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2,2-Dimethyl-5-(phenylthiomethylene)-1,3-dioxane-4,6-dione

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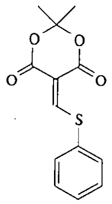
Abstract

The determination of the structure of the title compound, $C_{13}H_{12}O_4S$, shows that the substitution of *S*-phenyl for *S*-methyl has only minor and local effects on the molecular geometry of 5-thiomethylene derivatives of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione).

Comment

As part of a continuing study (Blake, Hunter & McNab, 1989; Blake, McNab & Monahan, 1991) of the geometry of 5-methylene derivatives of Meldrum's acid we report the structure of the 5-phenylthiomethylene compound (I).



(I)

The structure of the corresponding *S*-methyl derivative has been reported previously (Blake, Hunter & McNab, 1989). Substitution of *S*-phenyl for *S*-methyl has no significant effect on the bond lengths within the molecule except that the S—CH_3 distance [1.807 (4) Å] is longer than the S—C_6H_5 distance [1.782 (5) Å]. The effect on the valence angles is also generally negligible, but the C=C—S angle is somewhat wider [128.3 (4)°] in the *S*-phenyl derivative than in its *S*-methyl analogue [126.0 (2)°]. The asymmetry in the exocyclic angles [122.0 (4) and 117.9 (5)°] subtended at C(1*p*) in (I) may be rationalized in terms of repulsion between a lone pair on the S atom and the π system of the phenyl ring. The atoms C(4), C(5), C(6), C(7) and S are coplanar (the mean deviation from the least-squares plane is 0.015 Å) and the normal to this plane makes an angle of 51.8° with that of the phenyl ring.

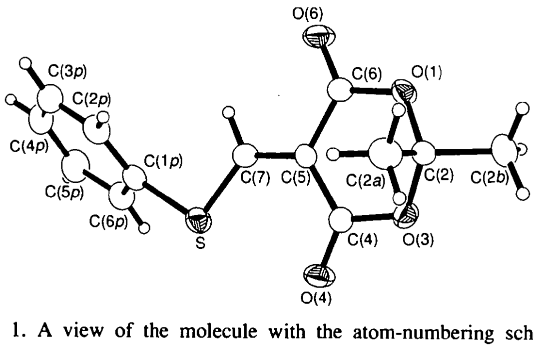


Fig. 1. A view of the molecule with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level.

Experimental

The title compound was prepared by the reaction of 5-methoxymethylene Meldrum's acid with thiophenol in acetonitrile (Hunter & McNab, 1993). Crystals were grown from ethyl acetate.

Crystal data

$C_{13}H_{12}O_4S$
$M_r = 264.29$
Monoclinic
$P2_1/c$
$a = 15.2742$ (14) Å
$b = 7.1069$ (6) Å
$c = 12.5036$ (13) Å
$\beta = 110.744$ (7)°
$V = 1269.3$ (2) Å^3
$Z = 4$
$D_x = 1.383$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 84 reflections
$\theta = 11–13°$
$\mu = 0.258$ mm^{-1}
$T = 298$ (2) K
Plate
$0.62 \times 0.47 \times 0.08$ mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω–2θ scans
Absorption correction: none
2333 measured reflections
1663 independent reflections
1147 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0496$
$\theta_{\rm max} = 22.52°$
$h = 0 \rightarrow 16$
$k = -7 \rightarrow 7$
$l = -13 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity variation: 1.0%

Refinement

Refinement on F^2
$R(F) = 0.0559$
$wR(F^2) = 0.1356$
$S = 1.146$
1645 reflections
164 parameters
H atoms were included in calculated positions
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 4.4915P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.042$

$\Delta\rho_{\rm max} = 0.378$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.250$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1994)
Extinction coefficient: 0.0060 (13)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
O(1)	0.2126 (2)	0.7640 (5)	0.4976 (3)	0.0463 (10)
C(2)	0.1187 (4)	0.7041 (8)	0.4837 (5)	0.0438 (14)
C(2*a*)	0.0502 (4)	0.7753 (8)	0.3746 (5)	0.058 (2)
C(2*b*)	0.1033 (4)	0.7704 (9)	0.5898 (5)	0.064 (2)
O(3)	0.1161 (3)	0.5008 (5)	0.4873 (3)	0.0455 (10)
C(4)	0.1507 (4)	0.4038 (8)	0.4176 (4)	0.0392 (14)
O(4)	0.1249 (3)	0.2441 (6)	0.3919 (4)	0.0549 (11)
C(5)	0.2209 (3)	0.4998 (7)	0.3841 (4)	0.0347 (13)
C(6)	0.2561 (4)	0.6858 (8)	0.4318 (5)	0.0419 (14)
O(6)	0.3221 (3)	0.7639 (5)	0.4215 (4)	0.0623 (13)
C(7)	0.2626 (4)	0.4143 (7)	0.3180 (4)	0.0402 (14)
S	0.23996 (11)	0.1997 (2)	0.25649 (14)	0.0507 (5)
C(1*p*)	0.3251 (4)	0.1915 (8)	0.1893 (5)	0.0427 (14)
C(2*p*)	0.3318 (4)	0.3314 (8)	0.1153 (5)	0.051 (2)
C(3*p*)	0.4001 (4)	0.3198 (9)	0.0676 (5)	0.056 (2)
C(4*p*)	0.4577 (4)	0.1661 (10)	0.0882 (5)	0.061 (2)
C(5*p*)	0.4493 (4)	0.0240 (10)	0.1579 (5)	0.063 (2)
C(6*p*)	0.3822 (4)	0.0357 (9)	0.2083 (5)	0.050 (2)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(2)	1.447 (6)	C(4)—C(5)	1.452 (7)
O(1)—C(6)	1.347 (6)	C(5)—C(7)	1.351 (7)
C(2)—C(2*a*)	1.484 (8)	C(5)—C(6)	1.471 (7)
C(2)—C(2*b*)	1.502 (7)	C(6)—O(6)	1.198 (6)
C(2)—O(3)	1.446 (7)	C(7)—S	1.688 (5)
O(3)—C(4)	1.357 (6)	S—C(1*p*)	1.782 (5)
C(4)—O(4)	1.208 (6)		
C(6)—O(1)—C(2)	119.2 (4)	C(7)—C(5)—C(4)	121.4 (5)
O(1)—C(2)—O(3)	109.1 (4)	C(7)—C(5)—C(6)	117.9 (5)
O(1)—C(2)—C(2*a*)	110.9 (5)	C(4)—C(5)—C(6)	120.4 (5)
O(3)—C(2)—C(2*a*)	110.5 (5)	O(6)—C(6)—O(1)	119.4 (5)
O(1)—C(2)—C(2*b*)	105.1 (4)	O(6)—C(6)—C(5)	124.9 (5)
O(3)—C(2)—C(2*b*)	105.8 (5)	O(1)—C(6)—C(5)	115.5 (5)
C(2*a*)—C(2)—C(2*b*)	115.1 (5)	C(5)—C(7)—S	128.3 (4)
C(4)—O(3)—C(2)	117.8 (4)	C(7)—S—C(1*p*)	100.3 (3)
O(4)—C(4)—O(3)	118.9 (5)	C(2*p*)—C(1*p*)—S	122.0 (4)
O(4)—C(4)—C(5)	124.8 (5)	C(6*p*)—C(1*p*)—S	117.9 (5)
O(3)—C(4)—C(5)	116.3 (5)		
C(4)—C(5)—C(7)—S	4.2 (8)	C(7)—S—C(1*p*)—C(2*p*)	−54.0 (5)
C(6)—C(5)—C(7)—S	177.6 (4)	C(7)—S—C(1*p*)—C(6*p*)	129.2 (5)
C(5)—C(7)—S—C(1*p*)	−178.6 (5)		

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

We thank DENI for a studentship (to MM) and the SERC for provision of a four-circle diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blake, A. J., Hunter, G. A. & McNab, H. (1989). *J. Chem. Res.* (*S*), pp. 118–119; *J. Chem. Res.* (*M*), pp. 0921–0943.

Blake, A. J., McNab, H. & Monahan, L. C. (1991). *J. Chem. Soc. Perkin Trans.* 2, pp. 2003–2010.

Hunter, G. A. & McNab, H. (1993). *Synthesis*, pp. 1067–1068.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1992). *SHELXTL/PC*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1994). *J. Appl. Cryst.* In preparation.

Stoe & Cie (1988*a*). *DIF*4. *Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1988*b*). *REDU*4. *Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

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Structural Investigation of Some Lactides

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Abstract

We determined the crystal structures of four lactides: (1) (3*S*,6*S*)-3-benzyl-6-methyl-1,4-dioxane-2,5-dione ($C_{12}H_{12}O_4$), (2) (3*RS*,6*SR*)-6-(1,1-dimethyl-2-methoxyethyl)-3-[(*SR*)-α-hydroxybenzyl]-3-methyl-1,4-dioxane-2,5-dione ($C_{17}H_{22}O_6$), (3) (3*RS*,6*SR*)-6-(1,1-dimethyl-2-methoxyethyl)-3-(1-hydroxy-1-methylethyl)-3-methyl-1,4-dioxane-2,5-dione ($C_{13}H_{22}O_6$) and (4) (3*S*,6*R*)-6-(1,1-dimethyl-2-methoxyethyl)-3-methyl-3-[(*S*)-3-oxocyclopentyl]-1,4-dioxane-2,5-dione ($C_{15}H_{22}O_6$). The structure of the lactide heterocycle in the title compounds is compared with the only four structures of this type previously reported. The geometrical parameters of this heterocycle agree with those found previously for carboxylic esters.

Comment

The structures of carboxylic ester groups have been investigated thoroughly (Schweizer & Dunitz, 1982). Lactides contain this fragment twice within a six-membered heterocycle. We have determined the crystal structures of four lactides and compared their structural parameters with those of carboxylic esters. We also studied the influence of substituents on the conformation of the dilactone ring. Compounds (2) and (3) crystallized as racemic mixtures, while (1)

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