Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0399$
$wR(F^2) = 0.1071$
$S = 1.089$
2056 reflections
344 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 1.11P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0048 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.1 (3), not reliably determined

Table 1. *Selected torsion angles (°)*

C8—O8—C7—C16	−123.0 (4)	O8—C7—C16—O11	2.3 (6)
C15—O11—C16—C7	172.6 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H41···O12	0.92	2.09	2.980 (4)	171
N6—H61···O12	0.96	2.02	2.896 (5)	150
N5—H51···O1	1.02	1.76	2.723 (5)	154
O12—H122···O9^{i}	0.83	1.87	2.697 (4)	168
O12—H121···O5^{ii}	0.96	2.01	2.961 (5)	170

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, -y, z - \frac{1}{2}$.

The poor quality of the available crystals limited the resolution of the data and led in turn to a lower data/parameter ratio (6:1) than was hoped for. At convergence, the mean s.u. on a C—C bond was 0.006 Å. The amide, ammonium and water H atoms were located by difference Fourier synthesis, but were refined with restraints to maintain the geometry derived from the difference map. All other H atoms were placed geometrically. The hydrogen-bonding calculations were performed using *PARST* (Nardelli, 1983).

Data collection: *CRYSOM* (Siefert, 1996). Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *XRAY*-80 (Stewart, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXL*93.

GH would like to thank the Spanish Ministry of Education for a postdoctoral fellowship.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1115). 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. (1997). C**53**, 801–803

1-(1,3-Benzothiazol-2-yl)-2-(2-bromo-5-nitrophenyl)ethanone

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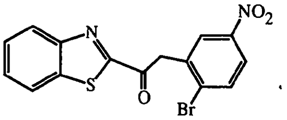
Abstract

The title compound, $C_{15}H_9BrN_2O_3S$, was isolated as an unexpected product from the reaction of the anion of sodium 2-(1,3-benzothiazolyl)ethanonitrile with α,2-dibromo-5-nitrotoluene. Its structure features a benzothiazole fragment and a bromo- and nitro-substituted phenyl ring linked by a methyl ketone group. The dihedral angle between the benzothiazole and phenyl rings is 103.7 (2)°. The benzothiazole fragment is planar, with a maximum deviation of 0.021 (2) Å. The nitro group is slightly rotated out of the phenyl-ring plane, with a O(2)—N(2)—C(14)—C(15) torsion angle of 16.4 (7)°.

Comment

As part of our continued interest in the synthesis of benzothiazolo[3,2-*a*]quinolinium salts (Cox *et al.*, 1982; Alegría *et al.*, 1993), we investigated the reaction of the anion of sodium 2-(1,3-benzothiazolyl)ethanonitrile with α,2-dibromo-5-nitrotoluene to give 2-(1,3-benzothiazolyl)-2-(2-bromo-5-nitrobenzyl)ethanonitrile. The title compound, (I), was unexpectedly obtained as a by-product. In order to identify this accidental product and confirm its chemical structure, the single-crystal X-ray structure analysis was carried out along with spectroscopic experiments such as NMR, FT–IR and mass spectroscopy.



(I)

The molecular structure of (I) is shown in Fig. 1. The structure consists of benzothiazole and 2-bromo-5-nitrophenyl groups linked by a methyl ketone group. The dihedral angle between the two aromatic rings is 103.7 (2)°. Since the benzothiazole ring is conjugated with the carbonyl group, the O(1)—C(8)—C(9) group is almost coplanar with the benzothiazole ring [dihedral angle 3.6 (5)°]. The C—N and S—C bond distances in the benzothiazole ring are comparable with those found in similar structures (Cox *et al.*, 1982; Alegría *et al.*, 1993). The structure is also consistent with all the spectroscopic data. In summary, the structure determination of the title compound by single-crystal X-ray crystallography confirmed that a different compound can also be formed under synthetic conditions. The formation of such a product is probably induced by dioxygen molecules in solution.

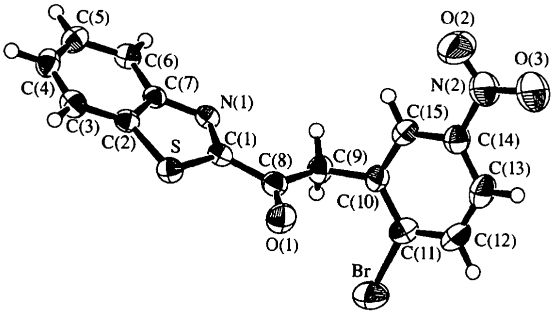


Fig. 1. An *ORTEP*II (Johnson, 1976) representation of the title compound showing 50% probability displacement ellipsoids.

Experimental

When sodium 2-(1,3-benzothiazolyl)ethanonitrile was allowed to react with α,2-dibromo-5-nitrotoluene in THF at 195 K, the title compound was obtained in 10% yield. After chromatographic separation, the compound (m.p. 417–419 K) was recrystallized from acetonitrile by slow evaporation of the solvent.

Crystal data

$C_{15}H_9BrN_2O_3S$
$M_r = 377.21$
Triclinic
$P\bar{1}$
$a = 5.6211\,(9)$ Å
$b = 7.356\,(1)$ Å
$c = 18.144\,(3)$ Å
$\alpha = 98.956\,(9)^\circ$
$\beta = 97.03\,(1)^\circ$
$\gamma = 99.326\,(9)^\circ$
$V = 722.9\,(2)$ Å^3
$Z = 2$
$D_x = 1.733$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 20$–25°
$\mu = 3.009$ mm^{-1}
$T = 295.2$ K
Platelet
0.40 × 0.35 × 0.05 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.566$, $T_{\max} = 0.860$
2972 measured reflections
2539 independent reflections

2056 reflections with $I > 2.5\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 24.97^\circ$
$h = 0 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -21 \rightarrow 21$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0317$
$wR = 0.0375$
$S = 1.766$
2056 reflections
199 parameters
H atoms: calculated and fixed

$w^{-1} = \sigma_c^2(F_o) + (p^2/4F_o^2)$, with $p = 0.03$
$(\Delta/\sigma)_{\max} = 0.0004$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Br—C(11)	1.892 (3)	N(1)—C(1)	1.298 (3)
S—C(1)	1.740 (3)	N(1)—C(7)	1.381 (3)
S—C(2)	1.730 (3)	N(2)—C(14)	1.472 (4)
O(1)—C(8)	1.209 (3)	C(1)—C(8)	1.479 (4)
O(2)—N(2)	1.210 (4)	C(8)—C(9)	1.513 (4)
O(3)—N(2)	1.200 (4)	C(9)—C(10)	1.508 (4)
C(1)—S—C(2)	88.5 (1)	N(1)—C(7)—C(2)	115.2 (2)
C(1)—N(1)—C(7)	109.9 (2)	N(1)—C(7)—C(6)	125.2 (2)
O(2)—N(2)—O(3)	123.1 (3)	O(1)—C(8)—C(1)	119.0 (2)
O(2)—N(2)—C(14)	118.6 (3)	O(1)—C(8)—C(9)	122.7 (2)
S—C(1)—N(1)	117.0 (2)	C(1)—C(8)—C(9)	118.3 (2)
S—C(1)—C(8)	117.2 (2)	C(8)—C(9)—C(10)	111.8 (2)
N(1)—C(1)—C(8)	125.8 (2)	Br—C(11)—C(10)	121.1 (2)
S—C(2)—C(3)	129.1 (2)	Br—C(11)—C(12)	117.6 (2)
S—C(2)—C(7)	109.5 (2)		

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4-*PC*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1:1 Deoxycholic Acid–Salicylic Acid Complex

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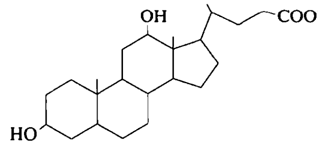
Abstract

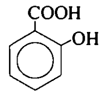
The 1:1 complex of deoxycholic acid [(3α,5β,12α)-3,12-dihydroxy-5-cholan-24-oic acid, $C_{24}H_{40}O_4$; DCA] and salicylic acid ($C_7H_6O_3$; SA) has been determined. The side-chain conformation of deoxycholic acid is *trans*, which is coupled with an intermediate conformation of ring *D*. No characteristic bilayer structure was found. Salicylic acid is trapped in a channel formed by DCA molecules.

Comment

Deoxycholic acid (DCA) is one of the bile acids having the interesting property of forming channel-type complexes with a wide variety of chemical compounds, for example, aliphatic and aromatic hydrocarbons, fatty acids, *etc.* (Giglio, 1984, and references therein). Many X-ray crystallographic studies have been carried out. Up to now, DCA–guest complexes have been grouped into three crystal systems, namely, orthorhombic, tetragonal and hexagonal. The first system is commonly observed and is able to include large non-polar molecules, while the rest can only accommodate small polar molecules such as ethanol and water (Coiro, Andrea & Giglio, 1979; Candeloro De Sanctis, Giglio, Petri & Quagliata, 1979). In this study, the crystal structure of DCA–SA (1/1) has been determined.



DCA



SA

The molecular structure is shown in Fig. 1. The DCA molecule is composed of four rings, *A*, *B*, *C* and *D*. Rings *A* and *B* are arranged in a *cis* manner resulting in the arched shape of the molecule. Rings *A*, *B* and *C* are considered to be rigid, whereas ring *D* is flexible and related to the conformation of the side chain. This feature varies among the DCA–guest complexes, although the side chain exhibits a '*gauche*' conformation and ring *D* approaches a 'half-chair' conformation in orthorhombic crystals (Giglio, 1984). The conformations in the present crystal are different. The conformation of ring *D* is suitably described by Δ, the phase angle of pseudo-rotation, and φ_m, the maximum angle of torsion (Altona, Geise & Romers, 1968). Selected torsion angles of the side chain are given in Table 1. The value of Δ in the DCA–SA complex is 14.5°. This value causes ring *D* to adopt a conformation intermediate between half chair and envelope. Five torsion angles of ring *D*, *i.e.* C17—C14—C15—C19, C18—C17—C14—C15, C19—C18—C17—C14, C15—C19—C18—C17

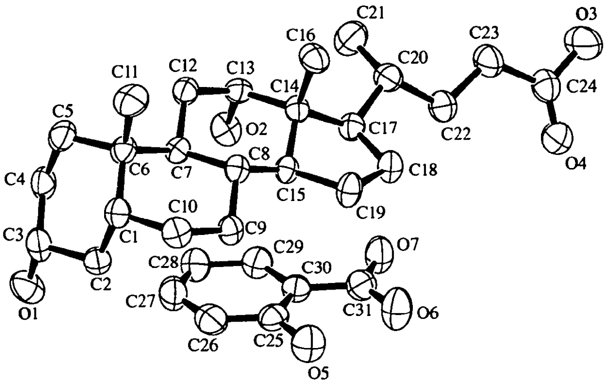


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the DCA–SA complex. Ellipsoids are drawn at the 50% probability level, while isotropic H-atom displacement parameters are represented by spheres of arbitrary size.