Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71381 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1053]

References

Akimoto, H. & Iitaka, Y. (1969). *Acta Cryst.* B**25**, 1491–1500.
Akimoto, H., Shiori, T., Iitaka, Y. & Yamada, S. (1968). *Tetrahedron Lett.* pp. 97–102.
Akimoto, H. & Yamada, S. (1968). *Tetrahedron Lett.* pp. 3967–3972.
Akimoto, H. & Yamada, S. (1971). *Tetrahedron*, **27**, 5999–6009.
B. A. Frenz & Associates, Inc. (1985). *SDP Structure Determination Package*. College Station, Texas, USA.
Hovorka, M., Gunterová, J. & Závada, J. (1990). *Tetrahedron Lett.* **31**, 413–416.
Hovorka, M., Ščigel, L., Gunterová, J., Tichý, M. & Závada, J. (1992). *Tetrahedron*, **48**, 9503–9516.
Hovorka, M. & Závada, J. (1991). *Org. Prep. Proc. Int.* **23**, 200–206.
Nardelli, M. (1991). *PARST. A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analysis*. Univ. of Parma, Italy.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1994). C**50**, 139–141

Structure of an Oxepino[2,3-*b*]indolizine Derivative

Akikazu Kakehi,* Kunio Kitajima, Suketaka Ito and Nobuo Takusagawa

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan

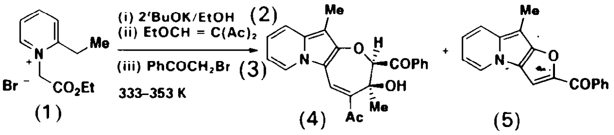
(*Received* 3 *March* 1993; *accepted* 30 *June* 1993)

Abstract

The pyrrole and pyridine rings in the indolizine skeleton of 4-acetyl-2-benzoyl-3-hydroxy-3,11-dimethyl-2,3-dihydrooxepino[2,3-*b*]indolizine, $C_{23}H_{21}NO_4$ (4), are planar, with mean deviations 0.007 (2) and 0.004 (3) Å, respectively, and are almost coplanar to one another with a dihedral angle of 2.2 (2)°. The seven-membered ring attached to positions 2 and 3 of the indolizine ring is slightly inclined to the indolizine ring by 6.1 (2)°. The phenyl ring in the benzoyl group at the 2 position of the oxepine ring is almost perpendicular to the indolizine ring with a dihedral angle of 91.8 (2)°. O4 of the acetyl group attached at the 4 position is hydrogen bonded to the 3-hydroxyl group in the same molecule [O4···O3 2.567 (3) Å].

Comment

An ethanolic solution (30 ml) of 2-ethyl-1-(ethoxycarbonylmethyl)pyridinium bromide (1) (3 mmol) was treated with potassium *tert*-butoxide (6 mmol) at 333–353 K in a water bath for 5 min. To the resulting solution, including 1-methyl-2(3*H*)-indolizinone (Kakehi, Ito, Watanabe, Kitagawa, Takeuchi & Hashimoto, 1980), ethoxymethyleneacetylacetone (2) (3 mmol) and phenacyl bromide (3) (3 mmol) were added and the mixture was then kept under the same conditions for 2 h. After removal of the solvent under reduced pressure, the residue was separated by column chromatography on alumina using ether and then chloroform to give (4) [27%, m.p. 472–474 K (from ethanol)] as orange prisms, together with 2-benzoyl-9-methylfuro[2,3-*b*]indolizine (5) (63%) (Kakehi, Ito, Ohizumi & Ito, 1983; Kakehi, Ito, Furuta & Todoroki, 1985). The acid-catalysed dehydration of (4) did not afford the corresponding fully conjugated oxepino[2,3-*b*]indolizine, rather its 3-methylene derivative.



The present study has been undertaken to confirm the chemical structure of the title compound (4) and to compare its structural features with those of some indolizines, especially those fused with oxygen-containing rings at the 2 and 3 positions. Comparative values of the selected bond lengths and angles for the indolizine moieties in the title compound (4) and other indolizine derivatives are summarized in Table 3. The bond distances and angles for the indolizine skeleton in (4) are similar to those in the non-fused ethyl 1-trifluoromethylindolizine-3-carboxylate (Pritchard, 1988), except the C5—C12 bond, which is more similar to the analogous bond in 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizin-2-one (Kakehi, Kitajima, Ito & Takusagawa, 1993) than that in 2-benzoyl-9-methylfuro[2,3-*b*]indolizine and 8-benzoyl-5,6-dihydro-4*H*-furo[2′,3′:4,5]pyrrolo-[3,2,1-*ij*]quinoline (Kakehi, Kitajima, Ito & Takusagawa, 1994). These deviations are relatively small, but a slight extension of the N1—C10 bond of the indolizine ring by ring fusion, and the C5—C12 bond by fusion of a non-aromatic ring such as an oxepine or 2-pyrone, can be seen. On the other hand, the considerably shortened distance between O3 and O4 indicates that the 3-hydroxyl group is hydrogen bonded to the carbonyl O atom in the 4-acetyl group but not with that in the 2-benzoyl group. The O3—H12···O4 angle is 153 (3)°.

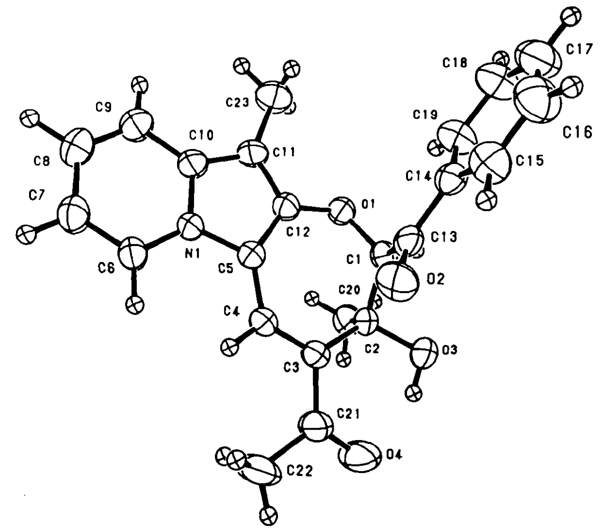


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (4) showing the atom-numbering system.

Experimental

Crystal data

$C_{23}H_{21}NO_4$
$M_r = 375.42$
Monoclinic
$C2/c$
$a = 23.204$ (3) Å
$b = 11.220$ (2) Å
$c = 16.139$ (3) Å
$\beta = 110.95$ (1)°
$V = 3924$ (1) Å^3
$Z = 8$
$D_x = 1.271$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 19.65$-$19.95°$
$\mu = 0.081$ mm^{-1}
$T = 297$ K
Prism
0.80 × 0.38 × 0.36 mm
Orange

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4848 measured reflections
4729 independent reflections
2435 observed reflections [$I > 3.00\sigma(I)$]
$R_{int} = 0.033$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 29$
$k = 0 \rightarrow 14$
$l = -20 \rightarrow 18$
3 standard reflections monitored every 150 reflections
intensity variation: average 0%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.054$
$S = 1.77$
2435 reflections
338 parameters
H atoms refined isotropically
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{max} = 0.18$

$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: analytical
Extinction coefficient: 0.31341×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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.

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

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

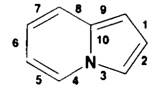
	x	y	z	B_{eq}
O1	0.33006 (7)	0.0160 (1)	0.0455 (1)	3.55 (7)
O2	0.37511 (8)	0.1838 (2)	0.2289 (1)	4.58 (8)
O3	0.32513 (8)	0.3364 (2)	0.0618 (1)	3.85 (8)
O4	0.4242 (1)	0.4487 (2)	0.0737 (2)	9.2 (1)
N1	0.48768 (9)	−0.0709 (2)	0.1368 (1)	3.18 (8)
C1	0.3227 (1)	0.1334 (2)	0.0761 (2)	3.2 (1)
C2	0.3560 (1)	0.2329 (2)	0.0459 (2)	3.2 (1)
C3	0.4259 (1)	0.2411 (2)	0.0926 (2)	3.9 (1)
C4	0.4622 (1)	0.1430 (2)	0.1181 (2)	3.8 (1)
C5	0.4443 (1)	0.0222 (2)	0.1121 (2)	3.2 (1)
C6	0.5510 (1)	−0.0647 (2)	0.1769 (2)	3.5 (1)
C7	0.5844 (1)	−0.1657 (3)	0.1977 (2)	4.1 (1)
C8	0.5553 (1)	−0.2772 (3)	0.1769 (2)	4.9 (1)
C9	0.4931 (1)	−0.2846 (3)	0.1366 (2)	3.6 (1)
C10	0.4571 (1)	−0.1797 (2)	0.1158 (2)	3.6 (1)
C11	0.3939 (1)	−0.1581 (2)	0.0792 (2)	3.6 (1)
C12	0.3869 (1)	−0.0361 (2)	0.0782 (2)	3.2 (1)
C13	0.3323 (1)	0.1316 (2)	0.1747 (2)	3.3 (1)
C14	0.2861 (1)	0.0669 (2)	0.2028 (2)	3.4 (1)
C15	0.2891 (1)	0.0790 (3)	0.2899 (2)	4.6 (1)
C16	0.2456 (2)	0.0246 (3)	0.3174 (2)	5.7 (2)
C17	0.1992 (2)	−0.0434 (3)	0.2592 (3)	5.9 (2)
C18	0.1959 (2)	−0.0564 (3)	0.1736 (3)	5.6 (2)
C19	0.2391 (1)	−0.0015 (3)	0.1449 (2)	4.6 (1)
C20	0.3420 (2)	0.2201 (3)	−0.0535 (2)	4.4 (1)
C21	0.4549 (1)	0.3571 (3)	0.0982 (3)	6.3 (2)
C22	0.5240 (2)	0.3717 (4)	0.1312 (6)	11.4 (3)
C23	0.3436 (2)	−0.2497 (3)	0.0516 (3)	5.4 (2)

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

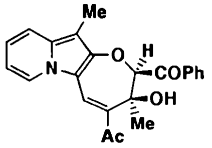
O1—C1	1.438 (3)	C3—C21	1.452 (4)
O1—C12	1.364 (3)	C4—C5	1.410 (3)
O2—C13	1.214 (3)	C5—C12	1.409 (3)
O3—C2	1.435 (3)	C6—C7	1.346 (4)
O4—C21	1.233 (3)	C7—C8	1.406 (4)
N1—C5	1.406 (3)	C8—C9	1.356 (4)
N1—C6	1.379 (3)	C9—C10	1.413 (4)
N1—C10	1.391 (3)	C10—C11	1.392 (3)
C1—C2	1.534 (3)	C11—C12	1.378 (3)
C2—C3	1.528 (3)	C11—C23	1.500 (4)
C2—C20	1.526 (4)	C13—C14	1.493 (3)
C3—C4	1.357 (3)	C21—C22	1.506 (5)
C1—O1—C12	118.5 (2)	N1—C6—C7	119.7 (2)
C5—N1—C6	129.0 (2)	C6—C7—C8	120.3 (3)
C5—N1—C10	109.4 (2)	C7—C8—C9	120.5 (3)
C6—N1—C10	121.6 (2)	C8—C9—C10	120.0 (3)
O1—C1—C2	114.9 (2)	N1—C10—C9	117.7 (2)
O1—C1—C13	110.8 (2)	N1—C10—C11	108.6 (2)

C2—C1—C13	116.0 (2)	C9—C10—C11	133.6 (2)
O3—C2—C1	101.0 (2)	C10—C11—C12	106.3 (2)
O3—C2—C3	111.9 (2)	C10—C11—C23	126.7 (3)
O3—C2—C20	109.4 (2)	C12—C11—C23	126.9 (3)
C1—C2—C3	117.1 (2)	O1—C12—C5	126.9 (2)
C1—C2—C20	108.8 (2)	O1—C12—C11	121.7 (2)
C2—C3—C4	122.3 (2)	C5—C12—C11	111.4 (2)
C2—C3—C21	118.1 (2)	O2—C13—C1	121.5 (2)
C4—C3—C21	119.1 (2)	O2—C13—C14	120.5 (2)
C3—C4—C5	128.7 (2)	C1—C13—C14	118.0 (2)
N1—C5—C4	122.2 (2)	O4—C21—C3	121.7 (3)
N1—C5—C12	104.3 (2)	O4—C21—C22	116.3 (3)
C4—C5—C12	133.4 (2)	C3—C21—C22	122.0 (3)

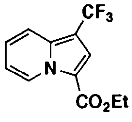
Table 3. *Comparison of indolizine ring geometry*



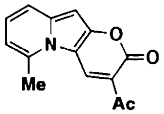
Compound	Fused ring	Bond length (Å) 1	2	3	4	5
(*a*)	7	1.378 (3)	1.409 (3)	1.406 (3)	1.379 (3)	1.346 (3)
(*b*)	None	1.382 (5)	1.370 (5)	1.407 (5)	1.372 (5)	1.362 (6)
(*c*)	6	1.368 (3)	1.411 (3)	1.403 (2)	1.386 (3)	1.367 (3)
(*d*)	5	1.388 (5)	1.373 (5)	1.379 (5)	1.381 (5)	1.335 (6)
(*e*)	5	1.394 (3)	1.384 (3)	1.379 (3)	1.377 (3)	1.350 (4)
		6	7	8	9	10
(*a*)	7	1.406 (4)	1.356 (4)	1.413 (4)	1.392 (3)	1.391 (3)
(*b*)	None	1.398 (6)	1.344 (5)	1.418 (5)	1.392 (5)	1.385 (5)
(*c*)	6	1.398 (4)	1.358 (4)	1.400 (3)	1.400 (3)	1.406 (3)
(*d*)	5	1.421 (6)	1.356 (6)	1.402 (6)	1.408 (5)	1.436 (5)
(*e*)	5	1.414 (4)	1.357 (4)	1.410 (3)	1.389 (3)	1.402 (3)



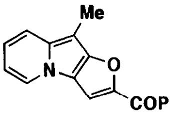
(*a*)



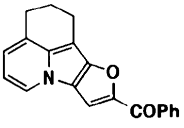
(*b*)



(*c*)



(*d*)



(*e*)

(*a*) 4-Acetyl-2-benzoyl-3-hydroxy-3,11-dimethyl-2,3-dihydrooxepino[2,3-*b*]-indolizine (this work); (*b*) ethyl 1-trifluoromethylindolizine-3-carboxylate (Pritcher, 1988); (*c*) 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizine-2-one (Kakehi *et al.*, 1993); (*d*) 2-benzoyl-9-methylfuro[2,3-*b*]indolizine (Kakehi *et al.*, 1994); (*e*) 8-benzoyl-5,6-dihydro-4*H*-furo[2′,3′:4,5]pyrrolo[3,2,1-*ij*]-quinoline (Kakehi *et al.*, 1994).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71449 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1052]

References

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kakehi, A., Ito, S., Furuta, H. & Todoroki, K. (1985). *J. Fac. Eng. Shinshu Univ.* pp. 1–7.

Kakehi, A., Ito, S., Ohizumi, T. & Ito, M. (1983). *Bull. Chem. Soc. Jpn*, **56**, 1219–1222.

Kakehi, A., Ito, S., Watanabe, K., Kitagawa, M., Taeuchi, S. & Hashimoto, T. (1980). *J. Org. Chem.* **45**, 5100–5104.

Kakehi, A., Kitajima, K., Ito, S. & Takusagawa, N. (1993). *Acta Cryst.* C**49**, 1230 1232.

Kakehi, A., Kitajima, K., Ito, S. & Takusagawa, N. (1994). *Acta Cryst.* Submitted.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Pritchard, R. G. (1988). *Acta Cryst.* C**44**, 1150–1152.

Acta Cryst. (1994). C**50**, 141–144

Structure of [1α(*E*),5α,6β,7α]-4-Methyl-7-(3-methyl-4-nitro-5-isoxazolyl)-5-nitro-6-phenyl-1-styryl-2-oxa-3-azabicyclo[3.2.0]hept-3-ene

DONATO DONATI*

Istituto di Chimica Organica, Pian dei Mantellini 44, 53100, Siena, Italy

MARIELLA FIORENZA AND PIERO SARTI-FANTONI

Dipartimento di Chimica Organica 'Ugo Schiff', and Centro di Studio CNR sulla Chimica e la Struttura dei Composti eterociclici e loro Applicazioni, via G. Capponi 9, 50121, Firenze, Italy

(*Received* 11 *February* 1993; *accepted* 22 *June* 1993)

Abstract

The title compound, $C_{24}H_{20}N_4O_6$, is a dimer obtained by irradiation of 3-methyl-4-nitro-5-styrylisoxazole. The relative configuration of the stereocentres and the conformation of the 2-oxa-3-azabicycloheptene ring is established.

Comment

During a study on the photoreactivity of 3-methyl-4-nitro-5-styrylisoxazole, as well as the expected photodimers deriving from 2 + 2 cycloaddition of two styryl moieties, the title dimer, obtained from 2 + 2 photocycloaddition of the double bond of the styryl moiety on the 4,5 positions of the isoxazole ring, was observed (Donati, Fiorenza & Sarti-Fantoni, 1979). To date, this case is the unique example of such unexpected photocycloaddition of isoxazoles. The latter photoreaction is highly stereo-

Acta Crystallographica Section C
ISSN 0108-2701 ©1994