N4—C4	1.405 (3)	C5—C6	1.386 (3)
N4—C7	1.366 (3)	C7—C8	1.502 (3)
N5—C5	1.468 (3)		
C4—N4—C7	125.4 (2)	N4—C4—C5	125.7 (2)
O5′—N5—O5	124.4 (2)	C3—C4—C5	117.7 (2)
O5′—N5—C5	118.5 (2)	N5—C5—C4	121.7 (2)
O5—N5—C5	117.0 (2)	N5—C5—C6	115.6 (2)
C2—C1—C6	121.2 (2)	C4—C5—C6	122.2 (2)
C2—C1—C9	120.1 (2)	C1—C6—C5	118.7 (2)
C6—C1—C9	118.6 (2)	O7—C7—N4	121.4 (2)
C1—C2—C3	119.6 (2)	O7—C7—C8	123.6 (2)
O3—C3—C2	123.1 (2)	N4—C7—C8	115.0 (2)
O3—C3—C4	116.4 (2)	O9—C9—O9′	124.2 (2)
C2—C3—C4	120.5 (2)	O9—C9—C1	115.6 (2)
N4—C4—C3	116.6 (2)	O9′—C9—C1	120.2 (2)
C7—N4—C4—C3	143.6 (2)	C2—C1—C9—O9	−5.4 (3)
C4—N4—C7—O7	0.1 (3)	C6—C1—C2—HC2	177 (1)
C4—N4—C7—C8	179.9 (2)	C2—C1—C6—HC6	−178 (1)
O5—N5—C5—C4	−40.6 (3)	HO9—O9—C9—C1	180.0
C9—C1—C2—C3	−177.7 (2)		

D—H···*A*	H···*A*	*D*—H···*A*
O9—HO9···O9′*	1.729	167.2
O3*—HO3*···O7	1.767	155.8
C9—O9′···HO9*		123.0
C7—O7···HO3*		125.0

* Denotes an atom of a symmetry-related molecule.

Profile analysis was performed on all reflections (Lehman & Larsen, 1974; Grant & Gabe, 1978). Intensities were corrected for Lorentz–polarization effects, linear decay and absorption. The Enraf–Nonius *MolEN* structure determination package (Fair, 1990) was used to solve and refine the structure. The H atoms attached to atoms C2, C6 and N4 were refined (positional and displacement parameters) and the H atoms attached to atoms O9 and O3 were located on a difference electron density map and were not refined, their displacement parameters being calculated based on the temperature factors of the atoms to which they were bonded ($1.45B_{eq}$). The H atoms on atoms C8, C8′ and C8″ were located or calculated and were not refined.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and root-mean-square amplitudes of anisotropic displacement have been deposited with the IUCr (Reference: PT1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-(2-Carboxybenzoyl)-2(3*H*)-benzothiazolone

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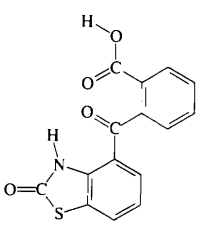
Abstract

Although 6-benzoyl-2(3*H*)-benzothiazolone derivatives are known, their 4-benzoyl analogues have not been described previously. The title compound [2-(2-oxo-3*H*-1,3-benzothiazol-4-oyl)benzoic acid, $C_{15}H_9NO_4S$] is the first of this series to be isolated and is characterized here. It was obtained in low yield in a one-step reaction from 3*H*-benzothiazolone and phthalic anhydride (in

the presence of aluminium chloride and dimethylformamide). The X-ray structure determination shows that there is no intramolecular hydrogen bonding, but there is a strong intermolecular hydrogen bond between neighbouring carboxyl groups. The dihedral angle between the 3*H*-benzothiazolone and benzoyl rings is 69.7 (4)°.

Comment

6-Benzoyl-2(3*H*)-benzoxazolone (Mairesse *et al.*, 1984) has shown particularly interesting analgesic properties (Bonte *et al.*, 1974, 1984) and is a valuable starting material for the design of new drugs. It seemed important to prepare the corresponding sulfur bioisosters, 6-benzoyl-2(3*H*)-benzothiazolones (Yous, Poupaert, Lesieur, Depreux & Lesieur, 1994; Follet-Houttemane, Boivin, Bonte & Lesieur, 1991), considering their greater chemical and metabolic stability. The development of synthetic compounds in this series (Taverne, 1995) led to 4-(2-carboxybenzoyl)-2(3*H*)-benzothiazolone (5% yield), as well as to the formation of 6-(2-carboxybenzoyl)-2(3*H*)-benzothiazolone (50% yield) under conditions previously described for 3*H*-benzoxazolone itself (Aichaoui, Lesieur & Henichart, 1992). ^{1}H NMR spectroscopy, including nuclear Overhauser effect spectroscopy (NOESY) transfer experiments, ascertained an S_E reaction resulting in these two isomers. Until now, no 4-acyl or aroyl derivative had been obtained from such a reaction. Thus, the title compound, (I), constitutes an original chemical and pharmacological basis for further development, and elucidation of its structural characteristics is essential for establishing its interaction with biological receptors.



(I)

The conformation determined by X-ray diffraction is shown in Fig. 1. The carboxylic acid function C17(=O20)—O21—H21 and the O19 atom of the ketone function C10=O19 are on the same side of the C10—C11 bond. The most important torsion angles are C9—C4—C10—O19 9.0 (3), C12—C11—C10—O19 64.5 (3), C11—C12—C17—O21 165.8 (3) and C11—C12—C17—O20 16.2 (2)°. There is strong conjugation between the O19 atom and the benzene ring due to the quasi-perfect flatness of this moiety. The H21 atom lies on the opposite side of the C12—C17 bond to the O19 atom and the H(N) atom is 2.153 (2) Å from the O19 atom, so that there is no intramolecular hydrogen bond. There is, however, a strong intermolecular hydrogen bond between two neighbouring carboxyl groups, as shown in Fig. 2. The 3*H*-benzothiazolone ring is roughly planar [maximum deviation from the least-squares plane is 0.013 (1) Å for the S atom]. The dihedral angle between the 3*H*-benzothiazolone and benzoyl rings is 69.7 (4)°. The O20—C17—O21 group is markedly twisted [19.1 (3)°] with respect to the neighbouring phenyl ring.

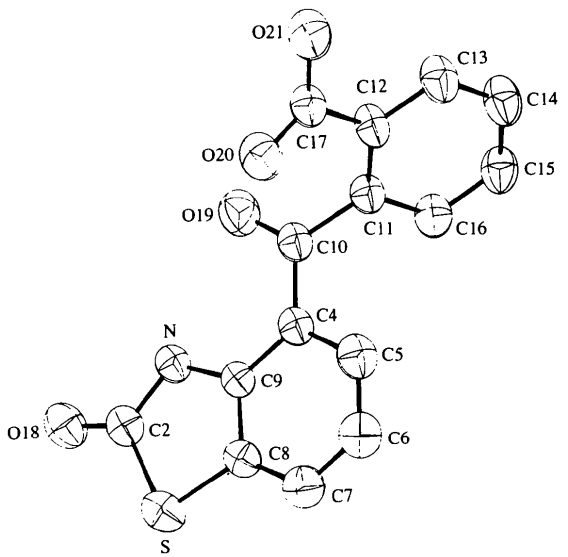


Fig. 1. *ORTEP*II (Johnson, 1976) drawing (50% probability ellipsoids) of the title compound showing the atom-labelling scheme.

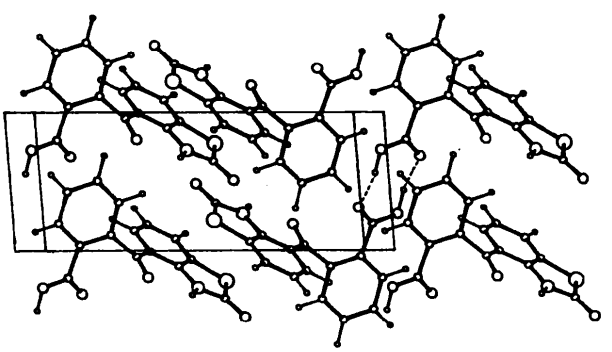


Fig. 2. Molecular packing of the title compound viewed down the *b* axis. Hydrogen bonds are illustrated by dotted lines.

Experimental

2(3*H*)-Benzothiazolone (1.2 eq.) was dissolved at 363 K in a mixture of aluminium chloride (9 eq.) and anhydrous dimethylformamide (2.8 eq.). Phthalic anhydride (1 eq.) was added and the mixture was stirred at 363 K for 3 h. After hydrolysis in ice–water, the resulting solid was dissolved in refluxing chloroform. 6-(2-Carboxybenzoyl)-2(3*H*)-benzothiazolone crystallized from the cold solution (50% yield). The concentrated filtrate was then boiled in acetone, whereupon the title compound precipitated. The crude precipitate was re-

crystallized from ethanol to yield pure 4-(2-carboxybenzoyl)-2(3*H*)-benzothiazolone in 5% yield. Single crystals were obtained by recrystallization from absolute ethanol solution (m.p. > 543 K). ^{1}H NMR (300 MHz, DMSO-d_6) δ (p.p.m.) 7.06 (H5, *dd*, J_{5-6} = 7.8, J_{5-7} = 1.0 Hz), 7.16 (H6, *dd*, J_{5-6} = 7.8, J_{6-7} = 7.8 Hz), 7.51 (H16, *dd*), 7.70 (H14, *ddd*), 7.78 (H15, *ddd*), 7.87 (H7, *dd*, J_{5-6} = 7.6, J_{5-7} = 1.0 Hz), 8.03 (H13, *dd*), 11.67 (NH, *s*, exchange with D_2O), 13.30 (COOH, *s*, exchange with D_2O); MS (FAB$^+$) *m/e* 300 (*M*H$^+$).

Crystal data

$C_{15}H_9NO_4S$
M_r = 299.2
Triclinic
$P\bar{1}$
a = 6.015 (2) Å
b = 8.052 (3) Å
c = 14.387 (5) Å
α = 98.83 (3)°
β = 94.21 (3)°
γ = 108.65 (3)°
V = 646.6 (4) Å^3
Z = 2
D_x = 1.537 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20–27°
μ = 0.215 mm^{-1}
T = 293 K
Plate
0.42 × 0.25 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3887 measured reflections
3764 independent reflections
2522 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.031
θ_{max} = 30°
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 20$
5 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
R = 0.0496
wR = 0.0557
S = 1.62
2522 reflections
193 parameters
$w = 1/[\sigma^2(F_o) + 0.001F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.03

$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) and Stewart, Davidson & Simpson (1965)

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

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

	x	y	z	U_{eq}
N	0.2704 (3)	0.0870 (2)	0.5807 (1)	0.049 (1)
S	0.2229 (2)	0.3604 (1)	0.5211 (1)	0.074 (1)
C2	0.3516 (4)	0.1896 (3)	0.5148 (1)	0.051 (2)
O18	0.4895 (3)	0.1719 (2)	0.4602 (1)	0.083 (2)
C9	0.1142 (3)	0.1359 (3)	0.6348 (1)	0.040 (2)
C8	0.0641 (4)	0.2830 (3)	0.6107 (1)	0.047 (2)
C7	−0.0887 (4)	0.3523 (3)	0.6565 (2)	0.064 (3)
C6	−0.1947 (5)	0.2732 (4)	0.7281 (2)	0.075 (3)
C5	−0.1487 (4)	0.1279 (3)	0.7529 (2)	0.068 (2)
C4	0.0046 (4)	0.0545 (3)	0.7069 (1)	0.050 (2)
C10	0.0458 (4)	−0.1047 (3)	0.7319 (1)	0.051 (2)
O19	0.1956 (3)	−0.1599 (3)	0.7000 (1)	0.098 (2)
C11	−0.1192 (4)	−0.2093 (3)	0.7922 (1)	0.052 (2)
C12	−0.0431 (4)	−0.2385 (3)	0.8805 (1)	0.054 (2)
C13	−0.2008 (4)	−0.3567 (4)	0.9259 (2)	0.070 (3)
C14	−0.4327 (4)	−0.4424 (4)	0.8854 (2)	0.072 (3)
C15	−0.5105 (4)	−0.4078 (4)	0.8000 (2)	0.059 (3)
C16	−0.3556 (4)	−0.2948 (3)	0.7534 (2)	0.058 (2)
C17	0.1977 (4)	−0.1346 (3)	0.9306 (1)	0.059 (2)
O20	0.3171 (3)	0.0054 (3)	0.9066 (1)	0.068 (2)
O21	0.2677 (3)	−0.1960 (3)	1.0002 (1)	0.076 (2)

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

S—C2	1.776 (3)	C10—O19	1.215 (3)
S—C8	1.734 (2)	C10—C11	1.504 (3)
C2—O18	1.209 (3)	C11—C12	1.399 (2)
C2—N	1.367 (2)	C12—C13	1.391 (4)
C9—N	1.376 (3)	C12—C17	1.484 (3)
C9—C8	1.397 (3)	C13—C14	1.379 (4)
C9—C4	1.405 (3)	C14—C15	1.383 (4)
C8—C7	1.377 (3)	C15—C16	1.372 (4)
C7—C6	1.383 (4)	C16—C11	1.395 (3)
C6—C5	1.376 (4)	C17—O20	1.243 (3)
C5—C4	1.398 (3)	C17—O21	1.283 (3)
C4—C10	1.471 (3)		
C2—S—C8	91.5 (1)	C4—C10—O19	122.2 (2)
S—C2—O18	123.7 (2)	C4—C10—C11	117.8 (2)
O18—C2—N	127.2 (2)	O19—C10—C11	119.7 (2)
S—C2—N	109.1 (2)	C10—C11—C12	123.3 (2)
C2—N—C9	115.8 (2)	C10—C11—C16	117.6 (2)
N—C9—C8	112.9 (2)	C16—C11—C12	118.8 (2)
C9—C8—S	110.8 (2)	C11—C12—C13	119.7 (2)
N—C9—C4	127.4 (2)	C11—C12—C17	121.1 (2)
C4—C9—C8	119.6 (2)	C13—C12—C17	119.0 (2)
C9—C8—C7	121.8 (2)	C12—C13—C14	120.5 (2)
S—C8—C7	127.4 (2)	C13—C14—C15	119.7 (3)
C8—C7—C6	118.6 (2)	C14—C15—C16	120.3 (3)
C7—C6—C5	120.6 (3)	C11—C16—C15	120.9 (2)
C6—C5—C4	121.8 (2)	C12—C17—O20	120.5 (2)
C5—C4—C9	117.6 (2)	C12—C17—O21	115.9 (2)
C9—C4—C10	121.7 (2)	O20—C17—O21	123.5 (2)
C5—C4—C10	121.2 (2)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21—H21···O20^i	1.12 (3)	1.49 (3)	2.610 (3)	172.5 (15)

Symmetry code: (i) $1-x, -y, 2-z$.

H atoms were located on difference electron density maps, then fixed at theoretical positions (C—H = 1.08, N—H = 1.01 Å, U = 0.07 Å^2), except for the H(O21) atom whose coordinates were refined.

Data collection and cell refinement were performed using *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction was carried out using *MolEN* (Fair, 1990). The structure was solved by direct methods using *SIR*88 (Burla *et al.*, 1989) and refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976), with anisotropic displacement parameters for all non-H atoms. Molecular graphics were prepared using *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1240). 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**, 1915–1917

Methyl 4-Oxo-*N*-(1-phenylethyl)-10-oxa-3-azatricyclo[5.2.1.$0^{1,5}$]dec-8-ene-6-carboxylate

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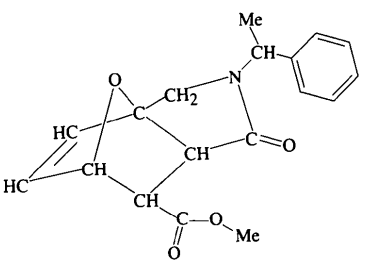
Abstract

The title compound, $C_{18}H_{19}NO_4$, is a precursor for numerous pharmacologically active compounds, the stereocontrol of the synthesis of which is of great importance.

Comment

The pyrrolidone ring is found in numerous natural products and a variety of pharmacologically active compounds (Marson, Grabowska, Walsgrove, Eggleston & Baurs, 1994). For example, pyrrolidone derivatives are used in the treatment of arteriosclerosis (Diaz, Monreal & Lucas, 1990). These molecules may act as potent neuroexitatory agents (Woo & Mullins, 1991) or neurotropic drugs (Toja, Gorini, Zirotti, Barzaghi & Galliani, 1987). Stereocontrol in the synthesis of these compounds is very important.

Our studies have demonstrated that stereocontrol can be achieved by the reaction of optically active furfurylamines with maleic anhydride. The mechanism of the reaction has been investigated previously with optically inactive compounds and proceeds by an intramolecular Diels–Alder reaction (Brun, Zylber, Pèpe & Reboul, 1994; Pèpe, Reboul, Brun & Zylber, 1995). With furfuryl *N*-1-phenylethylamine (*S*), the title compound, (I), is obtained as two diastereomeric adducts in a 65/35 ratio. These can be isolated in their pure forms. The cleavage of the oxa bridge of such systems leads to various functionalized disubstituted pyrrolidones with absolute control of the configuration of the different asymmetric centres (Ager & East, 1993).



(I)

The molecular configuration observed in the crystal studied here confirms the stereocontrol of the synthesis. The interatomic distances in the title compound have standard values and the only intermolecular contacts found are of van der Waals nature.

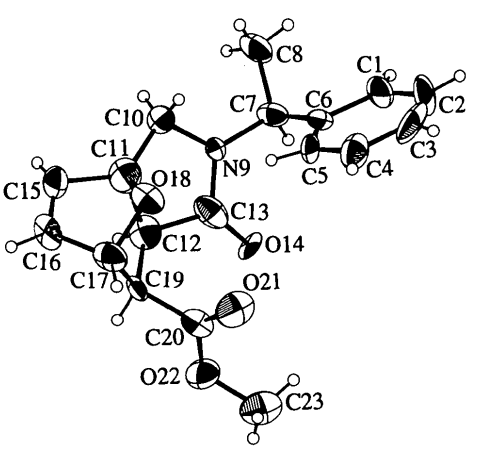


Fig. 1. An *ORTEP*II drawing (Johnson, 1976) of the title compound with displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are drawn as small spheres of arbitrary radii.