12)	3721 (4)	3422 (3)
C(3)	2897 (12)	4230 (4)	2857 (3)
C(4)	3346 (11)	3524 (4)	2173 (3)
C(5)	4801 (13)	3915 (5)	1569 (3)
C(6)	5174 (14)	3059 (5)	944 (3)
C(7)	6917 (15)	3438 (7)	290 (3)
H(1)	171	529	426
H(2)	−151	437	419
H(3)	199	380	463
H(4)	372	516	292
H(5)	572	483	157
H(6)	795	434	28
H(7)	872	277	29
H(8)	539	335	−24

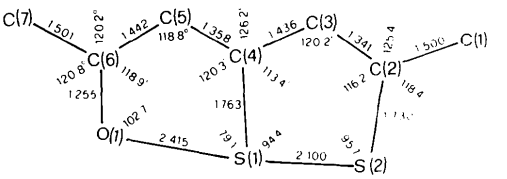


Fig. 1. Bond distances (Å), angles (°), and numbering of the atoms for the title compound. Mean e.s.d.'s are: $\sigma_{S-S} = 0{\cdot}003$, $\sigma_{O-S} = 0{\cdot}004$, $\sigma_{C-S} = 0{\cdot}005$, $\sigma_{O-C} = 0{\cdot}006$, $\sigma_{C-C} = 0{\cdot}007$ Å and $\sigma_{\hat{S}} = 0{\cdot}2$, $\sigma_{\hat{O}} = 0{\cdot}3$, $\sigma_{\hat{C}} = 0{\cdot}4°$.

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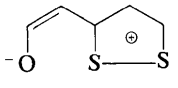
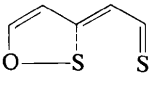
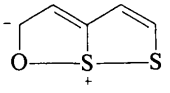
lengths, angles and the numbering of the atoms are shown in Fig. 1.*

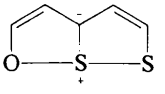
Discussion

In the chain of C atoms there is an alternation of long and short distances, characteristic of conjugated systems. The two C–S bond lengths (1·730 and 1·763 Å) are between single- and double-bond values, 1·82 and 1·61 Å (Hordvik & Sletten, 1966). The S–S bond length of 2·100 Å is the generally accepted value for a S–S single bond in a *cis*-planar disulphide group (Hordvik, 1966). On the other hand, the S–O distance (2·415 Å) is shorter than the sum of constant energy radii, 2·58 Å (Huggins, 1953), so that partial bonding between O and S exists; this may be explained by limit formulae such as:


(*a*)


(*b*)


(*c*)

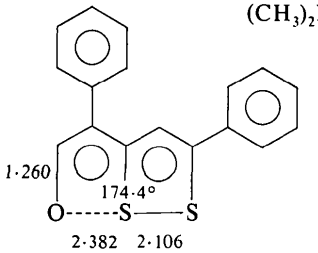

(*d*)

Moreover, the C–O bond (1·255 Å) is significantly longer than the value, 1·22 Å, expected for a double bond (Rabinovich & Schmidt, 1967), so that the molecule apparently tends to adjust itself to attain a S–S–O linear sequence; the $\widehat{SSO}$ angle is 173·5°.

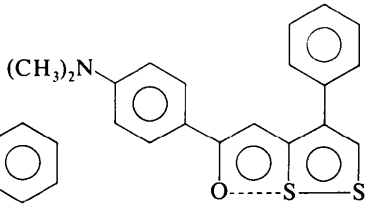
Our structure determination gives another example of the tendency of formally divalent S to be involved in intramolecular contacts (Johnson, Reid & Paul, 1971).

The molecule is nearly planar, the two planes through S(1)S(2)C(1)C(2)C(3)C(4) and O(1)S(1)C(4)C(5)C(6)C(7) are bent by 3·0°.

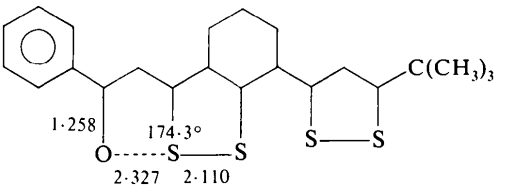
It may be interesting to compare the results of the structure determinations of similar compounds with our results (distances in Å):



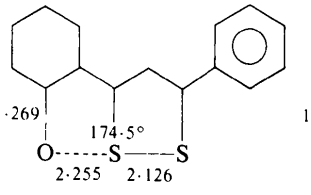
(III)
(Hordvik, Sletten & Sletten, 1969)



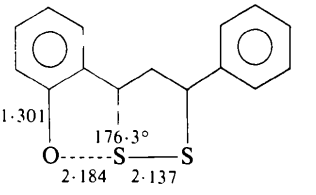
(IV)
(Hordvik & Sæthre, 1972)



(V)
(Sletten & Velsvik, 1973)



(VI)
(Pinel, Mollier, Llaguno & Paul, 1971)



(VII)
(Llaguno, Paul, Pinel & Mollier, 1972).

In all these compounds the S–S bond either has the value of a single bond or is slightly larger, the C–O bond is around the 1·26 Å value (except for the last compound, 1·30 Å), the distance S–O only ranges from 2·443 to 2·184 Å (our value is nearer to the larger value); in fact, there are no substituents in the chain of C atoms to enhance the negative charge of limit formulae (*c*) and (*d*).

The crystal packing has no particular feature. All the intermolecular contacts are at normal van der Waals distances.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34587 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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