gram(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*2.1 (McArdle, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

The authors thank Norwich Eaton Pharmaceuticals, Inc. (Norwich, New York) for providing the crystals. One of them (TAO) is indebted to the Research Council of the Katholieke Universiteit Leuven (Belgium) for a Senior Fellowship (No. F/92/32).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1116). 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. (1995). C**51**, 1306–1310

Two Methyl-Substituted Carbapenem Antibiotic Precursors

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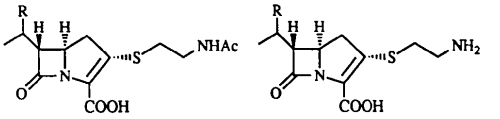
(*Received* 5 *October* 1994; *accepted* 12 *December* 1994)

Abstract

Carbapenem antibiotics are characterized by the presence of the 7-oxo-1-azabicyclo[3.2.0]hept-2-ene-2-carboxylic acid system. These new bicyclic β-lactam antibiotics are rapidly degraded by dehydropeptidase-I. The introduction of a methyl group at the C1 position of the carbapenem skeleton improves the dehydropeptidase stability. The crystal structure determinations of two synthetic methyl-substituted carbapenem precursors, 4-benzyl-6-methoxy-3-propylsulfonyl-2-{2,2,2′,2′-tetramethyl-[4,4′-bi([1,3]dioxolanyl)-5-yl]}-1-azabicyclo[3.2.0]heptane-7-one, $C_{27}H_{39}NO_8S$, and 3-ethylthio-4-(2-furylmethyl)-6-methoxy-2-{2,2,2′,2′-tetramethyl-[4,4′-bi([1,3]dioxolanyl)-5-yl]}-1-azabicyclo[3.2.0]heptane-7-one, $C_{24}H_{35}NO_7S$, established their stereochemistry unambiguously. The absolute configuration was deduced from that of the chiral D-glucosamine auxiliary.

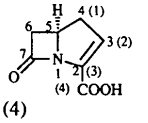
Comment

Carbapenem antibiotics such as PS-5, (1) (Yamamoto *et al.*, 1980), PS-6, (2) (Ishikura, 1979), and thienamycin, (3) (Kahan *et al.*, 1979), comprise an interesting family of streptomycete metabolites characterized by the presence of the 7-oxo-1-azabicyclo[3.2.0]hept-2-ene-2-carboxylic acid system (4).



(1) R = H
(2) R = Me

(3)

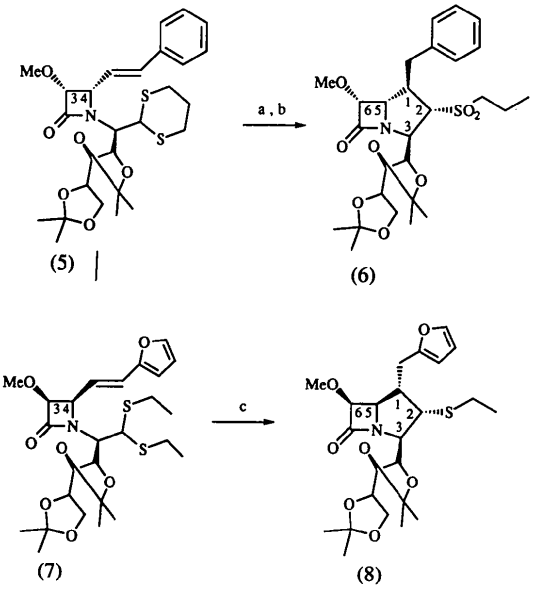


(4)

The potent antibacterial properties and the challenging chemical problems have made these new bicyclic β-lactams major synthetic objectives. A disadvantage of these compounds is that they are rapidly degraded in the kidney by dehydropeptidase-I (DHP-I) (Kahan *et al.*, 1979). The introduction of a methyl group into the 1-position of the carbapenem skeleton considerably improves the DHP stability (Neu, Novelli & Chin, 1989).

The synthesis of 1,2,3,6-tetrasubstituted carbapenem (6) from the readily available 1,3,4-trisubstituted azetidin-2-ones (5) (Barton *et al.*, 1990), in which the five-membered ring is formed by radical cyclization, has been reported recently (Anaya *et al.*, 1993). In continuing to explore the use of radical cyclization in the preparation of methyl-substituted carbapenem antibiotic precursors, we have synthesized compound (8) in 62% yield from the monocyclic β-lactam (7), which was obtained by Staudinger reaction using D-glucosamine as the chiral auxiliary (to be published). The X-ray struc-

ture determinations of compounds (6) and (8), reported here, were undertaken to establish unambiguously their stereochemistry.



The molecular structures of compounds (6) and (8) are shown in Figs. 1 and 2, respectively, the absolute configuration of the C3 atom being assigned an *R* configuration in view of the D-glucosamine origin. In both structures, the two rings of the carbapenem system are *cis*-fused but the system is convex in (6) while it is concave in (8).

In compound (6), the substituents at C1 and C2 are *trans* to each other while in (8) they are *cis*. The methoxy groups of (6) and (8) have opposite configurations and are in both cases *trans* to the neighboring side-chains at C1 (benzyl and furfuryl, respectively). The absolute configuration of (6) was deduced to be 1*R*,2*S*,3*R*,5*S*,6*R* and for (8) 1*S*,2*S*,3*R*,5*R*,6*S*.

In compound (6), the lactam ring is bent with a mean value of 14.5 (8)° for the torsion angles; the pyrrolidine ring is in a half-chair conformation [atoms N4 and C5 are −0.174 (6) and 0.244 (7) Å, respectively, away from the plane formed by the other three atoms]; the dihedral angle between the two fused rings is 121 (1)°; and the N4 atom is pyramidal [sum of bond angles = 332.3 (6)°]. The propyl chain fixed to the sulfone group is disordered with two positions of equal weight (0.50) and practically symmetrical about the line bisecting the angle formed by O—S—O [respective torsion angles: S18—C21—C22—C23 = 150 (2) and S18—C21′–C22′–C23′ = −173 (2)°].

In compound (8), the lactam ring is nearly planar [mean value of torsion angles = 6.3 (5)°]; the five-membered ring exhibits an envelope conformation with atom C1 as the flap, out of the mean plane of the other four atoms by 0.587 (5) Å; the dihedral angle between the two fused rings is 138 (1)°; and the N4 atom is also pyramidal [sum of bond angles = 340.8 (4)°]. The ethyl chain fixed on the S17 atom is disordered with a majority in the extended conformation [weight 0.667, torsion angle C2—S17—C18—C19 = −171.3 (7)°] and a minority in the bent conformation [weight 0.333, torsion angle C2—S17—C18′–C19′ = 66 (1)°].

Crystal packing of both structures shows only normal van der Waals contacts.

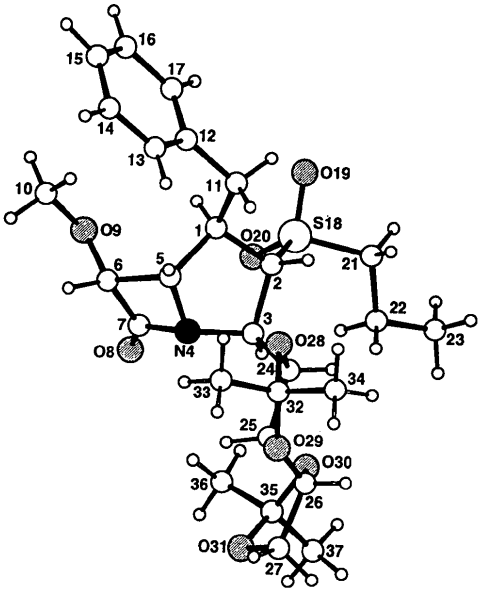


Fig. 1. Perspective view of compound (6). For clarity only one position of the disordered propyl chain has been depicted.

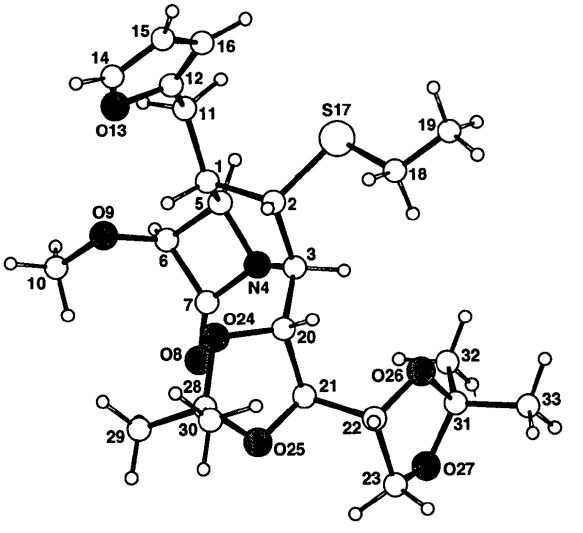


Fig. 2. Perspective view of compoud (8). For clarity only the majority position of the disordered ethyl chain has been depicted.

Experimental

Compound (6)

Crystal data

$C_{27}H_{39}NO_8S$
$M_r = 537.67$
Orthorhombic
$P2_12_12_1$
$a = 7.244\ (5)$ Å
$b = 14.863\ (8)$ Å
$c = 27.308\ (12)$ Å
$V = 2940.2\ (28)$ Å^3
$Z = 4$
$D_x = 1.21$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 16 reflections
$\theta = 4.0$–$25.0°$
$\mu = 1.32$ mm^{-1}
$T = 293$ K
Prism
$0.53 \times 0.20 \times 0.10$ mm
Colourless

Data collection

Philips PW100 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2979 measured reflections
2979 independent reflections
1661 observed reflections $[I > 2.5\sigma(I)]$
$\theta_{max} = 68.01°$
$h = 0 \rightarrow 28$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 180 min
intensity decay: 5%

Refinement

Refinement on F
$R = 0.068$
$wR = 0.093$
$S = 1.10$
1656 reflections
319 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.005220F^2]$
$(\Delta/\sigma)_{max} = 0.06$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (6)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
C1	0.6121 (11)	0.9957 (5)	0.2506 (3)	0.051 (7)
C2	0.6899 (11)	1.0242 (4)	0.2005 (3)	0.051 (7)
C3	0.5897 (10)	0.9683 (5)	0.1600 (3)	0.050 (7)
N4	0.4465 (8)	0.9206 (4)	0.1882 (2)	0.050 (6)
C5	0.4919 (11)	0.9122 (5)	0.2396 (3)	0.048 (7)
C6	0.2807 (10)	0.9203 (5)	0.2499 (3)	0.052 (7)
C7	0.2685 (11)	0.9512 (6)	0.1981 (3)	0.058 (8)
O8	0.1573 (8)	0.9879 (5)	0.1718 (2)	0.080 (7)
O9	0.2165 (8)	0.9802 (4)	0.2841 (2)	0.059 (6)
C10	0.2040 (13)	0.9422 (6)	0.3319 (4)	0.079 (11)
C11	0.7690 (11)	0.9779 (8)	0.2867 (3)	0.073 (10)
C12	0.7030 (11)	0.9614 (8)	0.3383 (3)	0.069 (10)
C13	0.6976 (16)	0.8752 (8)	0.3581 (4)	0.090 (13)
C14	0.638 (2)	0.8595 (12)	0.4053 (7)	0.13 (2)
C15	0.593 (3)	0.9333 (19)	0.4341 (6)	0.16 (3)
C16	0.592 (2)	1.0177 (13)	0.4160 (5)	0.12 (2)
C17	0.6520 (16)	1.0325 (9)	0.3677 (4)	0.092 (13)
S18	0.6647 (5)	1.1421 (2)	0.1927 (1)	0.094 (4)
O19	0.7432 (15)	1.1860 (4)	0.2331 (3)	0.126 (12)
O20	0.4768 (17)	1.1617 (5)	0.1810 (4)	0.136 (14)
C21	0.8381 (17)	1.1684 (15)	0.1519 (4)	0.095 (7)
C22	0.771 (3)	1.1500 (15)	0.1010 (3)	0.116 (8)
C23	0.862 (5)	1.213 (2)	0.0655 (6)	0.177 (14)
C21′	0.7209 (19)	1.1738 (17)	0.1340 (4)	0.115 (9)
C22′	0.925 (2)	1.1647 (18)	0.1274 (6)	0.118 (9)
C23′	0.980 (4)	1.202 (2)	0.0783 (8)	0.186 (15)
C24	0.7194 (12)	0.9034 (4)	0.1354 (3)	0.052 (8)
C25	0.6326 (13)	0.8369 (5)	0.0996 (3)	0.066 (9)
C26	0.6407 (15)	0.8617 (8)	0.0478 (4)	0.086 (12)
C27	0.525 (2)	0.8047 (10)	0.0137 (5)	0.12 (2)
O28	0.7996 (8)	0.8476 (3)	0.1713 (2)	0.060 (5)
O29	0.7362 (11)	0.7580 (4)	0.1063 (3)	0.104 (9)
O30	0.5631 (11)	0.9482 (5)	0.0414 (2)	0.093 (9)
O31	0.3557 (15)	0.8483 (10)	0.0132 (4)	0.150 (17)
C32	0.8276 (17)	0.7600 (6)	0.1518 (4)	0.081 (11)
C33	0.746 (3)	0.6972 (8)	0.1890 (6)	0.17 (3)
C34	1.029 (2)	0.7428 (11)	0.1435 (5)	0.15 (2)
C35	0.395 (2)	0.9427 (11)	0.0150 (4)	0.106 (17)
C36	0.237 (2)	0.9833 (14)	0.0422 (5)	0.15 (2)
C37	0.415 (2)	0.9782 (15)	−0.0350 (5)	0.17 (3)

Table 2. *Selected geometric parameters* (Å, °) *for* (6)

C1—C2	1.541 (11)	S18—O20	1.428 (12)
C1—C5	1.545 (10)	S18—C21	1.725 (13)
C1—C11	1.527 (11)	S18—C21′	1.719 (12)
C2—C3	1.560 (10)	C21—C22	1.496 (16)
C2—S18	1.774 (7)	C22—C23	1.50 (3)
C3—N4	1.472 (10)	C21′—C22′	1.50 (2)
C3—C24	1.506 (11)	C22′—C23′	1.50 (3)
N4—C5	1.448 (10)	C24—C25	1.526 (11)
N4—C7	1.394 (10)	C24—O28	1.410 (9)
C5—C6	1.560 (11)	C25—C26	1.463 (14)
C6—C7	1.488 (12)	C25—O29	1.404 (11)
C6—O9	1.371 (9)	C26—C27	1.511 (19)
C7—O8	1.210 (10)	C26—O30	1.413 (14)
O9—C10	1.427 (12)	C27—O31	1.39 (2)
C11—C12	1.510 (12)	O28—C32	1.422 (10)
C12—C13	1.391 (16)	O29—C32	1.407 (13)
C12—C17	1.377 (16)	O30—C35	1.421 (15)
C13—C14	1.38 (2)	O31—C35	1.43 (2)
C14—C15	1.39 (3)	C32—C33	1.501 (19)
C15—C16	1.35 (3)	C32—C34	1.497 (19)
C16—C17	1.409 (18)	C35—C36	1.49 (2)
S18—O19	1.402 (9)	C35—C37	1.471 (18)
C2—C1—C5	104.7 (6)	O19—S18—O20	117.9 (6)
C2—C1—C11	110.4 (6)	O19—S18—C21	96.1 (7)
C5—C1—C11	114.0 (6)	O19—S18—C21′	120.6 (7)
C1—C2—C3	108.2 (6)	O20—S18—C21	120.2 (7)
C1—C2—S18	109.9 (5)	O20—S18—C21′	87.8 (7)
C3—C2—S18	113.2 (5)	S18—C21—C22	108.7 (12)
C2—C3—N4	102.4 (6)	C21—C22—C23	110.0 (18)
C2—C3—C24	111.5 (6)	S18—C21′—C22′	108.8 (13)
N4—C3—C24	111.4 (6)	C21′—C22′—C23′	109.4 (18)
C3—N4—C5	112.8 (6)	C3—C24—C25	116.4 (7)
C3—N4—C7	126.7 (6)	C3—C24—O28	108.8 (6)
C5—N4—C7	92.8 (6)	C25—C24—O28	103.6 (6)
C1—C5—N4	104.3 (6)	C24—C25—C26	116.1 (8)
C1—C5—C6	117.1 (6)	C24—C25—O29	103.7 (7)
N4—C5—C6	86.9 (5)	C26—C25—O29	108.4 (8)
C5—C6—C7	84.9 (6)	C25—C26—C27	115.6 (10)
C5—C6—O9	120.3 (6)	C25—C26—O30	109.4 (8)
C7—C6—O9	115.2 (6)	C27—C26—O30	102.3 (9)
N4—C7—C6	91.7 (6)	C26—C27—O31	103.6 (11)
N4—C7—O8	130.3 (8)	C24—O28—C32	109.6 (6)
C6—C7—O8	138.0 (8)	C25—O29—C32	110.5 (7)
C6—O9—C10	112.9 (6)	C26—O30—C35	110.6 (9)
C1—C11—C12	113.3 (7)	C27—O31—C35	106.5 (12)
C11—C12—C13	121.5 (9)	O28—C32—O29	106.5 (8)
C11—C12—C17	120.2 (9)	O28—C32—C33	105.1 (10)
C13—C12—C17	118.3 (10)	O28—C32—C34	110.6 (9)
C12—C13—C14	121.8 (12)	O29—C32—C33	113.4 (10)
C13—C14—C15	118.0 (16)	O29—C32—C34	108.8 (9)
C14—C15—C16	121.9 (19)	C33—C32—C34	112.3 (11)
C15—C16—C17	119.2 (15)	O30—C35—O31	104.0 (11)
C12—C17—C16	120.5 (11)	O30—C35—C36	112.5 (12)
C2—S18—O19	108.9 (5)	O30—C35—C37	111.4 (12)
C2—S18—O20	109.1 (5)	O31—C35—C36	105.2 (12)
C2—S18—C21	103.1 (6)	O31—C35—C37	109.8 (12)
C2—S18—C21′	111.0 (7)	C36—C35—C37	113.3 (13)
C5—C1—C2—C3	9.4 (6)	C2—C3—C24—C25	172.7 (9)
C1—C2—C3—N4	7.0 (6)	C2—C3—C24—O28	56.2 (7)
C2—C3—N4—C5	−22.9 (6)	C3—C24—C25—C26	97.2 (9)

C3—N4—C5—C1	29.4 (6)	C3—C24—C25—O29	−144.0 (9)
N4—C5—C1—C2	−22.4 (6)	C24—C25—C26—C27	−169.2 (13)
C7—N4—C5—C6	14.7 (8)	C24—C25—C26—O30	−54.4 (9)
N4—C5—C6—C7	−13.8 (7)	C24—C25—O29—C32	20.0 (8)
C5—C6—C7—N4	14.3 (8)	C25—O29—C32—O28	−7.5 (8)
C6—C7—N4—C5	−15.4 (8)	O29—C32—O28—C24	−9.6 (7)
O8—C7—C6—O9	−44.7 (8)	C32—O28—C24—C25	21.2 (7)
C1—C5—C6—O9	−25.6 (6)	O28—C24—C25—O29	−24.7 (7)
C5—C6—O9—C10	−90.1 (8)	O29—C25—C26—C27	74.6 (11)
C6—C5—C1—C11	122.9 (8)	O29—C25—C26—O30	−170.6 (11)
C5—C1—C11—C12	−69.9 (8)	O30—C26—C27—O31	−29.3 (12)
C2—C1—C11—C12	172.6 (10)	C26—C27—O31—C35	36.8 (12)
C1—C11—C12—C13	103.4 (11)	C27—O31—C35—O30	−29.8 (12)
C1—C11—C12—C17	−78.7 (10)	O31—C35—O30—C26	10.1 (10)
C11—C1—C2—C3	132.5 (8)	C35—O30—C26—C27	11.3 (10)
C11—C1—C2—S18	−103.5 (7)	C3—C2—S18—C21	−84.5 (7)
C1—C2—C3—C24	−112.3 (8)	C3—C2—S18—C21′	−50.7 (7)
C1—C2—S18—O19	53.2 (6)	C2—S18—C21—C22	83.2 (10)
C1—C2—S18—O20	−76.7 (6)	S18—C21—C22—C23	149.8 (19)
C1—C2—S18—C21	154.5 (8)	C2—S18—C21′—C22′	−70.7 (11)
C1—C2—S18—C21′	−171.7 (9)	S18—C21′—C22′—C23′	−173 (2)
S18—C2—C3—C24	125.7 (7)		

Compound (8)

Crystal data

$C_{24}H_{35}NO_7S$
M_r = 481.61
Tetragonal
$P4_1$
a = 10.136 (6) Å
c = 25.026 (12) Å
V = 2571.1 (24) Å^3
Z = 4
D_x = 1.24 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 8.1–16.3°
μ = 1.43 mm^{-1}
T = 293 K
Prism
0.53 × 0.53 × 0.26 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4718 measured reflections
2231 independent reflections
1807 observed reflections [$I > 3.0\sigma(I)$]

R_{int} = 0.036
θ_{max} = 64.74°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 29$
3 standard reflections
frequency: 166 min
intensity decay: 4%

Refinement

Refinement on F
R = 0.048
wR = 0.052
S = 0.61
1801 reflections
295 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.000124F^2]$

$(\Delta/\sigma)_{max}$ = 0.04
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (8)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	1.1475 (4)	0.4068 (4)	0.2196 (2)	0.051 (4)
C2	1.0471 (5)	0.3559 (4)	0.2616 (2)	0.053 (5)
C3	0.9488 (4)	0.4714 (4)	0.2695 (2)	0.050 (4)
N4	0.9682 (4)	0.5516 (4)	0.2209 (2)	0.054 (4)
C5	1.0603 (5)	0.4891 (5)	0.1837 (2)	0.055 (5)
C6	1.1031 (6)	0.6261 (6)	0.1650 (2)	0.067 (6)
C7	1.0139 (5)	0.6772 (5)	0.2100 (2)	0.056 (5)
O8	0.9909 (4)	0.7828 (3)	0.2289 (2)	0.079 (4)
O9	1.2367 (4)	0.6497 (4)	0.1710 (2)	0.089 (5)
C10	1.2728 (10)	0.7743 (7)	0.1506 (5)	0.146 (13)
C11	1.2311 (5)	0.3031 (5)	0.1898 (2)	0.064 (5)
C12	1.3178 (6)	0.2209 (6)	0.2227 (2)	0.072 (6)
O13	1.4272 (5)	0.2778 (5)	0.2417 (2)	0.111 (6)
C14	1.4942 (9)	0.1815 (11)	0.2694 (4)	0.133 (13)
C15	1.4330 (11)	0.0703 (10)	0.2675 (4)	0.123 (12)
C16	1.3179 (7)	0.0932 (6)	0.2370 (4)	0.104 (9)
S17	0.9629 (2)	0.2080 (1)	0.2385	0.090 (2)
C18	0.8906 (11)	0.1616 (10)	0.3007 (3)	0.107 (4)
C19	0.8286 (11)	0.0380 (9)	0.3035 (5)	0.104 (3)
C18′	0.980 (2)	0.0752 (13)	0.2835 (6)	0.101 (6)
C19′	0.9104 (19)	0.115 (2)	0.3290 (8)	0.090 (6)
C20	0.9674 (4)	0.5450 (4)	0.3219 (2)	0.046 (4)
C21	0.8722 (4)	0.6597 (4)	0.3331 (2)	0.054 (5)
C22	0.7533 (5)	0.6193 (5)	0.3665 (2)	0.065 (6)
C23	0.6607 (6)	0.7300 (6)	0.3782 (3)	0.084 (7)
O24	1.0942 (3)	0.6044 (3)	0.3246 (2)	0.052 (3)
O25	0.9505 (3)	0.7484 (3)	0.3635 (2)	0.077 (4)
O26	0.6768 (3)	0.5283 (4)	0.3365 (2)	0.077 (4)
O27	0.5712 (5)	0.7244 (5)	0.3355 (3)	0.114 (7)
C28	1.0853 (5)	0.7102 (5)	0.3625 (2)	0.061 (5)
C29	1.1684 (6)	0.8226 (5)	0.3427 (3)	0.082 (7)
C30	1.1250 (7)	0.6641 (6)	0.4173 (3)	0.085 (7)
C31	0.5580 (6)	0.5931 (6)	0.3197 (3)	0.075 (6)
C32	0.5471 (12)	0.5884 (10)	0.2599 (4)	0.152 (14)
C33	0.4448 (6)	0.5200 (8)	0.3456 (3)	0.096 (8)

Table 4. *Selected geometric parameters* (Å, °) *for* (8)

C1—C2	1.551 (7)	S17—C18	1.784 (8)
C1—C5	1.512 (7)	S17—C18′	1.762 (13)
C1—C11	1.543 (7)	C18—C19	1.404 (14)
C2—C3	1.550 (6)	C18′—C19′	1.40 (2)
C2 S17	1.819 (5)	C20—C21	1.536 (6)
C3—N4	1.476 (6)	C20—O24	1.421 (5)
C3—C20	1.520 (7)	C21—C22	1.524 (7)
N4—C5	1.463 (6)	C21—O25	1.420 (6)
N4—C7	1.382 (6)	C22—C23	1.492 (8)
C5—C6	1.528 (7)	C22—O26	1.420 (7)
C6—C7	1.534 (8)	C23—O27	1.403 (9)
C6—O9	1.383 (7)	O24—C28	1.435 (6)
C7—O8	1.194 (6)	O25—C28	1.421 (6)
O9—C10	1.410 (9)	O26—C31	1.435 (7)
C11—C12	1.466 (8)	O27—C31	1.395 (8)
C12—O13	1.337 (8)	C28—C29	1.501 (8)
C12—C16	1.343 (9)	C28—C30	1.505 (8)
O13—C14	1.376 (12)	C31—C32	1.501 (11)
C14—C15	1.288 (15)	C31—C33	1.512 (9)
C15—C16	1.414 (13)		
C2—C1—C5	101.7 (4)	C2—S17—C18	97.6 (3)
C2—C1—C11	117.5 (4)	C2—S17—C18′	112.4 (6)
C5—C1—C11	114.1 (4)	S17—C18—C19	117.6 (7)
C1—C2—C3	104.9 (4)	S17—C18′—C19′	104.5 (12)
C1—C2—S17	111.6 (3)	C3—C20—C21	116.8 (4)
C3—C2—S17	111.2 (3)	C3—C20—O24	111.2 (4)
C2—C3—N4	103.0 (4)	C21—C20—O24	103.8 (3)
C2—C3—C20	113.6 (4)	C20—C21—C22	113.2 (4)
N4—C3—C20	115.1 (4)	C20—C21—O25	103.1 (4)
C3—N4—C5	111.8 (4)	C22—C21—O25	108.5 (4)
C3—N4—C7	135.6 (4)	C21—C22—C23	113.8 (5)
C5—N4—C7	93.4 (4)	C21—C22—O26	108.4 (4)
C1—C5—N4	103.5 (4)	C23—C22—O26	104.4 (4)
C1—C5—C6	121.2 (4)	C22—C23—O27	103.1 (5)
N4—C5—C6	89.0 (4)	C20—O24—C28	106.9 (3)
C5—C6—C7	85.1 (4)	C21—O25—C28	110.8 (4)
C5—C6—O9	113.7 (5)	C22—O26—C31	108.5 (4)
C7—C6—O9	116.0 (5)	C23—O27—C31	108.5 (5)
N4—C7—C6	91.8 (4)	O24—C28—O25	106.0 (4)
N4—C7—O8	133.0 (5)	O24—C28—C29	108.3 (4)
C6—C7—O8	135.2 (5)	O24—C28—C30	110.8 (4)
C6—O9—C10	111.8 (5)	O25—C28—C29	109.8 (4)
C1—C11—C12	116.3 (4)	O25—C28—C30	109.0 (4)

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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Acta Cryst. (1995). **C51**, 1310–1314

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

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(*Received* 5 *November* 1993; *accepted* 24 *April* 1995)

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