C11—C12—O13	116.9 (5)	C29—C28—C30	112.8 (5)
C11—C12—C16	134.3 (6)	O26—C31—O27	105.8 (5)
O13—C12—C16	108.7 (6)	O26—C31—C32	109.9 (6)
C12—O13—C14	106.4 (6)	O26—C31—C33	106.7 (5)
O13—C14—C15	111.4 (9)	O27—C31—C32	108.7 (6)
C14—C15—C16	105.9 (9)	O27—C31—C33	114.7 (5)
C12—C16—C15	107.6 (7)	C32—C31—C33	110.8 (6)
C5—C1—C2—C3	−35.7 (4)	C11—C1—C2—C3	−161.0 (5)
C1—C2—C3—N4	19.7 (4)	C1—C2—C3—C20	−105.4 (5)
C2—C3—N4—C5	4.4 (4)	S17—C2—C3—C20	133.8 (4)
C3—N4—C5—C1	−27.2 (4)	C2—C3—C20—C21	−179.1 (5)
N4—C5—C1—C2	37.7 (4)	C2—C3—C20—O24	62.1 (4)
C7—N4—C5—C6	−6.5 (5)	C7—N4—C3—C20	8.6 (4)
N4—C5—C6—C7	5.9 (5)	N4—C3—C20—O24	−56.4 (4)
C5—C6—C7—N4	−6.3 (5)	C3—C20—C21—C22	94.6 (5)
C6—C7—N4—C5	6.5 (5)	C20—C21—C22—C23	179.4 (6)
O8—C7—C6—O9	59.9 (6)	O25—C21—C22—C23	65.7 (5)
C7—C6—O9—C10	−86.8 (6)	C20—C21—C22—O26	−65.0 (5)
C1—C5—C6—O9	17.0 (4)	O24—C20—C21—O25	−25.6 (4)
C5—C6—O9—C10	176.8 (7)	C20—C21—O25—C28	11.0 (4)
C6—C5—C1—C11	−97.6 (5)	C21—O25—C28—O24	7.6 (4)
C5—C1—C11—C12	179.8 (6)	O25—C28—O24—C20	−24.9 (4)
C2—C1—C11—C12	−61.4 (5)	C28—O24—C20—C21	31.1 (4)
C1—C11—C12—O13	−74.6 (6)	C21—C22—C23—O27	90.7 (6)
C1—C11—C12—C16	109.9 (7)	O26—C22—C23—O27	−27.2 (5)
C11—C1—C2—S17	−40.5 (4)	C22—C23—O27—C31	31.8 (5)
C1—C2—S17—C18	167.3 (5)	C23—O27—C31—O26	−23.9 (5)
C2—S17—C18—C19	−171.3 (7)	O27—C31—O26—C22	5.4 (5)
C1—C2—S17—C18′	124.2 (7)	C31—O26—C22—C23	13.5 (5)
C2—S17—C18′—C19′	66.3 (11)		

In (6), the propyl chain on S18 is disordered over two positions (site occupancy factors of 0.5), so in the refinement, distances and angles for this chain were constrained, and displacement parameters kept isotropic. Isotropic displacement parameters of the H atoms were equal to $1.10U_{eq}$ of the parent atom.

In (8), the ethyl chain fixed on S17 is also disordered over two positions (site occupancy factors of 0.67 and 0.33), so, in the refinement, distances and angles for this chain were constrained, and atomic displacement parameters kept isotropic. Isotropic displacement parameters of the H atoms were equal to $1.10U_{eq}$ of the parent atom.

Data collection: Philips PW1100/20 software for (6); Enraf–Nonius CAD-4 software for (8). Data reduction: *PHIL* (Riche, 1981) for (6); *NONIUS* (Riche, 1989) for (8). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELX*76 (Sheldrick, 1976); molecular graphics: *R3M* (Riche, 1983); *ORTEP* (Johnson, 1965); software used to prepare material for publication: *ACTACIF* (Riche, 1992).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Keto and Enol Tautomers of 4-Benzoyl-3-methyl-1-phenyl-5(2*H*)-pyrazolone

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Abstract

The tautomeric keto and enol forms of 4-benzoyl-3-methyl-1-phenyl-5(2*H*)-pyrazolone, $C_{17}H_{14}N_2O_2$, have been prepared and their crystal structures characterized

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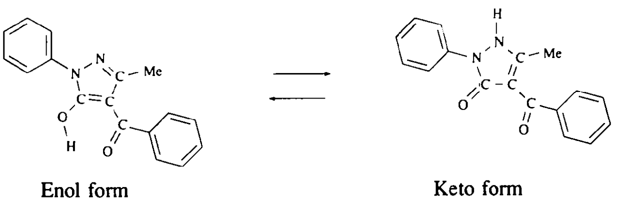
by X-ray analysis. The unit cell of the enol form, 4-benzoyl-5-hydroxy-3-methyl-1-phenylpyrazole, contains two structural conformers. The intramolecular distances in the enol form [2.621 (3) and 2.663 (2) Å] indicate the presence of hydrogen bonds, while the corresponding distance in the keto form [3.079 (3) Å] does not. In the keto form there is an intermolecular hydrogen bond [2.673 (3) Å] between the imino N(2) atom and the carbonyl O(1) atom.

Comment

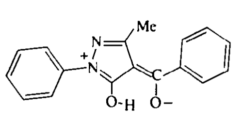
4-Benzoyl-3-methyl-1-phenyl-5(2*H*)-pyrazolone (1) is used widely as an extraction reagent in the separation of trace metals (Akama, Nakai & Kawamura, 1976, 1981; Umetani, Sasayama & Matsui, 1982; Akama, Tong, Ishima & Kajitani, 1992). Further, a number of studies (Akama, Saito, Hayashi, Sato, Tanaka & Kanno, 1993; Zeigan, Engelhardt & Uhlemann, 1981; Maquestiau, Van Haverbeke & Muller, 1975; Wamhoff, Schramm & Korte, 1971) have been made on the keto–enol tautomerism of (1). The structures of the keto form of (1) (O'Connell, Ramsay & Steel, 1985) and a Cu complex of (1) (Miao, Liu & Li, 1991) have been determined, but the crystal structure of the enol form has not yet been determined. This work describes the crystal and molecular structure of the enol form, and provides a more precise structure of the keto form.



(1)

The molecular structures of the two independent molecules of the enol form and that of the keto form are shown in Fig. 1.

Bond lengths and angles for the two forms of (1) are given in Tables 3 and 4. The N—N bond lengths average 1.387 (3) Å and range from 1.383 (3) to 1.390 (3) Å. The C=O bond lengths of the carbonyl groups that participate in hydrogen bonds [enol form, C(7)—O(2) 1.247 (3) and 1.244 (3) Å; keto form, C(5)—O(1) 1.246 (3) Å] are longer than that of the C=O group in the keto form that is not a proton acceptor [C(7)—O(2) 1.226 (3) Å]. The greater double-bond character of the C(5*a*)=C(4*a*) and N(2*a*)=C(3*a*) bonds in the enol form and the C(4)=C(3) bond in the keto form was confirmed by the shorter bond lengths. The lengths of the N(1)—C(5) and C(4)—C(7) bonds in the enol form are considerably shorter than those in keto form, though they are both single bonds. These differences can be explained if there is a substantial contribution from the resonance structure shown below. This structure would be expected to increase the strength of the intramolecular hydrogen bond seen in the enol form.



In the IR spectra (KBr pellets) of the crystals of (1), the colorless keto form of (1) exhibits a characteristic broad strong band centered at 2550 cm^{-1}, which is attributed to a stretching of the intermolecular N—H···O hydrogen bond. The enol form of (1) shows a broad band at around 3100 cm^{-1}, which is attributed to the O—H vibration of the intramolecular hydrogen bond.

The UV spectra of (1) in *n*-hexane and methanol are shown in Fig. 2. Compound (1) exhibits different absorption spectra in solvents of different polarities. The wavelength of the absorption maxima of (1) in methanol is about 15 nm shorter than that in *n*-hexane.

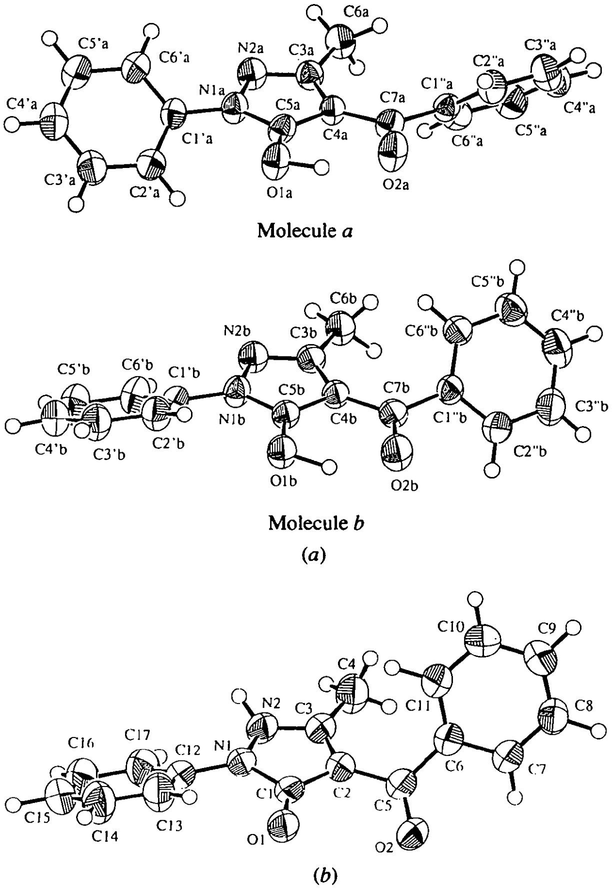


Fig. 1. Molecular structures of (*a*) the enol and (*b*) the keto tautomers of (1), with the atom-numbering scheme. Ellipsoids are drawn at 50% probability.

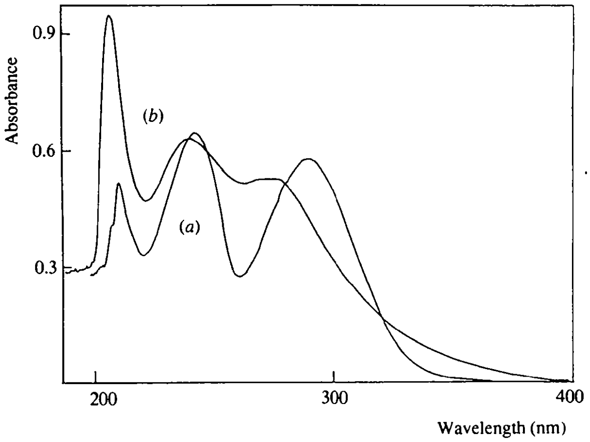


Fig. 2. UV spectra of (1) (4.49×10^{-5} mol l^{-1}): (a) in n-hexane; (b) in methanol.

Experimental

Compound (1) was synthesized and purified as reported previously (Jensen, 1959). Crystals of the enol and keto forms were grown from n-hexane and methanol, respectively.

Enol form

Crystal data

$C_{17}H_{14}N_2O_2$
$M_r = 278.31$
Monoclinic
$C2/c$
$a = 14.298$ (3) Å
$b = 14.400$ (3) Å
$c = 27.187$ (3) Å
$\beta = 91.54$ (1)°
$V = 5595.5$ (18) Å^3
$Z = 16$
$D_x = 1.321$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 16 reflections
$\theta = 20.05$–$20.77°$
$\mu = 0.713$ mm^{-1}
$T = 296$ (1) K
Prismatic
$0.30 \times 0.30 \times 0.15$ mm
Yellow

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction: none
3875 measured reflections
3693 independent reflections
2541 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.012$
$\theta_{max} = 55°$
$h = 0 \rightarrow 15$
$k = -15 \rightarrow 0$
$l = -28 \rightarrow 28$
3 standard reflections monitored every 150 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.038$
$wR = 0.056$
$S = 1.21$
2541 reflections
380 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 4.9×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Keto form

Crystal data

$C_{17}H_{14}N_2O_2$
$M_r = 278.31$
Monoclinic
$P2_1/a$
$a = 11.440$ (4) Å
$b = 9.110$ (7) Å
$c = 13.510$ (9) Å
$\beta = 90.8$ (3)°
$V = 1407$ (1) Å^3
$Z = 4$
$D_x = 1.313$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10$–$20°$
$\mu = 0.088$ mm^{-1}
$T = 293$ K
Prismatic
$0.50 \times 0.10 \times 0.05$ mm
Colorless

Data collection

Rigaku RAXIS IIc imaging plate system
Absorption correction: none
2192 measured reflections
2192 independent reflections

1784 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 26.25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 11$
$l = -16 \rightarrow 16$

Refinement

Refinement on F
$R = 0.063$
$wR = 0.077$
$S = 2.19$
1784 reflections
191 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 3.93852×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for the enol form*

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

	x	y	z	B_{eq}
O(1*a*)	0.1304 (1)	1.0063 (1)	0.05686 (6)	4.47 (5)
O(2*a*)	0.1225 (2)	1.0446 (1)	−0.03899 (6)	5.07 (5)
N(1*a*)	0.1276 (2)	0.8460 (1)	0.06650 (7)	3.67 (5)
N(2*a*)	0.1234 (2)	0.7662 (2)	0.03790 (8)	3.92 (6)
C(5*a*)	0.1306 (2)	0.9219 (2)	0.03759 (9)	3.49 (6)
C(4*a*)	0.1306 (2)	0.8932 (2)	−0.01120 (8)	3.24 (6)
C(3*a*)	0.1254 (2)	0.7940 (2)	−0.00805 (9)	3.45 (6)
C(6*a*)	0.1216 (2)	0.7211 (2)	−0.04703 (10)	4.41 (7)
C(7*a*)	0.1282 (2)	0.9608 (2)	−0.05000 (9)	3.51 (6)
C(1″*a*)	0.1308 (2)	0.9372 (2)	−0.10319 (9)	3.26 (6)
C(2″*a*)	0.0716 (2)	0.9852 (2)	−0.13553 (10)	4.30 (7)
C(3″*a*)	0.0733 (2)	0.9676 (2)	−0.1852 (1)	5.17 (8)
C(4″*a*)	0.1348 (2)	0.9036 (2)	−0.2033 (1)	5.26 (8)
C(5″*a*)	0.1949 (2)	0.8568 (2)	−0.1719 (1)	4.95 (8)
C(6″*a*)	0.1929 (2)	0.8731 (2)	−0.12176 (9)	3.97 (7)
C(1′*a*)	0.1234 (2)	0.8394 (2)	0.11851 (9)	3.40 (6)
C(2′*a*)	0.1690 (2)	0.9024 (2)	0.14874 (10)	4.25 (7)
C(3′*a*)	0.1620 (2)	0.8944 (2)	0.1988 (1)	4.85 (8)
C(4′*a*)	0.1113 (2)	0.8238 (2)	0.2192 (1)	4.91 (8)
C(5′*a*)	0.0675 (2)	0.7605 (2)	0.1889 (1)	4.96 (8)
C(6′*a*)	0.0727 (2)	0.7677 (2)	0.13845 (10)	4.23 (7)
O(1*b*)	0.1352 (1)	0.7524 (1)	0.43821 (6)	4.28 (5)
O(2*b*)	0.1229 (2)	0.8024 (1)	0.53052 (7)	5.30 (5)
N(1*b*)	0.1332 (2)	0.5904 (1)	0.43356 (7)	3.70 (5)
N(2*b*)	0.1270 (2)	0.5148 (1)	0.46503 (8)	3.96 (6)
C(5*b*)	0.1346 (2)	0.6701 (2)	0.45983 (9)	3.49 (6)
C(4*b*)	0.1320 (2)	0.6477 (2)	0.50948 (9)	3.41 (6)

C(3*b*)	0.1260 (2)	0.5484 (2)	0.50974 (9)	3.54 (6)
C(6*b*)	0.1141 (2)	0.4817 (2)	0.55076 (10)	4.37 (7)
C(7*b*)	0.1308 (2)	0.7210 (2)	0.54530 (9)	3.60 (6)
C(1″*b*)	0.1374 (2)	0.7047 (2)	0.59947 (9)	3.43 (6)
C(2″*b*)	0.0849 (2)	0.7589 (2)	0.6301 (1)	4.54 (7)
C(3″*b*)	0.0902 (2)	0.7463 (2)	0.6805 (1)	5.31 (8)
C(4″*b*)	0.1509 (2)	0.6814 (2)	0.7005 (1)	5.36 (8)
C(5″*b*)	0.2063 (2)	0.6299 (2)	0.6703 (1)	4.78 (7)
C(6″*b*)	0.1996 (2)	0.6412 (2)	0.61999 (9)	3.96 (7)
C(1′*b*)	0.1306 (2)	0.5754 (2)	0.38176 (9)	3.69 (6)
C(2′*b*)	0.1711 (2)	0.6380 (2)	0.35056 (10)	4.39 (7)
C(3′*b*)	0.1669 (2)	0.6214 (2)	0.3003 (1)	5.04 (8)
C(4′*b*)	0.1231 (2)	0.5440 (2)	0.2816 (1)	5.28 (8)
C(5′*b*)	0.0837 (2)	0.4815 (2)	0.3132 (1)	5.65 (9)
C(6′*b*)	0.0875 (2)	0.4967 (2)	0.3635 (1)	4.74 (8)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²) *for the keto form*

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

	x	y	z	$B_{\rm eq}$
O(1)	0.3480 (1)	0.1695 (2)	0.6953 (1)	4.89 (5)
O(2)	0.4333 (1)	0.3549 (2)	0.8726 (1)	5.53 (5)
N(1)	0.1555 (2)	0.2411 (2)	0.6744 (1)	4.14 (5)
N(2)	0.0797 (2)	0.3329 (2)	0.7238 (2)	4.47 (5)
C(3)	0.1280 (2)	0.3719 (3)	0.8103 (2)	4.32 (6)
C(4)	0.2410 (2)	0.3178 (3)	0.8159 (2)	4.11 (6)
C(5)	0.2610 (2)	0.2363 (3)	0.7268 (2)	4.07 (6)
C(6)	0.0606 (2)	0.4689 (3)	0.8764 (2)	5.90 (8)
C(7)	0.3304 (2)	0.3376 (3)	0.8942 (2)	4.23 (6)
C(1″)	0.2952 (2)	0.3308 (3)	0.9998 (2)	4.16 (6)
C(2″)	0.3648 (2)	0.4016 (3)	1.0718 (2)	4.64 (6)
C(3″)	0.3366 (2)	0.3967 (3)	1.1700 (2)	5.24 (7)
C(4″)	0.2409 (3)	0.3146 (3)	1.2001 (2)	5.68 (8)
C(5″)	0.1735 (3)	0.2401 (3)	1.1306 (2)	5.62 (8)
C(6″)	0.1994 (2)	0.2506 (3)	1.0308 (2)	4.87 (7)
C(1′)	0.1314 (2)	0.1974 (3)	0.5755 (2)	4.47 (6)
C(2′)	0.1864 (3)	0.0739 (4)	0.5382 (2)	6.01 (8)
C(3′)	0.1596 (3)	0.0289 (5)	0.4428 (2)	7.4 (1)
C(4′)	0.0827 (3)	0.1055 (5)	0.3841 (2)	7.16 (10)
C(5′)	0.0292 (3)	0.2270 (5)	0.4216 (2)	7.16 (10)
C(6′)	0.0529 (2)	0.2747 (4)	0.5172 (2)	5.99 (8)

Table 3. *Selected geometric parameters* (Å, °) *for the enol form*

O(1*a*)—O(2*a*)	2.663 (2)	O(1*b*)—O(2*b*)	2.621 (3)
O(1*a*)—C(5*a*)	1.323 (3)	O(1*b*)—C(5*b*)	1.323 (3)
O(2*a*)—C(7*a*)	1.247 (3)	O(2*b*)—C(7*b*)	1.244 (3)
N(1*a*)—N(2*a*)	1.387 (3)	N(1*b*)—N(2*b*)	1.390 (3)
N(1*a*)—C(5*a*)	1.348 (3)	N(1*b*)—C(5*b*)	1.351 (3)
N(1*a*)—C(1′*a*)	1.420 (3)	N(1*b*)—C(1′*b*)	1.424 (3)
N(2*a*)—C(3*a*)	1.313 (3)	N(2*b*)—C(3*b*)	1.309 (3)
C(5*a*)—C(4*a*)	1.390 (3)	C(4*b*)—C(5*b*)	1.389 (3)
C(4*a*)—C(3*a*)	1.433 (3)	C(3*b*)—C(4*b*)	1.432 (3)
C(4*a*)—C(7*a*)	1.436 (3)	C(4*b*)—C(7*b*)	1.436 (4)
C(3*a*)—C(6*a*)	1.491 (4)	C(3*b*)—C(6*b*)	1.485 (4)
C(7*a*)—C(1″*a*)	1.487 (3)	C(7*b*)—C(1″*b*)	1.492 (4)
N(2*a*)—N(1*a*)—C(5*a*)	110.3 (2)	N(2*b*)—N(1*b*)—C(5*b*)	109.9 (2)
N(2*a*)—N(1*a*)—C(1′*a*)	120.0 (2)	N(2*b*)—N(1*b*)—C(1′*b*)	119.3 (2)
C(5*a*)—N(1*a*)—C(1′*a*)	129.6 (2)	C(5*b*)—N(1*b*)—C(1′*b*)	130.6 (2)
N(1*a*)—C(5*a*)—C(4*a*)	108.4 (2)	N(1*b*)—C(5*b*)—C(4*b*)	108.4 (2)
N(1*a*)—N(2*a*)—C(3*a*)	106.2 (2)	N(1*b*)—N(2*b*)—C(3*b*)	106.5 (2)
O(1*a*)—C(5*a*)—N(1*a*)	120.9 (2)	O(1*b*)—C(5*b*)—N(1*b*)	121.7 (2)
C(5*a*)—C(4*a*)—C(3*a*)	103.8 (2)	C(5*b*)—C(4*b*)—C(3*b*)	103.9 (2)
C(5*a*)—C(4*a*)—C(7*a*)	119.9 (2)	C(5*b*)—C(4*b*)—C(7*b*)	119.3 (2)
N(2*a*)—C(3*a*)—C(4*a*)	111.3 (2)	N(2*b*)—C(3*b*)—C(4*b*)	111.3 (2)
N(2*a*)—C(3*a*)—C(6*a*)	117.4 (2)	N(2*b*)—C(3*b*)—C(6*b*)	117.5 (2)
O(2*a*)—C(7*a*)—C(4*a*)	118.7 (2)	O(2*b*)—C(7*b*)—C(4*b*)	118.4 (2)
C(4*a*)—C(7*a*)—C(1″*a*)	124.0 (2)	C(4*b*)—C(7*b*)—C(1″*b*)	123.5 (2)
C(5*a*)—O(1*a*)—H(1*a*)	101.7	C(5*b*)—O(1*b*)—H(1*b*)	103.6

O(1*a*)—C(5*a*)—N(1*a*)—N(2*a*)	176.8 (2)
O(2*a*)—C(7*a*)—C(4*a*)—C(5*a*)	−2.8 (4)
O(2*a*)—C(7*a*)—C(1″*a*)—C(2″*a*)	−41.3 (4)
N(1*a*)—N(2*a*)—C(3*a*)—C(4*a*)	−0.2 (3)
N(1*a*)—N(2*a*)—C(3*a*)—C(6*a*)	−180.0 (2)
N(1*a*)—C(5*a*)—C(4*a*)—C(3*a*)	1.2 (3)
N(1*a*)—C(5*a*)—C(4*a*)—C(7*a*)	176.6 (2)
N(2*a*)—N(1*a*)—C(5*a*)—C(4*a*)	−1.4 (3)
N(2*a*)—C(3*a*)—C(4*a*)—C(5*a*)	−0.6 (3)
C(5*a*)—N(1*a*)—N(2*a*)—C(3*a*)	1.0 (3)
C(5*a*)—N(1*a*)—C(1′*a*)—C(2′*a*)	−35.2 (4)
C(4*a*)—C(5*a*)—N(1*a*)—C(1′*a*)	−177.7 (2)
O(1*b*)—C(5*b*)—N(1*b*)—N(2*b*)	−176.3 (3)
O(2*b*)—C(7*b*)—C(4*b*)—C(5*b*)	7.0 (4)
O(2*b*)—C(7*b*)—C(1″*b*)—C(2″*b*)	37.2 (4)
N(1*b*)—N(2*b*)—C(3*b*)—C(4*b*)	−0.2 (3)
N(1*b*)—N(2*b*)—C(3*b*)—C(6*b*)	176.6 (2)
N(1*b*)—C(5*b*)—C(4*b*)—C(3*b*)	−1.8 (3)
N(1*b*)—C(5*b*)—C(4*b*)—C(7*b*)	−178.7 (2)
N(2*b*)—N(1*b*)—C(5*b*)—C(4*b*)	1.8 (3)
N(2*b*)—C(3*b*)—C(4*b*)—C(5*b*)	1.3 (3)
C(5*b*)—N(1*b*)—N(2*b*)—C(3*b*)	−1.0 (3)
C(5*b*)—N(1*b*)—C(1′*b*)—C(2′*b*)	30.6 (4)
C(4*b*)—C(5*b*)—N(1*b*)—C(1′*b*)	176.8 (2)

Table 4. *Selected geometric parameters* (Å, °) *for the keto form*

O(1)—O(2)	3.079 (3)	C(4)—C(3)	1.385 (3)
O(1)—C(5)	1.246 (3)	C(4)—C(7)	1.472 (3)
O(2)—C(7)	1.226 (3)	C(3)—C(6)	1.480 (4)
N(1)—C(5)	1.391 (3)	C(7)—C(1″)	1.490 (3)
N(1)—C(1′)	1.418 (3)	N(2)—H(2N)	0.95
N(2)—C(3)	1.334 (3)	N(1)—N(2)	1.383 (3)
C(5)—C(4)	1.435 (4)		
N(2)—N(1)—C(5)	108.6 (2)	C(5)—C(4)—C(7)	123.3 (2)
N(2)—N(1)—C(1′)	120.7 (2)	N(2)—C(3)—C(4)	109.1 (2)
C(5)—N(1)—C(1′)	128.8 (2)	N(2)—C(3)—C(6)	118.3 (3)
N(1)—C(5)—C(4)	105.3 (2)	O(2)—C(7)—C(4)	120.3 (2)
N(1)—N(2)—C(3)	109.2 (2)	C(4)—C(7)—C(1″)	119.3 (2)
O(1)—C(5)—N(1)	122.2 (2)	N(1)—N(2)—H(2N)	119.4
C(5)—C(4)—C(3)	107.4 (2)	C(3)—N(2)—H(2N)	123.8

O(1)—C(5)—N(1)—N(2)	−175.0 (2)
O(2)—C(7)—C(4)—C(5)	37.3 (4)
O(2)—C(7)—C(1″)—C(2″)	26.1 (3)
N(1)—N(2)—C(3)—C(4)	5.5 (3)
N(1)—N(2)—C(3)—C(6)	−179.1 (2)
N(1)—C(5)—C(4)—C(3)	−2.6 (3)
N(1)—C(5)—C(4)—C(7)	178.7 (2)
N(2)—N(1)—C(5)—C(4)	5.8 (3)
N(2)—C(3)—C(4)—C(5)	−1.8 (3)
C(5)—N(1)—N(2)—C(3)	−7.2 (3)
C(5)—N(1)—C(1′)—C(2′)	37.4 (3)
C(4)—C(5)—N(1)—C(1′)	169.7 (2)

The structures were solved (Sheldrick, 1985; Beurskens, Admiraal, Beurskens, Bosman, Garcia-Granda, Gould, Smits & Smykalla, 1992) by direct methods and were refined by full-matrix least squares. H atoms were geometrically positioned, excluding those of the hydroxyl (enol form), imino (keto form) and methyl groups which were located in difference Fourier maps. Computations were performed using the *TEXSAN* program package (Molecular Structure Corporation, 1989) on an Iris Indigo computer at the Rigaku Corporation.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK0003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three Lactone Fused Perhydroisoxazolo[2,3-*a*]pyridines: a Conformational Study

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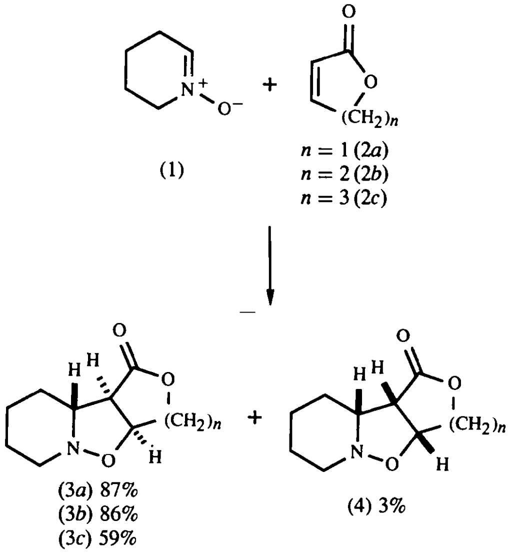
Abstract

(3a*RS*,9a*SR*,9b*SR*)-Octahydro-1*H*-furo[3′,4′:4,5]isoxazolo[2,3-*a*]pyridin-1-one ($C_9H_{13}NO_3$), (4a*RS*,10a*RS*,10b*RS*)-octahydro-1*H*,3*H*-pyrano[3′,4′:4,5]isoxazolo[2,3-*a*]pyridin-1-one ($C_{10}H_{15}NO_3$), and (5a*RS*,11a*RS*,11b*RS*)-decahydro-1*H*-oxepino[3′,4′:4,5]isoxazolo[2,3-*a*]pyridin-1-one ($C_{11}H_{17}NO_3$), *exo* products of the reaction between 3,4,5,6-tetrahydropyridine 1-oxide and five-, six- and seven-membered α,β-unsaturated lactones, adopt, in the solid state, the preponderant conformation observed in chloroform or acetone solution. The perhydroisoxazolo[2,3-*a*]pyridine substructure presents a *cis* fusion when the lactone ring is five-membered and a *trans* fusion when it is six- or seven-membered. In the three compounds, the piperidine ring exhibits a more or less distorted chair conformation depending on the product. The lactone ring conformation involves a local pseudo twofold axis running through the carbonyl C atom (five-membered lactone) or through the midpoint of the C—C bond that joins the carbonyl group to the ring junction (six- and seven-membered lactones). On the other hand, the isoxazolidine ring shows an envelope conformation when the lactone ring is six- or seven-membered, whereas an intermediate conformation between the envelope and the half-chair is observed when the lactone is five-membered.

Comment

The 1,3-dipolar cycloaddition of nitrones to alkenes has proved to be a powerful synthetic tool for the preparation of nitrogen-containing natural products (for recent reviews, see Tufariello, 1984; Torssell, 1988; Annunziata, Cinquini, Cozzi & Raimondi, 1989). Electron-deficient unsymmetrically 1,2-disubstituted olefins add regiospecifically to nitrones affording only isoxazolidines with the electron-withdrawing group attached to the 4-position. In this context, the reactions between the nitrone (1) and α,β-unsaturated lactones (2*a*)–(2*c*) have been studied (Cid *et al.*, 1993). In this cycloaddition, *exo* adducts have been obtained as major or exclusive products.



The cycloadducts formed contain the perhydroisoxazolo[2,3-*a*]pyridine substructure which may exist in solution as a mixture of one rigid *trans* and two flexi-

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