

Two Methylsulfonylmethylene Derivatives of Meldrum's Acid

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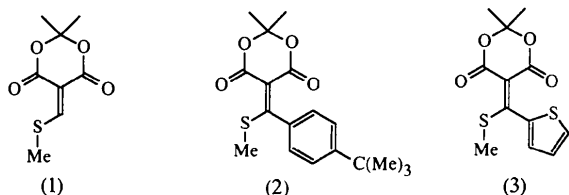
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Abstract

Functionalization of methylsulfonylmethylene Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) with aryl or thienyl substituents, to give 5-[(*p*-*tert*-butylphenyl)(methylsulfonyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione, C₁₈H₂₂O₄S, and 2,2-dimethyl-5-[(methylsulfonyl)(2-thienyl)methylene]-1,3-dioxane-4,6-dione, C₁₂H₁₂O₄S₂, results in a lengthening of the C—S single bond and the adoption of essentially a boat conformation by the Meldrum's acid heterocycle.

Comment

We have previously published the crystal structure of methylsulfonylmethylene Meldrum's acid, (1) (Blake *et al.*, 1989), and as part of a continuing study on the effects of substitution on the structural chemistry of Meldrum's acid derivatives, we report here the effect of the replacement of the methylene H atom with an aryl group, (2), and with a 2-thienyl group, (3). This latter substituent exhibits twofold rotational disorder and so, in this case, our comments are restricted to the remainder of the molecule.



The S1—C7 bond lengths in (2) and (3) [1.738 (1) and 1.744 (4) Å, respectively] are significantly longer than the corresponding distance in (1) [1.694 (3) Å], and this may reflect the electron donation by the additional ring into the methylenedioxy unit. There appears to be a consistent trend towards a more single-bond character in the C5—C7 bonds of (2) and (3) [1.368 (2) and 1.377 (5) Å, respectively] than in (1) [1.356 (4) Å]. The dioxanedione ring in (3) has local mirror symmetry to within experimental error, but in

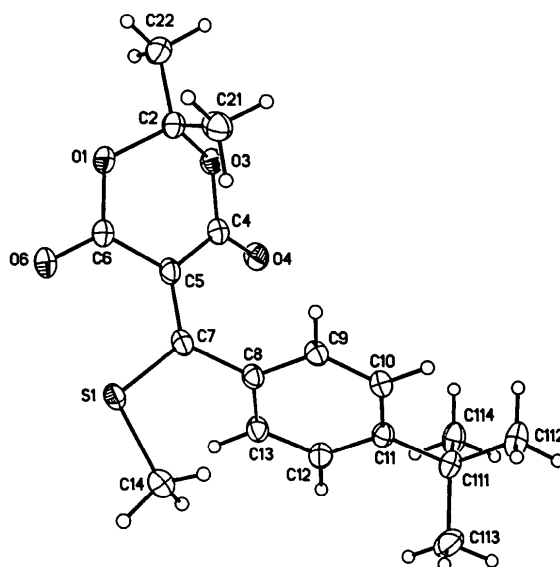


Fig. 1. A view of (2) with the atom-numbering scheme. Displacement ellipsoids enclose 30% probability surfaces.

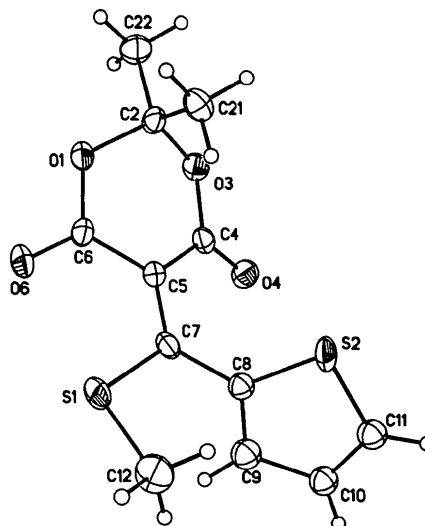


Fig. 2. A view of (3) with the atom-numbering scheme. Displacement ellipsoids enclose 30% probability surfaces. The minor disorder component is not shown.

(2), C4—C5 is significantly longer [1.485 (2) Å] than C5—C6 [1.467 (2) Å].

There is a substantial difference between the angle at the S atom in (1) [100.94 (16)°] and the related angles at S1 in (2) and (3) [104.94 (7) and 104.1 (2)°, respectively], which may be due to steric interaction with the additional phenyl or thiophene rings. Similarly, the angle C5—C7—S1 is much smaller in (2) [120.3 (1)°] and (3) [121.2 (3)°] than in (1) [126.16 (3)°], as is the angle C4—C5—C6 [116.4 (1) and 115.6 (3)° in (2) and (3),

compared with 120.2(3)° in (1)]. Whereas the dioxanedione ring systems in (2) and (3) can be described as being mainly in a boat conformation (16% chair, 1% twist boat, 83% boat in both cases; Gould *et al.*, 1995), in (1), the O1—C6—C5—C4—O3 moiety is effectively planar, the ring being 31% chair, 1% twist boat and 68% boat. Qualitatively expressed, a second substituent on C7 apparently induces a distortion of the dioxanedione ring, which forces C7 and the O4 and O6 carbonyl groups in opposite directions with respect to the best O1—C6—C5—C4—O3 plane. The plane of the aryl ring in (2) lies at 114.2(1)° with respect to the S1—C7—C8 plane, which itself makes an angle of only 9.4(1)° with the C4—C5—C6 plane; the corresponding parameters for (3) are 114.1(2) and 5.6(3)°, respectively.

Experimental

Compounds (2) and (3) were prepared according to the procedures described by Hunter & McNab (1995). Crystals of (2) were grown by slow evaporation of an acetone solution, while those of (3) were grown by sublimation.

Compound (2)

Crystal data

C₁₈H₂₂O₄S
M_r = 334.43
 Triclinic
P $\bar{1}$
a = 9.4818 (9) Å
b = 9.7365 (14) Å
c = 10.6089 (10) Å
 α = 93.469 (8)°
 β = 113.697 (5)°
 γ = 97.890 (8)°
V = 881.08 (16) Å³
Z = 2
D_s = 1.26 Mg m⁻³
D_m not measured

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
 ω - θ scans with on-line profile fitting (Clegg, 1981)
 Absorption correction: ψ scans (North *et al.*, 1968)
T_{min} = 0.405, *T_{max}* = 0.673

Refinement

Refinement on *F*²
R = 0.0338
 ωR = 0.0402

Cu *K* α radiation
 λ = 1.54180 Å
 Cell parameters from 60 reflections
 θ = 20–22°
 μ = 1.73 mm⁻¹
T = 220.0 (2) K
 Block
 0.43 × 0.39 × 0.23 mm
 Orange

7548 measured reflections
 3123 independent reflections
 2785 reflections with *I* > 2 σ (*I*)
R_{int} = 0.014
 θ_{\max} = 70.17°
h = -11 → 11
k = -11 → 11
l = -7 → 12
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.0%

(Δ/σ)_{max} = 0.005
 $\Delta\rho_{\max}$ = 0.23 e Å⁻³
 $\Delta\rho_{\min}$ = -0.22 e Å⁻³

S = 1.1073
 2785 reflections
 209 parameters
 H atoms placed geometrically after each cycle
 Weighting: Chebyshev polynomial (Carruthers & Watkin, 1979)

Extinction correction: Larson (1970)
 Extinction coefficient: 50 (3)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °) for (2)

S1—C7	1.738 (1)	O4—C4	1.200 (2)
S1—C14	1.801 (2)	C4—C5	1.485 (2)
O1—C2	1.444 (2)	C5—C6	1.467 (2)
O1—C6	1.353 (2)	C5—C7	1.368 (2)
C2—O3	1.436 (2)	O6—C6	1.204 (2)
O3—C4	1.353 (2)	C7—C8	1.488 (2)
C7—S1—C14	104.94 (7)	S1—C7—C5	120.3 (1)
C4—C5—C6	116.4 (1)	S1—C7—C8	118.4 (1)
C4—C5—C7	121.6 (1)	C5—C7—C8	121.3 (1)
C6—C5—C7	121.8 (1)		

Compound (3)

Crystal data

C₁₂H₁₂O₄S₂
M_r = 284.34
 Triclinic
P $\bar{1}$
a = 6.137 (8) Å
b = 7.170 (8) Å
c = 15.00 (3) Å
 α = 79.00 (8)°
 β = 84.36 (11)°
 γ = 83.08 (8)°
V = 641.2 (15) Å³
Z = 2
D_s = 1.473 Mg m⁻³
D_m not measured

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
 ω -2 θ scans
 Absorption correction: none
 3309 measured reflections
 2200 independent reflections

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.061
 ωR (*F*²) = 0.187
S = 1.152
 2200 reflections
 166 parameters
 H atoms riding
 $\omega = 1/[\sigma^2(F_o^2) + (0.0945P)^2 + 1.3847P]$
 where *P* = (*F_o*² + 2*F_c*²)/3

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 50 reflections
 θ = 9.5–16.0°
 μ = 0.418 mm⁻¹
T = 150.0 (2) K
 Block
 0.55 × 0.55 × 0.40 mm
 Colourless

2068 reflections with *I* > 2 σ (*I*)
R_{int} = 0.022
 θ_{\max} = 25.09°
h = -7 → 7
k = -8 → 8
l = 0 → 17
 3 standard reflections
 frequency: 60 min
 intensity decay: 4%

(Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max}$ = 0.49 e Å⁻³
 $\Delta\rho_{\min}$ = -0.72 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. Selected geometric parameters (Å, °) for (3)

O1—C6	1.365 (5)	C5—C7	1.377 (5)
O1—C2	1.443 (5)	C5—C6	1.472 (5)
C2—O3	1.435 (4)	C6—O6	1.207 (5)
O3—C4	1.355 (4)	C7—C8	1.473 (5)
C4—O4	1.223 (4)	C7—S1	1.744 (4)
C4—C5	1.472 (5)	S1—C12	1.817 (5)
C7—C5—C4	123.4 (3)	C5—C7—S1	121.2 (3)
C7—C5—C6	120.8 (3)	C8—C7—S1	116.8 (2)
C4—C5—C6	115.6 (3)	C7—S1—C12	104.1 (2)
C5—C7—C8	122.0 (3)		

The thienyl ring in (3) exhibits twofold rotational disorder about the C7—C8 axis and the two components were restrained during refinement to be geometrically similar. The relative occupancy was refined to 0.681 (5) for the major component. The S atoms in both components were refined with anisotropic displacement parameters; the higher-occupancy C atoms were modelled with independent isotropic displacement parameters, while a common isotropic displacement parameter was refined for the remainder.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1990a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1994) for (2); *SHELXTL* (Sheldrick, 1994) for (3). Program(s) used to refine structures: *CRYSTALS* (Watkin *et al.*, 1996) for (2); *SHELXL96* (Sheldrick, 1996) for (3). For both compounds, molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1192). Services for accessing these data are described at the back of the journal.

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Chasmaconitine 0.5-Methanol Solvate†

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Abstract

The crystal structure of chasmaconitine hemimethanol solvate, C₃₄H₄₇NO₉·0.5CH₄O, a C₁₉ norditerpenoid alkaloid, isolated from the roots of *Aconitum chasmanthum* Stapf ex Holmes of Pakistani origin, contains discrete molecules separated by normal van der Waals distances. The fused-ring system contains one boat, one half-chair, two envelope and two chair conformations. The molecular dimensions are normal with no interactions between the alkaloid and the disordered solvate molecules; the mean bond distances are C_{sp³}—N 1.467 (14), C_{sp³}—C_{sp³} 1.54 (2), C_{sp³}—O 1.42 (2), C_{sp²}—O 1.337 (5) and C=O 1.197 (5) Å.

Comment

Aconitum chasmanthum Stapf ex Holmes is a small herbaceous shrub which grows wild in Kashmir, Hattian and Rescuta Top. It contains a large number of norditerpenoid alkaloids, e.g. chasmaconitine and chasmanthine (Achmatowicz & Marion, 1964), homochasmanine (Achmatowicz & Marion, 1965), indaconitine (Miana *et al.*, 1971) and chasmanine (Pelletier *et al.*, 1984). The pharmacological properties of the diterpenoid alkaloids which include the control and induction of cardiac arrhythmia, effects on smooth and skeletal muscles, central nervous activity and analgesia, have been reviewed (Benn & Jacyno, 1983; Pelletier & Page, 1986; Amiya

† Alternative name: (1 α ,6 α ,14 α ,16 β)-20-ethyl-13-hydroxy-1.6.16-trimethoxy-4-(methoxyethyl)aconitane-8,14-diyl 8-acetate 14-benzoate 0.5-methanol solvate.