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Acta Cryst. (1993). C**49**, 1230–1232

Structure of a Pyrano[2,3-*b*]indolizine

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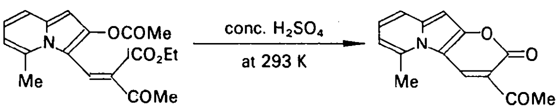
(*Received* 24 *January* 1992; *accepted* 3 *December* 1992)

Abstract

The pyrrole and pyridine rings in the indolizine skeleton of 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizin-2-one are planar [mean deviations 0.003 (2) and 0.003 (2) Å, respectively] and inclined at 0.5 (2)° to one another. The planar [mean deviation 0.004 (2) Å] 2-pyrone ring, fused at the 2 and 3 positions of the indolizine ring, is also coplanar with the indolizine ring [dihedral angle 1.1 (2)°]. The delocalized ring system extends to the fused pyrone ring as indicated by the shortened C4—C3 bond of 1.375 (3) Å. The acetyl group at the 3 position is also coplanar with the pyrone ring [dihedral angle 0.5 (2)°].

Comment

Treatment of ethyl 2-acetyl-3-(2-acetoxy-5-methylindolizin-3-yl)acrylate (1) (329 mg, 1 mmol) with concentrated sulfuric acid (1 ml) at room temperature for 12 h gave the title compound 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizin-2-one (2) in a 12% yield (Kakehi, Ito, Murakami & Sano, 1984).



(1) (2)

The present study was undertaken to confirm the chemical structure of the title compound and to compare the structural features of many indolizine derivatives of physicochemical and pharmaceutical interest. The bond distances and angles for the indolizine skeleton in the title compound are closer to those of 1-acetoxy-2,3-diphenylindolizine (Wadsworth, Bender, Smith, Luss & Weidner, 1986) and ethyl 1-trifluoromethylindolizine-3-carboxylate (Pritchard, 1988), than to those of ethyl 3,4-dihydrocyclopenta[*hi*]indolizine-1-carboxylate (Kakehi, Kitajima, Ito & Takusagawa, 1992); this is because, in contrast to the annelation of a five-membered ring at the 1 and 8 positions of an indolizine ring, the less-hindered pyrone ring attached to the 2 and 3 positions does not cause a large distortion of the skeleton. On the other hand, the distances and angles for the 2-pyrone ring are similar to those found in various 2-pyrone derivatives (Thailambal & Vasantha Pattabhi, 1987; Thailambal, Vasantha Pattabhi & Gabe, 1986), except for the shortened C3—C4 and lengthened C4—C11 bonds. The shortening of the C3—C4 bond suggests that the 2-pyrone moiety of the title compound (2) has a different resonance structure from pyrone itself because the fused indolizine ring changes the resonance system of the pyrone moiety. Compared with the pyrone moiety in coumarin (Gavuzzo, Mazza & Giglio, 1974) and coumarin derivatives (Vasudevan, Puttaraja & Kulkarni, 1991), the pyrone ring in (2) is again characterized by its shortened C3—C4 and lengthened O1—C1 bonds, reflecting the difference between the aromatic systems of the indolizine and the benzene. The widening [129.5 (2)°] of the angle C2—C1—O2 in the pyrone moiety in (2) is probably enhanced by the steric interactions between the 3-acetyl group and O2. Such widening was observed in the case of 3-acetyl-4-hydroxy-6-phenyl-2-pyrone (Thailambal & Vasantha Pattabhi, 1985). A comparison of selected bond lengths and angles for the 2-pyrone moieties in the title compound (2) and other 2-pyrone and coumarin derivatives is summarized in Table 3.

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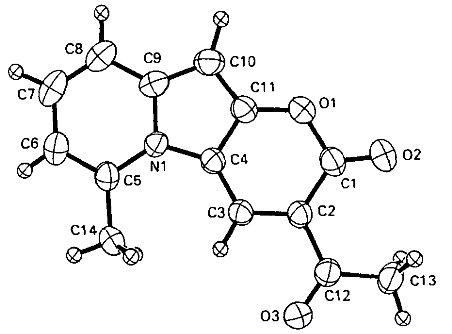


Fig. 1. *ORTEP* (Johnson, 1976) drawing of the title compound (2) showing the atomic numbering system.

Experimental

Crystal data

$C_{14}H_{11}NO_3$
M_r = 241.25
Triclinic
$P\bar{1}$
a = 8.311 (3) Å
b = 10.552 (3) Å
c = 7.508 (5) Å
α = 97.45 (4)°
β = 115.59 (3)°
γ = 104.36 (2)°
V = 553.8 (5) Å^3
Z = 2

D_x = 1.447 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 19.51–19.96°
μ = 0.96 mm^{-1}
T = 293 K
Planar
0.90 × 0.40 × 0.12 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
ω-2θ scans
Absorption correction: none
2715 measured reflections
2540 independent reflections
1665 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.013
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 13$
$l = -9 \rightarrow 8$
3 standard reflections monitored every 150 reflections intensity variation: −0.1%

Refinement

Refinement on F
Final R = 0.044

$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.15 e Å^{-3}

wR = 0.055
S = 1.84
1665 reflections
208 parameters
All H-atom parameters refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max}$ = 0.00

Extinction correction: analytical
Extinction coefficient: 0.42007 × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

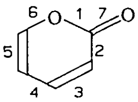
$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O1	0.3198 (2)	0.0620 (1)	0.8529 (2)	4.06 (5)
O2	0.4362 (2)	0.2686 (2)	0.8368 (3)	5.13 (6)
O3	−0.0995 (2)	0.3151 (2)	0.6334 (3)	5.01 (6)
N1	−0.1220 (2)	−0.1609 (2)	0.7552 (2)	2.92 (5)
C1	0.2946 (3)	0.1841 (2)	0.8087 (3)	3.52 (7)
C2	0.1055 (3)	0.1897 (2)	0.7368 (3)	2.98 (6)
C3	−0.0414 (3)	0.0811 (2)	0.7145 (3)	2.90 (6)
C4	−0.0099 (3)	−0.0355 (2)	0.7599 (3)	2.87 (6)
C5	−0.3138 (3)	−0.2103 (2)	0.6952 (3)	3.34 (6)
C6	−0.3857 (4)	−0.3382 (2)	0.7076 (4)	4.08 (8)
C7	−0.2732 (4)	−0.4189 (2)	0.7759 (4)	4.47 (8)
C8	−0.0854 (4)	−0.3699 (2)	0.8344 (3)	4.07 (8)
C9	−0.0047 (3)	−0.2390 (2)	0.8261 (3)	3.42 (7)
C10	0.1802 (3)	−0.1646 (2)	0.8738 (3)	3.99 (8)
C11	0.1739 (3)	−0.0430 (2)	0.8320 (3)	3.36 (7)
C12	0.0612 (3)	0.3136 (2)	0.6868 (3)	3.45 (7)
C13	0.2119 (4)	0.4349 (3)	0.7049 (4)	4.21 (8)
C14	−0.4306 (3)	−0.1235 (3)	0.6183 (4)	4.09 (8)

Table 2. *Geometric parameters* (Å, °)

O1—C1	1.414 (3)	C3—C4	1.375 (3)
O1—C11	1.358 (2)	C4—C11	1.411 (3)
O2—C1	1.200 (2)	C5—C6	1.367 (3)
O3—C12	1.223 (3)	C6—C7	1.398 (4)
N1—C4	1.403 (2)	C7—C8	1.358 (4)
N1—C5	1.386 (3)	C8—C9	1.400 (3)
N1—C9	1.406 (3)	C9—C10	1.400 (3)
C1—C2	1.445 (3)	C10—C11	1.368 (3)
C2—C3	1.382 (3)		
C1—O1—C11	121.4 (2)	N1—C5—C6	117.6 (2)
C4—N1—C9	108.1 (2)	C5—C6—C7	122.3 (2)
C5—N1—C9	121.5 (2)	C6—C7—C8	119.8 (2)
O1—C1—O2	114.1 (2)	C7—C8—C9	120.1 (2)
O1—C1—C2	116.4 (2)	N1—C9—C8	118.7 (2)
O2—C1—C2	129.5 (2)	N1—C9—C10	109.1 (2)
C1—C2—C3	121.2 (2)	C9—C10—C11	105.9 (2)
C2—C3—C4	120.3 (2)	O1—C11—C4	121.1 (2)
N1—C4—C11	105.2 (2)	C4—C11—C10	111.7 (2)
C3—C4—C11	119.6 (2)		

Table 3. *Comparison of the pyrone-ring geometry* (Å, °)



Bond length							Bond angle	
1	2	3	4	5	6	7	2–7	Reference
1.414 (3)	1.445 (3)	1.382 (3)	1.375 (3)	1.411 (3)	1.358 (2)	1.200 (2)	129.5 (2)	(*a*)
1.373 (5)	1.462 (7)	1.355 (6)	1.429 (7)	1.391 (7)	1.383 (5)	1.203 (6)	127.6 (4)	(*b*)
1.367 (2)	1.433 (3)	1.341 (2)	1.424 (2)	1.398 (2)	1.382 (2)	1.224 (2)	125.9 (2)	(*c*)
1.383 (1)	1.432 (1)	1.351 (2)	1.432 (1)	1.383 (1)	1.380 (1)	1.213 (1)	127.1 (1)	(*d*)
1.367 (4)	1.448 (5)	1.344 (5)	1.431 (5)	1.395 (4)	1.378 (4)	1.204 (4)	125.6 (3)	(*e*)
1.394 (7)	1.438 (8)	1.400 (8)	1.406 (8)	1.348 (8)	1.364 (7)	1.205 (7)	128.5 (5)	(*f*)

References: (*a*) 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizine-2-one (present work); (*b*) 3-(bromoacetyl)coumarin (Vasudevan *et al.*, 1991); (*c*) 7-hydroxycoumarin (Ueno, 1985); (*d*) 7-ethoxycoumarin (Ueno, 1985); (*e*) coumarin (Gavuzzo *et al.*, 1974); (*f*) 3-acetyl-4-hydroxy-6-phenyl-2-pyrone (Thailambal & Vasantha 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 (*MITHRIL*; Gilmore, 1984) utilizing the *TEXSAN* (Molecular Structure Corporation, 1985) system.

The authors are grateful to the Ministry of Education, Science and Culture for the financial support of this work (Grant-in-Aid for Scientific Research Nos. 02453085 and 03650669).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55926 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1004]

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Acta Cryst. (1993). C**49**, 1232–1234

Structure of the γ Phase of Erucic Acid

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(*Received* 19 *June* 1992; *accepted* 4 *January* 1993)

Abstract

The hydrocarbon chains on either side of the *cis*-olefin group in 13-docosenoic acid adopt all-*trans* conformation and form an orthorhombic subcell with parallel skeletal planes. Both the methyl- and carboxyl-terminal polymethylene chains are inclined toward the interface of the dimer layers by 34°. The torsion angles of the *cis*-olefin group, C—C—C=C—C—C, are -129, 0 and 127° from the carboxyl side.

Comment

The structure determination of the γ phase of erucic acid was undertaken to confirm that this phase is isomorphous to the low-melting phase of oleic acid (Abrahamsson & Ryderstedt-Nahringbauer, 1962), and to elucidate the dynamic features of the acyl chain. We have shown that *cis*-mono-unsaturated fatty acids crystallize in various phases, among which some reversible or irreversible solid-state phase transitions take place. In the case of erucic acid, four polymorphic phases (α, $\alpha 1$, γ and $\gamma 1$) and two types of reversible phase transition ($\gamma \Longleftrightarrow \alpha$ and $\gamma 1 \Longleftrightarrow \alpha 1$) have been found. We found that the γ phase is quite similar to the low-melting phase of oleic acid in its vibrational spectrum, crystal habit and thermal behaviour (Suzuki, Sato, Yoshimoto,