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Crystal and Molecular Structure of (S)-α-(*p*-Bromobenzenesulphonamido)-β-propiothiolactone*

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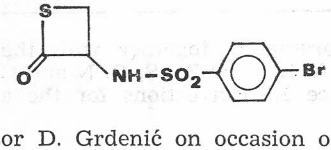
(S)-α-(p-Bromobenzenesulphonamido)-β-propiothiolactone, $C_9H_8NO_3S_2Br$, crystallizes in the orthorhombic system with $a = 1.0125(2)$, $b = 1.2439(1)$ and $c = 0.9304(3)$ nm, $Z = 4$ in space group $P2_12_12_1$. The compound is isostructural with the analogous chloro derivative. The crystal structure has been refined from diffractometer data to conventional R and R_G values of 0.045 and 0.048 for 2277 reflections with $I \geq 2\sigma(I)$. The heterocyclic four-membered ring has a puckering angle of 8.9(4)°. The dihedral angle between the best planes of the β-propiothiolactone and benzene rings is 84.1(2)°. The structure consists of discrete molecules connected along the a axis by intermolecular hydrogen bonds N—H...O of 291.9(7) pm.

INTRODUCTION

A series of chemical studies has recently been carried out on the polymerization reactions which α-substituted β-propiothiolactones undergo both in bulk and in solution[1-3]. This type of polymerization is important because the monomeric unit has a chiral carbon atom. The optically active polymers may be of chemical and biological interest because they represent a new class of nonamide-bonded polycysteines. The rate of polymerization is dependent on the nature of the substituent in the p-position on the benzene ring[4,5]. In order to study the possible effect of the p-substituent on the geometry of the heterocyclic ring and of intermolecular contacts on bulk polymerization[6], the crystal and molecular structures of some α-substituted β-propiothiolactones have been determined[7-12]. Here we report on the structure of (S)-α-(p-bromobenzenesulphonamido)-β-prophiothiolactone.



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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

EXPERIMENTAL

The crystals of the title compound are colourless prisms elongated along [100]. Preliminary cell dimensions and space group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were refined by least-squares using 15 $(\Theta\chi\varphi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal Data. — $C_9H_8NO_3S_2Br$, M = 322.21, orthorhombic, $a = 1.0125(2)$, $b = 1.2439(1)$, $c = 0.9304(3)$ nm, $V = 1.1718(4)$ nm^3, $Z = 4$, $D_m = 1.83$ (by flotation), $D_c = 1.826$ Mg m^{-3}. F(000) = 640. CuKα radiation; $\lambda = 154.18$ pm; μ (CuKα) = 8.070 mm^{-1}. Space group $P2_12_12_1$ from systematic absences.

Intensity Data, Structure Determination and Refinement. — Intensity data were collected on a Siemens single-crystal diffractometer up to Θ 70° by use of the $\omega - 2\,\Theta$ scan method and the »five points« technique[13] (Ni-filtered CuKα radiation). 2474 independent reflections were measured, of wich 2277, having intensities $I \geq 2\sigma(I)$, were used in the crystal analysis. The size of the crystal specimen was 0.14 × 0.14 × 0.33 mm. The data were corrected for Lorentz-polarization effects, but not for absorption.

The initial positions of the heavy atoms were taken from our earlier study of the isomorphous chloro derivative[7], whose intensities were measured photometrically. The refinement was carried out first with isotropic and then with anisotropic thermal parameters, reducing the R factor to 0.056. A difference electron-density synthesis located the hydrogen atoms close to the expected positions. A few least-squares cycles were then computed, including the hydrogen atoms with isotropic thermal parameters, to give the final conventional R factor of 0.045.

TABLE I

Fractional Atomic Coordinates (x 10^4, for H Atoms x 10^3) and Equivalent or Isotropic Thermal Parameters (pm^2) with Estimated Standard Deviations

$$U_{eq} = 1/3\, \Sigma_i\, \Sigma_j\, U_{ij}\, a_i^*\, a_j^*\, \vec{a}_i \cdot \vec{a}_j$$

	x	y	z	U_{eq}	U_{iso}
Br	285(1)	—1407(1)	2757(1)	69.0(6)	
S(1)	2722(3)	4146(1)	—1424(2)	73.0(8)	
S(2)	4317(2)	2536(1)	3233(2)	44.7(5)	
O(1)	1888(5)	2320(4)	—82(6)	38(2)	
O(2)	3726(5)	3318(3)	4166(5)	59(2)	
O(3)	5619(5)	2109(3)	5335(5)	60(2)	
N	4431(5)	3052(4)	1645(5)	44(2)	
C(1)	2522(6)	3139(4)	—111(7)	46(2)	
C(2)	3403(7)	3685(5)	994(6)	45(2)	
C(3)	3857(10)	4578(5)	—40(9)	67(3)	
C(4)	3205(5)	1445(4)	3096(6)	39(2)	
C(5)	3602(6)	507(4)	2416(8)	50(2)	
C(6)	2710(7)	—339(4)	2317(8)	54(2)	
C(7)	1466(6)	—229(4)	2897(7)	46(2)	
C(8)	1059(7)	690(5)	3566(7)	51(2)	
C(9)	1950(7)	1550(5)	3685(7)	48(2)	
H(1)	509(8)	280(5)	125(8)		12(2)
H(2)	285(5)	403(4)	176(6)		5(2)
H(31)	474(12)	439(9)	—32(13)		16(5)
H(32)	347(10)	526(8)	40(11)		14(4)
H(5)	457(6)	58(6)	212(9)		11(3)
H(6)	307(5)	—93(4)	178(6)		5(2)
H(8)	13(10)	73(7)	398(10)		15(4)
H(9)	188(9)	223(5)	433(8)		7(2)

All calculations were performed on the CDC Cyber 76 computer using the SHELX-76 system of programmes[17]. Lists of structure factors and anisotropic thermal parameters are available on request.

TABLE II

Interatomic Distances (pm) with e.s.d.'s in Parentheses

S(1) — C(1)	176.2(6)	C(6) — C(7)	137.6(8)
S(1) — C(3)	180.8(8)	C(7) — C(8)	136.5(8)
C(1) — C(2)	152.1(8)	C(8) — C(9)	140.4(8)
C(2) — C(3)	154.0(9)	C(7) — Br	189.5(5)
C(1) — O(1)	120.5(7)	N — H(1)	82(8)
N — C(2)	143.8(7)	C(2) — H(2)	101(4)
N — S(2)	161.5(5)	C(3) — H(31)	96(11)
S(2) — O(2)	143.5(4)	C(3) — H(32)	102(10)
S(2) — O(3)	144.9(5)	C(5) — H(5)	102(5)
S(2) — C(4)	176.7(5)	C(6) — H(6)	96(5)
C(4) — C(5)	138.7(7)	C(8) — H(8)	102(9)
C(4) — C(9)	139.0(8)	C(9) — H(9)	103(6)
C(5) — C(6)	138.9(8)		

TABLE III

Bond Angles (°) with e.s.d.'s in Parentheses

C(1) — S(1) — C(3)	77.9(3)	O(3) — S(2) — C(4)	108.2(2)
S(1) — C(1) — C(2)	94.8(4)	N — S(2) — C(4)	106.5(2)
S(1) — C(3) — C(2)	92.4(4)	S(2) — C(4) — C(5)	119.6(4)
C(1) — C(2) —C(3)	94.3(5)	S(2) — C(4) — C(9)	118.8(4)
O(1) — C(1) — S(1)	132.7(5)	C(5) — C(4) — C(9)	121.6(5)
O(1) — C(1) — C(2)	132.4(5)	C(4) — C(5) — C(6)	118.6(5)
C(1) — C(2) — N	117.7(5)	C(5) — C(6) — C(7)	119.6(5)
C(3) — C(2) — N	116.2(6)	C(6) — C(7) — C(8)	122.5(5)
C(2) — N — S(2)	123.4(4)	C(7) — C(8) — C(9)	118.7(6)
O(2) — S(2) — O(3)	120.7(3)	C(8) — C(9) — C(4)	119.0(5)
O(2) — S(2) — N	108.3(2)	C(6) — C(7) — Br	118.2(4)
O(3) — S(2) — N	104.9(3)	C(8) — C(7) — Br	119.1(5)
O(2) — S(2) — C(4)	107.4(3)		

TABLE IV

Selected Torsion Angles (°) with e.s.d.'s in Parentheses

S(1) — C(1) — C(2) — C(3)	—6.6(5)
C(1) — C(2) — C(3) — S(1)	—6.5(5)
C(1) — S(1) — C(3) — C(2)	5.7(4)
C(3) — S(1) — C(1) — C(2)	5.8(4)
C(3) — S(1) — C(1) — O(1)	—175.8(7)
S(1) — C(1) — C(2) — N	—129.3(5)
O(1) — C(1) — C(2) — N	52.2(9)
O(1) — C(1) — C(2) — C(3)	174.9(7)
N — C(2) — C(3) — S(1)	130.2(5)
C(1) — C(2) — N — S(2)	—101.2(6)
C(3) — C(2) — N — S(2)	148.2(5)
C(2) — N — S (2) — C(4)	73.5(5)
C(2) — N — S(2) — O(2)	—41.8(6)
C(2) — N — S(2) — O(3)	—171.9(5)
O(2) — S(2) — C(4) — C(5)	—171.2(5)
O(2) — S(2) — C(4) — C(9)	8.4(6)
O(3) — S(2) — C(4) — C(5)	—39.4(6)
O(3) — S(2) — C(4) — C(9)	140.2(5)
N — S(2) — C(4) — C(5)	73.0(5)
N — S(2) — C(4) — C(9)	—107.4(5)

RESULTS AND DISCUSSION

The molecular conformation and the atomic numbering scheme is illustrated in Figure 1. Interatomic distances and angles with their standard deviations are given in Tables II and III, while selected torsion angles are listed in Table IV. Projection of the molecule along the bond S(2)-N is shown in Figure 2. Molecular packing with the hydrogen bonding scheme is illustrated in Figure 3. Details of least-squares planes calculated for various parts of the molecule are given in Table VI.

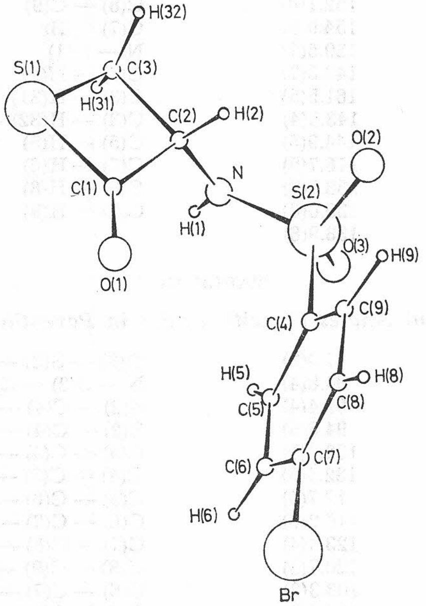

Figure 1. Perspective drawing of the molecule.

The main feature of interest is the geometry and conformation of the heterocyclic four-membered ring. In general the puckering of four- membered rings depends on the balance between two opposing forces in the molecule: the ring strain (caused by the narrowing of the ring angles and by the cross-ring repulsion) and the torsional strain (caused by the non-bonded interactions among vicinal substituents).

As expected and shown by the torsion angles (Table IV) the thietane ring is not planar. The puckering angles between the planes defined by S(1), C(1), C(2) and S(1), C(3), C(2) and by C(1), C(2), C(3) and C(1), S(1), C(3) are 8.9(4) and 8.4(5)°, respectively. This conformation is consistent with those reported in several other recent X-ray structural investigations (Table V). No strict correlation can be established between puckering angles and steric hindrance of the vicinal substituents. However, we can say that smaller puckering angles (~ 10°) have been observed when some of the substituents on C(sp^3) atoms are hydrogens, while greater puckering angles (~ 20°) have been observed for the ring with bulky substituents on vicinal carbons. This is also evident in *cis*-2,2-diphenyl-3,4-dichlorothietane[23] with the puckering angle B = 28.9° and in 5,7-diazo-3-cyano-3,5,7-trimethyl-6-oxo-1-thiaspiro [3,5]nonane[24] with the puckering angle B = 18°.

TABLE V

Geometrical Data of Thietane Rings, Distances in pm and Angles in Degrees

	S—C(sp^3)	S—C(sp^2)	C—S—C	Puckering angles		Ref.
				A*	B**	
3-(*p*-ClPh—SO_2—NH—)thietan-2-one	185(2)	176(2)	78(1)	13	—	7,8
3-(Ph—SO_2—NH—)thietan-2-one	184.0(9)	179.1(8)	77.6(4)	11.2	—	9
3-(*p*-CH_3OPh—SO_2—NH—)thietan-2-one	182.2(5)	175.5(4)	77.1(2)	8.3	—	10
3-(*p*-O_2N—SO_2—NH—)thietan-2-one	183.2(5)	176.3(5)	77.3(2)	8.7	—	11
2-(R_2C=)thietane	182.3(8)	177.3(6)	77.5(3)	0	0	18
2-($R_2'C$=)thietane	184(1)	174.9(6)	76.5(4)	—	5	19
2-(R—N=)-3,3-dimethyl-4,4-diphenylthietane	186.8(3)	177.7(5)	77.0(2)	21	20	20
2-(R—N=)-3-methyl-4-ethoxythietane	187.1	173.9	76.4	0	0	21
Dispiro compound***	183.4(5)	176.1(6)	78.0(2)	9.7(4)	—	22
Present structure	180.8(8)	176.2(6)	77.9(3)	8.9(4)	8.4(5)	

* A = dihedral angle between the S(1), C(1), C(2) and S(1), C(3), C(2) planes.

** B = dihedral angle between the C(1), S(1), C(3) and C(1), C(2), C(3) planes.

*** 2-isopropylidene-1,1,7,7,9,9-hexamethyl-3,5,10,11-tetrathiodispiro[3.1.3.2]undecane-8-thione.

TABLE VI

Least-Squares Planes and Atomic Distances from These Planes. The Plane Equations Are of the Form $PX+QY+RZ=S$, Where X, Y and Z are in pm Relative to Orthogonal Axes

(a) Plane:		P	Q	R	S
I	S(1), C(1), C(2)	—79.31	48.61	36.70	—16.50
II	S(1), C(2), C(3)	—70.03	61.04	37.02	72.76
III	S(1), C(1), C(3)	—72.90	53.47	42.74	18.22
IV	C(1), C(2), C(3)	—76.87	56.98	29.06	23.18
V	S(1), C(1), C(2), O(1)	78.74	—49.41	—36.85	11.07
VI	S(1), C(1), C(2), C(3), O(1)	76.97	—50.82	—38.65	01.81
VII	C(4), C(5), C(6) C(7), C(8), C(9)	—33.25	36.08	—87.14	—294.29

(b) Deviations in pm From Planes:

V		VI		VII	
S(1)	0.0	S(1)	—0.5	C(4)	0.2
C(1)	0.9	C(1)	0.3	C(5)	—0.1
C(2)	—0.3	C(2)	—5.3	C(6)	0.0
O(1)	—0.3	C(3)	10.8	C(7)	—0.2
		O(1)	1.6	C(8)	0.5
				C(8)	—0.6
				S(2)	0.7
				Br	—2.0

(c) Dihedral angle Between Planes (°)

I, II	8.9(4)	V, II	8.3(4)
III, IV	8.4(5)	VI, VII	84.1(2)

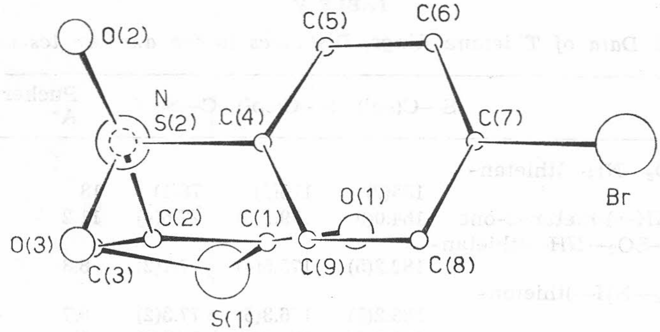

Figure 2. Projection of the molecule looking along S(2)—N bond.

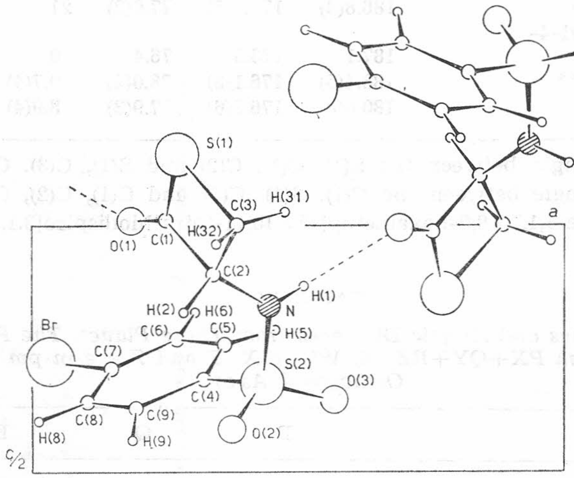

Figure 3. Molecular packing along [010].

The S^{II}—C(sp^3) and S^{II}—C(sp^2) distances (180.8(8)) and 1.76.2(6) pm) indicate single bonds and agree well with the values reported by Argay et al.[25], (179,6 and 176.8 pm) and by Bocelli and Grenier-Loustalot (180.9 and 176.5 pm). The C—S—C angle of 77.9(3)° is comparable to other values found in thietane rings (Table V).

The bond lengths and bond angles in the arylsulphonamide group agree with the values typical for S^{VI} atoms in *N*-sulphonylsulphilimines[27] and other sulphonamide compounds[28-31]. The atoms around the sulphur atom S(2) are arranged in an approximately tetrahedral coordination with an enlarged O—S—O angle, 120.7(3)°, as expected. All the other angles are below the tetrahedral value. The shortening of all bond lengths around S(2) may suggest that 3d orbitals are used in π-bond formation[32]. The S^{VI}—N bond distance of 161.5(5) pm is comparable to the mean value of 161 pm for four benzenesulphonamides[30] and 161.0 pm for *N*-substituted pyrole derivative[33].

The C—C distances in the benzene ring are influenced by the substituents: those neighbouring the SO_2 group are approximately 2 pm longer than those neighbouring the Br atom.

TABLE VII

Selected Intermolecular Distances (pm)

$N\ldots O(1)^{I}$	291.9(7)
$H(1)\ldots O(1)^{I}$	213(8)
$S(1)\ldots Br^{I}$	402.3(3)
$Br\ldots O(1)^{II}$	367.8(5)
$Br\ldots S(1)^{II}$	403.2(2)
$Br\ldots C(1)^{II}$	367.5(6)
$O(1)\ldots Br^{III}$	346.8(5)
$C(1)\ldots Br^{III}$	363.2(6)
$S(1)\ldots Br^{III}$	462.4(2)
$S(1)\ldots O(2)^{IV}$	352.2(4)
$S(1)\ldots O(3)^{IV}$	329.1(5)

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference molecular at x, y, z:

I $x + 1/2, -y + 1/2, -z$
II $-x + 1/2, -y, z + 1/2$
III $-x, y + 1/2, -z + 1/2$
IV $-x + 1/2, -y + 1, z - 1/2$
V $x - 1/2, -y + 1/2, -z$

Projection along the S(2)—N bond is shown in Figure 2. The two rings are almost perpendicular to each other (dihedral angle between the mean planes is 84.1(2)°).

The intermolecular hydrogen bond N—H(1)... O(1) of 291.9(7) pm along the *a* axis is another important feature of the title compound. The angle N—H(1)... O(1) is 162(6)°. The other intermolecular distances are given in Table VII. It is worth mentioning (in the sense of the possibility of bulk polymerization) that the distances between the Br atom and the atoms which are included in polymerization S(1) and C(1) are 403.2(2), 367.5(6) and 462.4(2), 363.2(6) pm, respectively. The S(1)—O(3) and S(1)—O(2) distances of 329.2(4) and 352.2(4) pm respectively suggest at most extremely weak interactions.

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SAŽETAK

Kristalna i molekularna struktura (S)-α-(*p*-brombenzensulfonamido-β-propiotiolaktona

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(S)-α-(*p*-Brombenzensulfonamido)-β-propiotiolakton, $C_9H_8NO_3S_2Br$, kristalizira u rompskom sustavu sa $a = 1,0125(2)$, $b = 1,2439(1)$ i $c = 0,9304(3)$ nm, $Z = 4$ u prostornoj grupi $P2_12_12_1$. Spoj je izostrukturan s analognim klor derivatom. Koristeći difraktometarske podatke struktura je utočnjena do vrijednosti za $R = 0,045$ i $R_6 = 0,048$ za 2277 refleksa sa $I \geq 2\sigma(I)$. Četveročlani heterociklički prsten nije planaran i kut izvijanja iznosi 8,9(4)°. Diedarski kut između ravnina položenih β-propiotiolaktonskim i benzenovim prstenom iznosi 84,1(2)°. Struktura se sastoji od molekula povezanih duž osi *a* intermolekulskom vodikovom vezom N—H... O od 291,9(7) pm.