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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1183). Services for accessing these data are described at the back of the journal.

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3-Cyano-6-(2-methoxyphenyl)-4-methylthio-2H-pyran-2-one

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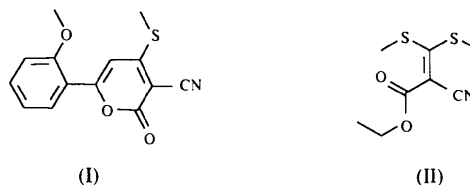
(Received 13 February 1997; accepted 14 May 1997)

Abstract

The molecule of the title compound, C₁₄H₁₁NO₃S, is approximately planar with the two six-membered rings inclined at an angle of 10.99 (12)°.

Comment

Compounds containing the pyrone nucleus, in particular the 4-hydroxy-2H-pyran-2-ones and their ether derivatives, have been found to have a variety of pharmacological properties (Israili & Smismann, 1976; Kretzschmar, Meyer, Teschendorf & Zoellner, 1969). Tominaga and other workers have extensively investigated the addition of enolate anions derived from ketones to doubly active ketene dithioacetals, which are versatile reagents and have been extensively utilized in organic synthesis to afford 4-methylthio-2H-pyran-2-ones (Hatada *et al.*, 1975). We have synthesized several 3-cyano-4-methylthio-6-aryl-2H-pyran-2-ones (δ -lactones) as synthons for the synthesis of different classes of heterocycles, such as pyrazoles, isoxazoles and pyrazolo/isoxazolo coumarins and triazoles (Singh *et al.*, 1995; Kumar, Kumar, Parmar & Errington, 1996). However, lactones having the aryl group possessing an *ortho* substituent are usually difficult to make due to steric hindrance. This paper reports the first preparation of a lactone containing an *ortho*-methoxyphenyl substituent, (I).



The molecular structure of the title compound is illustrated in Fig. 1. The bond lengths and angles are largely unexceptional (Allen *et al.*, 1987). As previously reported (Azim, Parmar & Errington, 1997), the C_{sp²}—S distance [1.734 (3) Å] is shorter than the C_{sp³}—S distance [1.796 (3) Å] and is indicative of some double bonding in the sp² case. The molecule is approximately planar, with the dihedral angle between the two six-membered rings equal to 10.99 (12)°. The ring substituents are approximately aligned with the ring planes as illustrated by torsion angles C7—S1—C3—C2 and C14—O3—C13—C12 of -177.22 (19) and

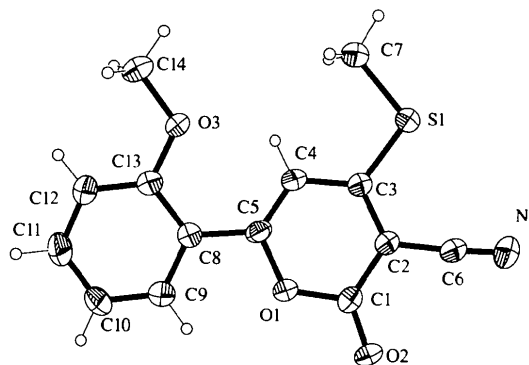


Fig. 1. View of the molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

4.0 (4)°, respectively. The two methyl groups point in the same direction with respect to bonded heteroatoms. The two six-membered rings bend away from one another in the sense that the bond angles C13—C8—C5 [123.6 (2)°] and C4—C5—C8 [127.9 (2)°] are both significantly greater than the expected 120°; this may be due to the steric effect of the *ortho* substituent.

Experimental

A mixture of ethyl 2-cyano-3,3-bis(methylthio)acrylate [(II); 4.34 g, 0.02 mol], 2-methoxyacetophenone (2.75 ml, 0.02 mol), powdered KOH (2.24 g, 0.04 mol) and DMF (50 ml) was stirred at 305 K for 8 h. The reaction mixture was poured onto 300 ml of ice water and stirred for 4 h. The yellow solid that separated was collected by filtration and washed with water; it crystallized out from acetone as fine bright orange crystals (900 mg, 17%; m.p. 470–471 K). IR (KBr) ν_{\max} : 2250 (C≡N), 1710 (C=O), 1605, 1565, 1490, 1280, 1160, 1010, 840, 760 and 620 cm^{-1} . UV (MeOH) λ_{\max} : 316 and 385 nm.

Crystal data

$\text{C}_{14}\text{H}_{11}\text{NO}_3\text{S}$	Mo $K\alpha$ radiation
$M_r = 273.30$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 3385 reflections
$P2_1/c$	$a = 9.1163 (9) \text{ \AA}$
$a = 9.1163 (9) \text{ \AA}$	$\theta = 2.27\text{--}23.38^\circ$
$b = 16.050 (2) \text{ \AA}$	$\mu = 0.260 \text{ mm}^{-1}$
$c = 8.7050 (8) \text{ \AA}$	$T = 230 (2) \text{ K}$
$\beta = 99.608 (2)^\circ$	Plate
$V = 1255.84 (17) \text{ \AA}^3$	$0.50 \times 0.31 \times 0.16 \text{ mm}$
$Z = 4$	Intense orange
$D_x = 1.445 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens SMART diffractometer	1789 independent reflections
ω scans	1373 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan SADABS (Sheldrick, 1996a)	$R_{\text{int}} = 0.046$
$T_{\min} = 0.77$, $T_{\max} = 0.96$	$\theta_{\max} = 23.38^\circ$
5252 measured reflections	$h = -10 \rightarrow 8$
	$k = -17 \rightarrow 16$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.006$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$\Delta\rho_{\max} = 0.234 \text{ e \AA}^{-3}$
$wR(F^2) = 0.123$	$\Delta\rho_{\min} = -0.311 \text{ e \AA}^{-3}$
$S = 0.992$	Extinction correction: none
1789 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
174 parameters	
H atoms riding	
$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

S1—C3	1.734 (3)	O3—C13	1.372 (3)
S1—C7	1.796 (3)	O3—C14	1.434 (3)
O1—C5	1.374 (3)	N1—C6	1.150 (3)
O1—C1	1.389 (3)	C2—C6	1.431 (4)
O2—C1	1.210 (3)	C5—C8	1.474 (3)

C3—S1—C7	104.14 (12)	O1—C5—C8	111.64 (19)
C5—O1—C1	123.07 (18)	N1—C6—C2	175.8 (3)
C13—O3—C14	118.9 (2)	C13—C8—C5	123.6 (2)
O2—C1—C2	127.5 (2)	C9—C8—C5	118.9 (2)
C4—C5—C8	127.9 (2)		
C7—S1—C3—C2	−177.22 (19)	C4—C5—C8—C13	−10.7 (4)
S1—C3—C4—C5	−177.32 (18)	C14—O3—C13—C12	4.0 (4)

The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω . The crystal-to-detector distance was 5.01 cm. Coverage of the unique set was over 99% complete to at least 23° in θ . Crystal decay, monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections, was found to be negligible. H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times U_{iso} of the parent atom.

Data collection: SMART (Siemens, 1994b). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: SHELXTL/PC (Siemens, 1994a). Program(s) used to refine structure: SHELXL96 (Sheldrick, 1996b). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXTL/PC.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher, McMeeking & Parkin, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1174). Services for accessing these data are described at the back of the journal.

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The Novel Fragrance 2-Isobutyl-4-oxo-5,5-dimethyltetrahydropyran as its 2,4-Dinitrophenylhydrazone Derivative

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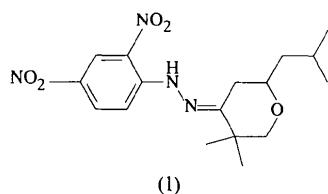
(Received 23 December 1996; accepted 6 June 1997)

Abstract

The structure of the title compound, 2-isobutyl-5,5-dimethyltetrahydropyran-4-one 2,4-dinitrophenylhydrazone, C₁₇H₂₄N₄O₅, was determined and the identity of the 2-isobutyl substituent, unclear from NMR spectroscopy, was confirmed.

Comment

2-Isobutyl-4-oxo-5,5-dimethyltetrahydropyran was prepared and organoleptically evaluated by Quest International as a potential novel fragrance ingredient. The evaluation was carried out by a panel of expert perfumers. The compound possessed a fruity odour of moderate intensity which, although predominantly rhubarb in character, was also perceived as having grapefruit, chemical, nitrile and urinous notes. The hybridization at C23, and hence the identity of the 2-isobutyl group, could not be assigned reliably from a proton NMR spectrum. In order to confirm the structure by X-ray crystallography, the ketone was converted into the corresponding crystalline 2,4-dinitrophenylhydrazone derivative, (1) (Fig. 1).



All H atoms, including those on C23, were evident in a difference synthesis and the bond lengths for C1—C23 and C23—C24 confirmed *sp*³ hybridization at C23.

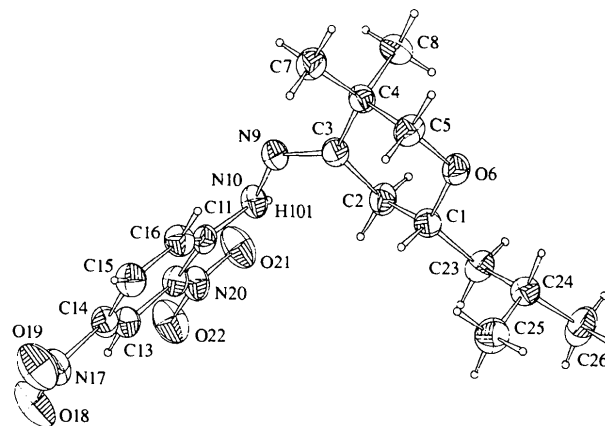


Fig. 1. The molecular structure of (1) with 50% probability displacement ellipsoids.

Experimental

The potential fragrance was prepared as a liquid by a standard six-step synthesis, starting from isopropyl methyl ketone (Rossiter, 1997) and converted to the corresponding 2,4-dinitrophenylhydrazone derivative. This was crystallized from ethanol/*n*-hexane.

Crystal data

C₁₇H₂₄N₄O₅
M_r = 364.40
 Triclinic
P $\bar{1}$
a = 6.681 (3) Å
b = 9.093 (1) Å
c = 16.067 (3) Å
 α = 70.89 (1)°
 β = 75.48 (3)°
 γ = 83.96 (4)°
V = 892.5 (5) Å³
Z = 2
D_x = 1.36 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 refined from ΔF (Walker
 & Stuart, 1983)
T_{min} = 0.67, *T_{max}* = 0.92
 4804 measured reflections
 3415 independent reflections

Refinement

Refinement on *F*²
R(*F*) = 0.055
 ωR (*F*²) = 0.177

Cu *K* α radiation
 λ = 1.5418 Å
 Cell parameters from 23
 reflections
 θ = 15–60°
 μ = 0.80 mm⁻¹
T = 293 K
 Plate
 0.60 × 0.50 × 0.10 mm
 Red

R_{int} = 0.019
 θ_{\max} = 71.93°
h = -7 → 8
k = -10 → 11
l = -11 → 19
 3 standard reflections
 frequency: 60 min
 intensity decay: 6.7%

$(\Delta/\sigma)_{\max}$ < 0.001
 $\Delta\rho_{\max}$ = 0.38 e Å⁻³
 $\Delta\rho_{\min}$ = -0.24 e Å⁻³