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Structure of 2-*exo*-(5,5-Dimethyl-1,3-dioxo-2-cyclohexylidene)-6,6-dimethyl-4,5,6,7-tetrahydro-1,3-benzoxathiol-4-one (EDDEO)

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Abstract. $C_{17}H_{20}O_4S$, m.p. 435 K, $M_r = 320{\cdot}4$, monoclinic, $P2_1/n$, $a = 26{\cdot}855$ (5), $b = 10{\cdot}515$ (2), $c = 5{\cdot}757$ (1) Å, $\beta = 93{\cdot}43$ (2)°, $V = 1622{\cdot}75$ Å^3, $Z = 4$, $D_m = 1{\cdot}270$, $D_x = 1{\cdot}311$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}21$ mm^{-1}, $F(000) = 680$, room temperature, final $R = 0{\cdot}086$ for 532 independent non-zero reflections. The main feature of the molecule is an approximately planar fused-ring system of the oxathiole with the cycloenone ring [maximum deviation from planarity of 0·37 (2) Å]. Both six-membered rings have envelope-like conformations with, in each case, five atoms coplanar and one atom displaced by *ca* 0·7 Å.

Introduction. In the course of a systematic investigation on the reactivity of phenyliodonium dimedonate it was found (Papadopoulou, 1984) that its reaction with CS_2 yields, along with two others, a new compound, the molecular structure of which could not be deduced from chemical and spectroscopic data. This necessitated the X-ray crystal structure analysis of the title compound, EDDEO, reported here.

Experimental. Pure, colourless, crystals of EDDEO kindly provided by Professor A. Varvoglis and Dr M. Papadopoulou. D_m measured by flotation in a KBr solution. Crystal 0·58 × 0·52 × 0·28 mm. Philips PW 1100 computer-controlled single-crystal diffractometer. Cell constants by least-squares analysis of θ angles of the 59 strongest reflexions. Graphite-monochromated Mo $K\alpha$ radiation. ω-scan mode. Three standard reflexions without significant intensity variation. 2341 reflexions measured; $\theta = 3$–22° (max. $hkl = 28$, 11, ± 6); 1977 unique reflexions. Only 532 with $I > 1{\cdot}7\sigma(I)$ due to the poor quality of the crystals. No absorption or extinction corrections. Space group $P2_1/n$ from systematic absences ($h0l$: $h + l = 2n$, $0k0$: $k = 2n$). Structure solved by direct methods with *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Full-matrix least-squares refinement with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Anisotropic temperature coefficients only for S, O and one of the C atoms due to the rather small data/parameter ratio. Inclusion of reflexions with $I < 1{\cdot}7\sigma(I)$ and block-diagonal refinement did not improve the accuracy of the atomic parameters. H atoms of the two rings at calculated positions, of methyl groups located on a difference Fourier map. H-atom coordinates not refined. H-atom isotropic temperature factors the same as those of the C atoms bonded to them. $\sum w(|F_o| - |F_c|)^2$ minimized. $w = 1/\{1 + [(F-B)/A]^2\}$ with $A = 20$, $B = 50$. $R = 0{\cdot}086$, $wR = 0{\cdot}085$, $S = 2{\cdot}52$. Max. $\Delta/\sigma = 0{\cdot}14$, ave. $\Delta/\sigma = 0{\cdot}03$. Max. and min. $\Delta\rho$ in final difference Fourier map 1·96 and −3·06 e Å^{-3} in the S region.

Discussion. The final positional parameters are given in Table 1.* Interatomic distances and angles are given in Table 2. The structure and conformation of the molecule are shown in Fig. 1. The main characteristic of the molecule is the roughly coplanar system of the oxathiole ($P1$) and the cycloenone ($P2$) rings [$P1 \wedge P2 = 3{\cdot}8$ (7)°].

The dimedone (5,5-dimethyl-1,3-cyclohexanedione) ring ($P3$) is rotated by an angle of 13·4 (7)° with respect to $P1$ and its two O atoms lie on either side of $P1$ at distances of −0·20 (4) and 0·15 (4) Å.

The $P1$ ring is planar to a good approximation [max. deviation 0·05 (1) Å], whereas the other two rings are in the form of 'open envelopes'. In $P2$ atom C(5) is 0·65 (3) Å off the plane defined by C(2), C(3), C(4), C(6), C(7) [max. deviation 0·02 (2) Å] which forms an angle of 133 (2)° with the plane of C(4), C(5), C(6). Similarly, in $P3$ atom C(13) is 0·75 (3) Å off the plane of C(10), C(11), C(12), C(14), C(15) [max. deviation 0·06 (2) Å], which forms an angle of 128 (2)° with the plane of C(12), C(13), C(14). So the characteristic 'envelope' conformation found in the structure of dimedone (Singh & Calvo, 1974; Semmingsen, 1974) is preserved also in the present case.

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* Lists of structure amplitudes, anisotropic thermal parameters, coordinates and isotropic temperature factors for H atoms, C—H bond distances and least-squares-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42396 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and isotropic temperature factors* (Å^2) *for the non-*H *atoms in EDDEO*

Here and throughout this paper the e.s.d.'s are given in parentheses and refer to the last digit.

	x	y	z	B_{eq}/B_{iso}
S	0·6538 (2)	0·0259 (5)	0·7910 (10)	2·0*
O(1)	0·702 (1)	0·199 (1)	0·580 (2)	3·1*
O(2)	0·720 (1)	−0·052 (1)	1·238 (3)	4·9*
O(3)	0·667 (1)	0·304 (2)	0·171 (3)	4·3*
O(4)	0·571 (1)	0·013 (2)	0·571 (3)	5·6*
C(1)	0·660 (1)	0·130 (2)	0·571 (4)	2·4
C(2)	0·714 (1)	0·074 (2)	0·881 (3)	1·0
C(3)	0·738 (1)	0·028 (2)	1·114 (3)	1·3
C(4)	0·788 (1)	0·094 (2)	1·175 (3)	2·3
C(5)	0·817 (1)	0·147 (2)	0·974 (4)	4·4*
C(6)	0·783 (1)	0·237 (2)	0·817 (4)	3·6
C(7)	0·734 (1)	0·163 (2)	0·762 (4)	2·9
C(8)	0·861 (1)	0·217 (2)	1·062 (4)	3·3
C(9)	0·834 (1)	0·031 (2)	0·834 (4)	3·6
C(10)	0·623 (1)	0·163 (2)	0·399 (3)	1·8
C(11)	0·626 (1)	0·262 (2)	0·219 (4)	2·0
C(12)	0·580 (1)	0·288 (2)	0·055 (3)	1·9
C(13)	0·528 (1)	0·255 (2)	0·158 (3)	0·7
C(14)	0·533 (1)	0·117 (2)	0·220 (4)	4·2
C(15)	0·576 (1)	0·096 (2)	0·413 (4)	2·6
C(16)	0·487 (1)	0·260 (2)	−0·040 (4)	2·4
C(17)	0·516 (1)	0·348 (2)	0·359 (4)	4·3

* $B_{eq} = \frac{8}{3}\pi^2$ trace $\tilde{\mathbf{U}}$.

Table 2. *Interatomic distances* (Å) *and angles* (°)

S–C(1)	1·69 (2)	C(1)–S–C(2)	84·7 (10)
S–C(2)	1·74 (2)	S–C(1)–C(10)	126·9 (17)
C(1)–C(10)	1·40 (3)	S–C(1)–O(1)	115·9 (15)
C(1)–O(1)	1·35 (3)	O(1)–C(1)–C(10)	116·7 (18)
O(1)–C(7)	1·36 (3)	C(1)–O(1)–C(7)	111·7 (16)
C(7)–C(2)	1·29 (3)	O(1)–C(7)–C(6)	120·4 (19)
C(2)–C(3)	1·54 (3)	Q(1)–C(7)–C(2)	110·5 (18)
C(3)–O(2)	1·22 (3)	C(2)–C(7)–C(6)	128·7 (20)
C(3)–C(4)	1·53 (3)	C(7)–C(2)–S	117·0 (15)
C(4)–C(5)	1·53 (3)	C(7)–C(2)–C(3)	121·8 (18)
C(5)–C(8)	1·46 (3)	S–C(2)–C(3)	120·3 (14)
C(5)–C(9)	1·55 (3)	C(2)–C(3)–O(2)	124·5 (17)
C(5)–C(6)	1·57 (3)	C(2)–C(3)–C(4)	111·9 (16)
C(6)–C(7)	1·55 (3)	O(2)–C(3)–C(4)	123·6 (17)
		C(3)–C(4)–C(5)	118·2 (17)
C(10)–C(11)	1·47 (3)	C(4)–C(5)–C(6)	110·0 (20)
C(11)–O(3)	1·24 (3)	C(4)–C(5)–C(8)	111·3 (19)
C(11)–C(12)	1·54 (3)	C(4)–C(5)–C(9)	106·5 (18)
C(12)–C(13)	1·59 (3)	C(8)–C(5)–C(9)	108·9 (21)
C(13)–C(16)	1·53 (2)	C(8)–C(5)–C(6)	109·2 (19)
C(13)–C(17)	1·54 (3)	C(5)–C(6)–C(7)	106·2 (19)
C(13)–C(14)	1·50 (3)		
C(14)–C(15)	1·56 (3)	C(1)–C(10)–C(11)	127·5 (19)
C(15)–O(4)	1·27 (3)	C(1)–C(10)–C(15)	114·6 (18)
C(15)–C(10)	1·47 (3)	C(11)–C(10)–C(15)	117·7 (17)
		C(10)–C(11)–O(3)	120·2 (18)
Possible hydrogen bonds		C(10)–C(11)–C(12)	119·0 (17)
C(4)···O(3$^{\mathrm{i}}$)	3·38 (3)	O(3)–C(11)–C(12)	119·4 (18)
H2(C4)···O(3$^{\mathrm{i}}$)	2·38	C(11)–C(12)–C(13)	115·2 (16)
C(6)···O(2$^{\mathrm{ii}}$)	3·39 (3)	C(12)–C(13)–C(14)	103·2 (15)
H1(C6)···O(2$^{\mathrm{ii}}$)	2·48	C(12)–C(13)–C(16)	108·3 (14)
C(14)···O(4$^{\mathrm{iii}}$)	3·39 (3)	C(12)–C(13)–C(17)	108·4 (15)
H1(C14)···O(4$^{\mathrm{iii}}$)	2·27	C(16)–C(13)–C(17)	114·2 (15)
		C(16)–C(13)–C(14)	105·3 (15)
Contact distances		C(17)–C(13)–C(14)	116·7 (17)
C(1)···O(2$^{\mathrm{iv}}$)	3·22 (3)	C(13)–C(14)–C(15)	111·4 (18)
C(2)···O(3$^{\mathrm{v}}$)	3·24 (2)	O(4)–C(15)–C(10)	119·8 (19)
C(7)···O(3$^{\mathrm{v}}$)	3·38 (3)		
C(3)···O(1$^{\mathrm{v}}$)	3·42 (2)	C(4)–H2(C4)···O(3$^{\mathrm{i}}$)	146·9
		C(6)–H1(C6)···O(2$^{\mathrm{ii}}$)	146·1
		C(14)–H1(C14)···O(4$^{\mathrm{iii}}$)	170·6

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

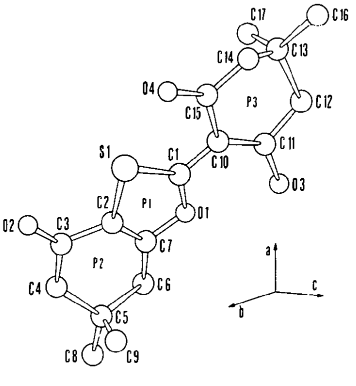

Fig. 1. Clinographic projection of the EDDEO molecule.

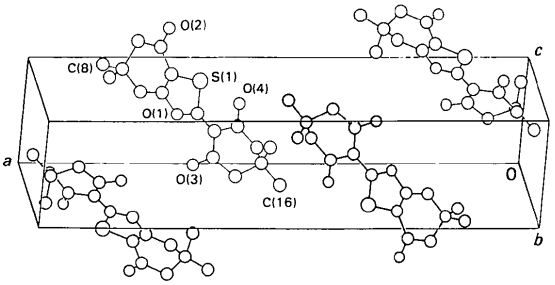

Fig. 2. Clinographic projection of the molecular packing in the unit cell.

A clinographic projection of the unit cell showing the molecular packing of EDDEO is shown in Fig. 2. Three rather doubtful intermolecular C—H···O hydrogen bonds and four possible C···O contacts between the molecules (Table 2) could be regarded as indicating a closely packed system.

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