Data collection

Rigaku AFC-5*R* diffractometer	R_{int} = 0.0413
ω–2θ scans	θ_{max} = 60°
Absorption correction: none	$h = -10 \rightarrow 0$
2696 measured reflections	$k = -11 \rightarrow 0$
2526 independent reflections	$l = -18 \rightarrow 19$
2086 reflections with $I > 3\sigma(I)$	3 standard reflections every 150 reflections intensity decay: 0.92%

Refinement

Refinement on *F*	$\Delta\rho_{max}$ = 0.17 e Å^{-3}
R = 0.0432	$\Delta\rho_{min}$ = −0.18 e Å^{-3}
wR = 0.0553	Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
S = 1.260	Extinction coefficient: 0.08 (1)
2086 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
388 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o) + 0.00090\|F_o\|^2]$	
$(\Delta/\sigma)_{max}$ = 0.0010	

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.432 (5)	C1—C7	1.505 (6)
O1—C2	1.426 (5)	C2—C3	1.543 (6)
O2—C1	1.423 (4)	C2—C8	1.556 (5)
O2—C3	1.414 (4)	C3—C21	1.545 (5)
O3—C8	1.431 (4)	C4—C5	1.515 (7)
O4—C21	1.424 (4)	C5—C6	1.471 (8)
C1—C4	1.509 (6)	C6—C7	1.544 (8)
C1—O1—C2	110.2 (3)	C3—C2—C8	118.1 (3)
C1—O2—C3	107.3 (3)	O2—C3—C2	102.1 (3)
O1—C1—O2	104.7 (3)	O2—C3—C21	109.5 (3)
O1—C1—C4	112.9 (3)	C2—C3—C21	118.4 (3)
O1—C1—C7	114.0 (4)	C1—C4—C5	104.1 (4)
O2—C1—C4	111.5 (3)	C4—C5—C6	106.3 (4)
O2—C1—C7	108.2 (3)	C5—C6—C7	108.5 (4)
C4—C1—C7	105.6 (3)	C1—C7—C6	103.6 (4)
O1—C2—C3	103.0 (3)	O3—C8—C2	107.2 (3)
O1—C2—C8	110.1 (3)	O4—C21—C3	106.6 (3)

Table 2. *Contact distances (Å)*

O3···O5	2.842 (4)	O5···O6^{ii}	2.701 (4)
O4···O6^{i}	2.672 (4)		

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

Data collection and cell refinement was carried out using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). The scan rate was 16° min^{-1} (in ω) and the scan width was (1.63 + 0.30tanθ)°. The ratio of peak counting time to background counting time was 2:1. Data reduction was performed using *TEXSAN* (Molecular Structure Corporation, 1993). The structure was solved with *SHELXS*86 (Sheldrick, 1985) and refined using *TEXSAN*. Refinement was by full-matrix least-squares methods, with anisotropic displacement parameters for all non-H atoms. Hydroxyl H atoms were located in difference Fourier maps and all other H atoms were placed in calculated positions. *TEXSAN* software was also used to prepare the material for publication.

The authors wish to thank Professor Noritake Yasuoka for valuable discussion.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 2*H*-Pyrano[3,2-*a*]indolizine Derivative

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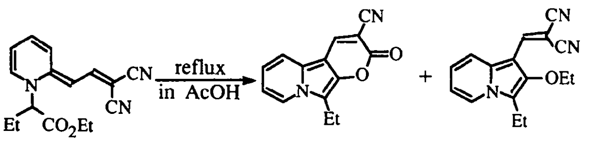
Abstract

The indolizine and pyrano[3,2-*a*]indolizine skeletons of 10-ethyl-2-oxo-2*H*-pyrano[3,2-*a*]indolizine-3-carbonitrile, $C_{14}H_{10}N_2O_2$, are planar [mean deviations 0.003 (2) and 0.019 (2) Å, respectively]. The planar pyrone ring [mean deviation 0.009 (2) Å], fused at the 1- and 2-positions of the indolizine ring, is also almost coplanar with the indolizine ring [dihedral angle 2.3 (1)°]. The delocalized ring system of the indolizine skeleton extends to the fused 2-pyrone ring, resulting in a significant decrease in the bond-alternation characteristics of the 2-pyrone moiety.

Comment

The present study has been undertaken in order to confirm the chemical structure of the title compound, (2), and to compare its geometry with those of a pyrano[2,3-*b*]indolizin-2-one (Kakehi, Kitajima, Ito & Takusagawa, 1993), a 2-pyrone (Thailambal & Pattabhi, 1985) and a coumarin derivative (Gavuzzo, Mazza & Giglio, 1974; Vasudevan, Puttaraja & Kulkarni, 1991; Ueno, 1985).



(1) (2) (3)

The pyrrole and pyridine rings in the indolizine skeleton of (2) are planar [mean deviations 0.005 (2) and 0.002 (2) Å, respectively] and are inclined at an angle of 0.1 (1)° with respect to one another. The planar 2-pyrone ring [mean deviation 0.009 (2) Å], fused at the 1- and 2-positions of the indolizine ring, is also coplanar with the indolizine ring [dihedral angle 2.3 (1)°]. The bond distances and angles for the indolizine and annelated 2-pyrone rings are very similar to those found in 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizin-2-one (Kakehi, Kitajima, Ito & Takusagawa, 1993), except for the shortened C10—C11 and lengthened C4—C11 bonds. These shortening and lengthening effects suggest that the resonance structure of the pyrrole moiety in the indolizine skeleton is greatly affected by the position of the annelated 2-pyrone ring.

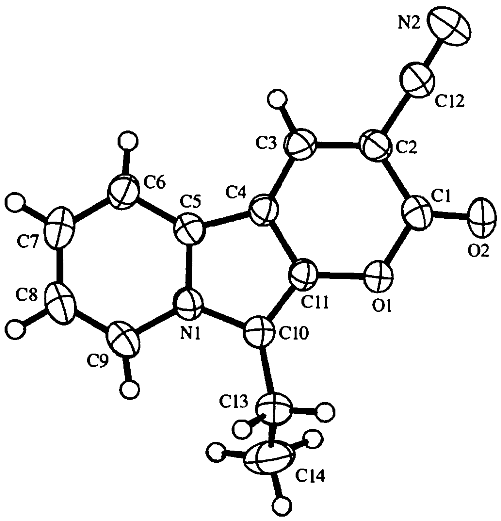


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atomic numbering system. Displacement ellipsoids are drawn at the 50% probability level.

Furthermore, the geometry of the 2-pyrone ring itself is deformed due to the resonance extending throughout the whole delocalized ring system. Evidently, the bond-alternation nature of the 2-pyrone ring in compound (2) and in pyrano[2,3-*b*]indolizin-2-one derivatives (Kakehi, Kitajima, Ito & Takusagawa, 1993) is weaker than that in coumarins (Gavuzzo, Mazza & Giglio, 1974; Vasudevan, Puttaraja & Kulkarni, 1991; Ueno, 1985) and 2-pyrone (Thailambal & Pattabhi, 1985). In other words, the more highly delocalized 2-pyrone rings in these pyranoindolizin-2-ones is attained by resonance with the indolizine ring. Comparisons of some bond lengths for the 2-pyrone moiety in the title compound with those found in other fused and non-fused 2-pyrone derivatives are summarized in Table 2; other selected geometric parameters are given in Table 1.

Experimental

An acetic acid solution (20 ml) of ethyl 2-[2-(3,3-dicyanoallylidene)-1,2-dihydropyridin-1-yl]butanoate [(1); 0.283 g, 1 mmol], readily obtainable from the alkaline treatment of 1-(1-ethoxycarbonylpropyl)-2-methylpyridinium bromide with (ethoxymethylidene)malononitrile, was heated under reflux for 2 h. After removal of the acetic acid under reduced pressure, the residue was separated by column chromatography on alumina using ether and then chloroform. The strongly fluorescent orange chloroform layers were combined and then concentrated at reduced pressure to give compound (2) (0.107 mg, 45%), together with a trace amount of 1-(2,2-dicyanovinyl)-2-ethoxy-3-ethylindolizine [(3); Kakehi, Ito & Matsubara, 1995]. For X-ray analysis, compound (2) was recrystallized from chloroform.

Crystal data

$C_{14}H_{10}N_2O_2$
$M_r = 238.25$
Triclinic
$P\bar{1}$
$a = 9.095$ (3) Å
$b = 9.160$ (3) Å
$c = 8.189$ (2) Å
$\alpha = 101.90$ (2)°
$\beta = 101.54$ (2)°
$\gamma = 59.34$ (2)°
$V = 570.6$ (3) Å^3
$Z = 2$
$D_x = 1.387$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 19.75$–$19.95°$
$\mu = 0.089$ mm^{-1}
$T = 295$ K
Prism
0.64 × 0.38 × 0.32 mm
Brown

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2792 measured reflections
2624 independent reflections
1895 reflections with $I > 3\sigma(I)$

$R_{int} = 0.012$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 11$
$k = -9 \rightarrow 11$
$l = -10 \rightarrow 10$
3 standard reflections every 150 reflections
intensity decay: 0.4%

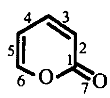
Refinement

Refinement on F	$\Delta\rho_{max} = 0.22$ e Å^{-3}
$R = 0.039$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
$wR = 0.048$	Extinction correction: Stout & Jensen (1968)
$S = 1.84$	Extinction coefficient: 0.13135×10^{-4}
1895 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
204 parameters	
H atoms refined with individual U_{iso}	
$w = 4F_o^2/\sigma^2(F_o^2)$	
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. *Selected geometric parameters (Å, °)*

N1—C5	1.394 (2)	C4—C5	1.413 (2)
N1—C9	1.373 (2)	C10—C11	1.360 (2)
N1—C10	1.401 (2)		
C1—O1—C11	119.6 (1)	C3—C4—C11	119.5 (1)
C5—N1—C10	111.3 (1)	C5—C4—C11	105.9 (1)
O1—C1—O2	116.9 (1)	N1—C5—C4	106.1 (1)
O1—C1—C2	117.3 (1)	N1—C10—C11	104.7 (1)
O2—C1—C2	125.8 (2)	O1—C11—C4	122.5 (1)
C1—C2—C3	122.5 (1)	C4—C11—C10	112.0 (1)
C2—C3—C4	118.5 (1)		

Table 2. *Comparison of 2-pyrone ring geometries (Å)*



Bond 1	2	3	4	5	6	7	Reference
1.385 (2)	1.456 (2)	1.371 (2)	1.385 (2)	1.409 (2)	1.372 (2)	1.202 (2)	(*a*)
1.414 (3)	1.445 (3)	1.382 (3)	1.375 (3)	1.411 (3)	1.358 (2)	1.200 (2)	(*b*)
1.367 (4)	1.448 (5)	1.344 (5)	1.431 (5)	1.395 (4)	1.378 (4)	1.204 (4)	(*c*)
1.373 (5)	1.462 (7)	1.355 (6)	1.429 (7)	1.391 (7)	1.383 (5)	1.203 (6)	(d)
1.383 (1)	1.432 (1)	1.351 (2)	1.432 (1)	1.383 (1)	1.380 (1)	1.213 (1)	(e)
1.394 (7)	1.438 (8)	1.400 (8)	1.406 (8)	1.348 (8)	1.364 (7)	1.205 (7)	(*f*)

References: (*a*) compound (2) (present work); (*b*) 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizin-2-one (Kakehi *et al.*, 1993); (*c*) coumarin (Gavuzzo *et al.*, 1974); (*d*) 3-bromoacetylcoumarin (Vasudevan *et al.*, 1991); (*e*) 7-ethoxycoumarin (Ueno, 1985); (*f*) 3-acetyl-4-hydroxy-6-phenyl-2-pyrone (Thailambal & Pattabhi, 1985).

Azimuthal scans of several reflections indicated no need for an absorption correction. The H atoms were located from a difference Fourier map and refined isotropically. The structure was solved by direct methods (*SIR*88; Burla *et al.*, 1989) utilizing the *TEXSAN* (Molecular Structure Corporation, 1985) system.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN*. Program(s) used to refine structure: *ORTEP*II (Johnson, 1976). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1120). 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. (1997). C**53**, 355–358

(1*R**,3*R**,4*S**)-4-(*tert*-Butyldiphenylsilyloxy)-6,7-dimethoxy-1-methyl-3-phenyl-1,2,3,4-tetrahydroisoquinoline

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Abstract

Ambiguous information obtained from ^{1}H NMR spectroscopy has prompted an investigation of the correct stereochemistry of the title compound, $C_{34}H_{39}NO_3Si$, by X-ray diffraction analysis. An uncommon pseudo-axial–axial *trans* conformation was observed for the substituents linked to the C-4 and C-3 atoms (IUPAC numbering). The pseudo-equatorial conformation of the methyl group joined to the C-1 atom was also confirmed.

Comment

In connection with previous studies of the stereoselective preparation of different isoquinolinic derivatives, a convenient method for the stereoselective