

O5	0.1102 (3)	0.3907 (3)	0.6088 (2)	0.0480 (7)
C1	0.5332 (4)	0.2431 (4)	0.7075 (4)	0.0416 (10)
C2	0.3712 (4)	0.1698 (3)	0.6471 (3)	0.0274 (8)
C3	0.2362 (4)	0.1986 (4)	0.7313 (3)	0.0336 (8)
C4	0.3193 (5)	0.2694 (5)	0.8541 (4)	0.0496 (10)
C5	0.4623 (6)	0.1742 (6)	0.9150 (4)	0.0632 (14)
C6	0.5955 (5)	0.1709 (5)	0.8338 (4)	0.0569 (13)
C7	0.5011 (5)	0.3970 (5)	0.7307 (4)	0.0560 (12)
C8	0.3897 (6)	0.4107 (5)	0.8307 (4)	0.0616 (13)
C9	0.4094 (4)	0.0125 (4)	0.6350 (3)	0.0346 (9)
C10	0.3632 (7)	-0.2193 (5)	0.6982 (5)	0.077 (2)
C11	0.2021 (4)	0.1563 (4)	0.4427 (3)	0.0303 (8)
C12	0.1412 (4)	0.2192 (4)	0.3182 (3)	0.0314 (8)
C13	0.0822 (5)	0.1301 (5)	0.2189 (3)	0.0415 (10)
C14	0.0142 (6)	0.1863 (5)	0.1038 (4)	0.0523 (11)
C15	0.0015 (5)	0.3291 (5)	0.0878 (3)	0.0487 (11)
C16	0.0602 (4)	0.4186 (5)	0.1848 (3)	0.0411 (9)
C17	0.1297 (4)	0.3636 (4)	0.3003 (3)	0.0351 (9)
C18	0.0853 (4)	0.2843 (4)	0.6803 (3)	0.0393 (9)

Table 2. Selected geometric parameters (Å, °)

N—C11	1.335 (4)	C2—C3	1.582 (5)
N—C2	1.481 (4)	C3—C4	1.560 (6)
C1—C7	1.529 (7)	C4—C8	1.513 (7)
C1—C6	1.555 (6)	C4—C5	1.552 (6)
C1—C2	1.558 (4)	C5—C6	1.522 (6)
C2—C9	1.552 (5)	C7—C8	1.545 (6)
C11—N—C2	119.7 (3)	C9—C2—C3	113.0 (3)
C9—O2—C10	116.9 (3)	C1—C2—C3	108.1 (3)
C7—C1—C6	108.9 (4)	C18—C3—C4	107.3 (3)
C7—C1—C2	110.3 (3)	C18—C3—C2	119.5 (3)
C6—C1—C2	108.1 (3)	C4—C3—C2	109.0 (3)
N—C2—C9	104.8 (3)	C8—C4—C5	108.3 (4)
N—C2—C1	109.4 (3)	C8—C4—C3	111.7 (3)
C9—C2—C1	107.6 (3)	C5—C4—C3	108.0 (4)
N—C2—C3	113.6 (3)		
C11—N—C2—C9	55.4 (4)	C1—C2—C9—O1	-65.7 (4)
C11—N—C2—C1	170.6 (3)	C3—C2—C9—O1	175.1 (3)
C11—N—C2—C3	-68.5 (4)	N—C2—C9—O2	-1328 (3)
C1—C2—C3—C4	-8.7 (4)	C3—C2—C9—O2	-8.5 (4)
C4—C5—C6—C1	-9.2 (6)	C2—N—C11—O3	-7.4 (5)
C1—C7—C8—C4	-11.8 (5)	C2—N—C11—C12	172.0 (3)
C10—O2—C9—O1	-7.0 (6)	N—C11—C12—C17	-37.1 (5)
C10—O2—C9—C2	176.6 (4)	N—C11—C12—C13	147.9 (3)
N—C2—C9—O1	50.8 (4)	C2—C3—C18—O4	149.4 (4)

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1992). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus (Sheldrick, 1989). Software used to prepare material for publication: SHELXL93. Geometrical calculations: PARST (Nardell, 1983).

This work was supported by the Dirección General de Investigación Científica y Técnica, project number PB94-0578.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1159). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2294–2296

[3-(4-Methylphenyl)-5-isoxazolyl]acetonitrile

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(Received 15 March 1996; accepted 16 April 1996)

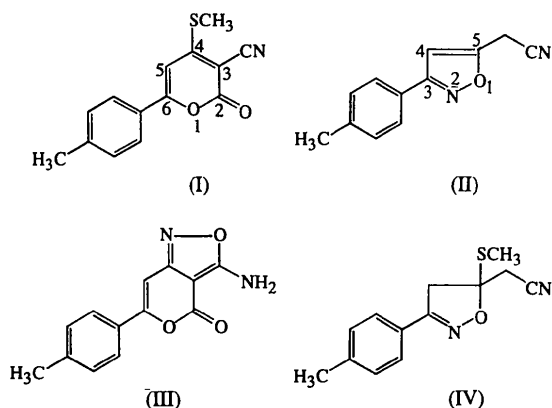
Abstract

An improved synthesis of the title compound, C₁₂H₁₀N₂O, via the reaction of 6-(4-methylphenyl)-4-methylthio-2-oxo-2H-pyran-3-carbonitrile and hydroxylamine hydrochloride in pyridine is reported. The isoxazole ring is planar and is inclined at an angle of 34.2(1)° with respect to the aromatic ring. All bond lengths and angles are unexceptional.

Comment

Isoxazoles are known to possess a range of biological activities, a particularly important example being antispasmodic activity (Naruto *et al.*, 1982, 1983). In this context, an interesting reaction has recently been reported (Ram, Hussaini, Singh & Shoeb, 1993) in which three different compounds [(II)–(IV)] having an isoxazole moiety are obtained in one step by the treatment of 6-(4-methylphenyl)-4-methylthio-

2-oxo-2*H*-pyran-3-carbonitrile, (I), with hydroxylamine hydrochloride in pyridine at 387 K. We have carried out the synthesis of a series of isoxazoles in higher yields by a modification of the above procedure, the objective being to extend the series and to obtain further derivatives for structure–activity studies. In our modified procedure, the title compound, (II), was obtained in 42% yield, compared with a yield of 20% in the earlier work.



The X-ray structure of (II) was determined in order to assign its constitution unambiguously (Fig. 1). All of the bond lengths and angles are unexceptional and those associated with the isoxazole ring are consistent with the expected bond orders and compare well with those reported previously (Simon, Sasvari, Dvortsak, Horvath & Harsanyi, 1974). The best plane through the five atoms of the isoxazole ring has an r.m.s. deviation of only 0.002 Å, compared with a value of 0.025 Å in the 4,5-dihydro derivative (Kumar, Vats, Parmar & Errington, 1996). The plane of the aromatic ring is inclined at an angle of 34.2 (1)° with respect to the plane of the isoxazole ring. The acetonitrile group is linear and its axis lies close to the plane of the isoxazole ring.

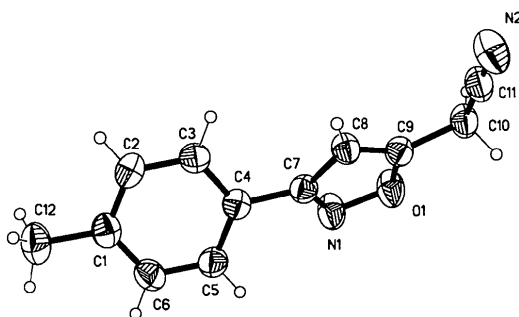


Fig. 1. View of the title molecule showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

The origin of the intermolecular forces is not obvious as all of the interatomic distances between non-H atoms in adjacent molecules exceed the sum of the van der Waals radii.

Experimental

6-(4-Methylphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile [(I), 8.995 g, 35 mmol] was dissolved in pyridine (70 ml) by heating the mixture at 343–353 K. Hydroxylamine hydrochloride (2.8 g, 40 mmol) was added and the mixture stirred at 343–353 K for 48 h. Pyridine was distilled off at reduced pressure and the residue taken up in ethyl acetate, washed with water and dilute HCl, and dried over Na₂SO₄. When the gummy mass obtained on removal of the ethyl acetate was chromatographed on silica gel, compound (II) eluted out with ethyl acetate–petroleum ether (1:8) and crystallized out from chloroform–petroleum ether (1:1) as fine needles (2.9 g; m.p. 370–371 K).

Crystal data

C₁₂H₁₀N₂O
M_r = 198.22
 Monoclinic
*P*2₁/*c*
a = 11.609 (8) Å
b = 5.717 (3) Å
c = 15.293 (8) Å
 β = 92.63 (5)°
V = 1013.9 (10) Å³
Z = 4
D_x = 1.299 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 20 reflections
 θ = 9–11°
 μ = 0.085 mm⁻¹
T = 240 (2) K
 Rod
 0.78 × 0.39 × 0.25 mm
 Orange

Data collection

Siemens *P3R3* diffractometer
 ω–2θ scans
 Absorption correction:
 none
 2063 measured reflections
 1800 independent reflections
 1568 observed reflections
 [*I* > 2σ(*I*)]
R_{int} = 0.0773

θ_{max} = 25.05°
h = 0 → 13
k = 0 → 6
l = –18 → 18
 3 standard reflections
 monitored every 200 reflections
 intensity decay: 10%

Refinement

Refinement on *F*²
R(*F*) = 0.0501
wR(*F*²) = 0.1532
S = 1.041
 1797 reflections
 138 parameters
 H-atom parameters not refined
w = 1/[σ²(*F_o*²) + (0.096*P*)² + 0.22*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.047

Δρ_{max} = 0.21 e Å⁻³
 Δρ_{min} = –0.22 e Å⁻³
 Extinction correction:
SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.18 (2)
 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 (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
O1	0.17055 (11)	0.1514 (2)	0.97028 (8)	0.0541 (4)
N1	0.22494 (14)	0.1519 (3)	1.05450 (9)	0.0527 (5)
N2	–0.00673 (15)	–0.5137 (3)	0.83885 (10)	0.0604 (5)
C1	0.38383 (13)	–0.2369 (3)	1.33066 (10)	0.0441 (5)

C2	0.38406 (15)	-0.3931 (3)	1.26054 (12)	0.0470 (5)
C3	0.32939 (14)	-0.3408 (3)	1.18107 (10)	0.0432 (4)
C4	0.27458 (13)	-0.1270 (3)	1.16806 (10)	0.0376 (4)
C5	0.27231 (15)	0.0285 (3)	1.23787 (11)	0.0438 (4)
C6	0.32584 (15)	-0.0263 (3)	1.31783 (11)	0.0476 (5)
C7	0.22228 (13)	-0.0651 (3)	1.08119 (10)	0.0374 (4)
C8	0.16821 (13)	-0.2139 (3)	1.01730 (10)	0.0394 (4)
C9	0.13807 (13)	-0.0699 (3)	0.95103 (10)	0.0394 (4)
C10	0.08036 (15)	-0.0987 (3)	0.86229 (11)	0.0456 (5)
C11	0.03111 (15)	-0.3314 (3)	0.84962 (10)	0.0449 (5)
C12	0.4452 (2)	-0.2944 (4)	1.41627 (13)	0.0620 (6)

Table 2. Selected geometric parameters (Å, °)

O1—C9	1.349 (2)	C1—C12	1.498 (2)
O1—N1	1.408 (2)	C7—C8	1.420 (2)
N1—C7	1.307 (2)	C8—C9	1.340 (2)
N2—C11	1.140 (3)		
C9—O1—N1	108.08 (12)	C9—C8—C7	104.2 (2)
C7—N1—O1	105.54 (13)	C8—C9—O1	110.52 (14)
N1—C7—C8	111.71 (14)	N2—C11—C10	179.2 (2)
C8—C7—C4	128.72 (15)		
C3—C4—C7—C8	33.6 (2)	C8—C9—C10—C11	10.4 (3)

Refinement was on F^2 for all reflections except for three flagged by the user for potential systematic errors. The temperature of the crystal was controlled using the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms, while H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of their attached atom.

Data collection: Siemens P3R3 system. Cell refinement: Siemens P3R3 system. Data reduction: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to solve structure: SHELXTL-Plus. Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXL93.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury (Allen *et al.*, 1991). NK thanks the Council of Scientific and Industrial Research (CSIR, New Delhi, India) for the award of a Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2296–2298

Bis[5,5-bis(4-methoxyphenyl)-3,3-dimethyl-2-tetrahydrofuranyl] Ether

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(Received 1 February 1996; accepted 25 March 1996)

Abstract

(2,2-Dimethyl-3-phenoxypropyl)bis(*p*-methoxyphenyl)methanol gave the title compound, C₄₀H₄₆O₇, an oxygen-bridged dimer, under conditions which yielded monomeric aldehydes from alcohols containing other substituents.

Comment

We are currently investigating the photochemical reactivity of a number of β,γ -unsaturated oxime derivatives, (I), under sensitized conditions using an electron-accepting sensitizer. The starting materials for this study are β,γ -unsaturated aldehydes, (II), readily made from cyclopropane esters, (III) (Julia & Baillarge, 1966; Zimmerman & Pratt, 1970). The use of a Grignard reagent converts the esters to the alcohols, (IV), which are then subjected to acid-induced ring opening. With the $R = C_6H_5$, p -^tBuC₆H₄, p -BrC₆H₄, p -ClC₆H₄ and p -CH(CH₃)₂C₆H₄ derivatives of (IV), this ring opening occurs readily. When *p*-cyanophenyl groups are the substituents [(IV); $R = p$ -CNC₆H₄], the ring opening, carried out using a mixture of acetone, concentrated hydrochloric acid and water (6:3:1) at reflux for 12 h, is an extremely slow process, presumably because conversion to the cation (V) is unfavourable. The *p*-methoxyphenyl derivative [(IV); $R = p$ -MeOC₆H₄], however, under the usual conditions (mixture of acetone, con-