Crystal and molecular structure of (S)-a-(pCyanobenzenesulphonamido)-B- propiothiolactone, C10H8N203S2

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Crystal and Molecular Structure of (S)-α-(*p*-Cyanobenzenesulphonamido)-β-propiothiolactone, $C_{10}H_8N_2O_3S_2$

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Crystals of the title compound are monoclinic, space group $P2_1$, with $a = 1.0018(2)$, $b = 0.9722(2)$, $c = 0.6262(1)$ nm, $\beta = 102.32(1)^\circ$ and $Z = 2$. The structure was solved by direct methods using 1113 reflections with $I \geq 2\sigma(I)$ and refined to a conventional R index of 0.051. The heterocyclic four-membered ring is bent and has a puckering angle of 18.7(7)°. The dihedral angle between the best planes of the β-propiothiolactone and benzene ring is 70.2(3)°. Discrete molecules are connected along the b axis by intermolecular hydrogen bonds N—H . . . 0 of 309.5(9) pm.

INTRODUCTION

The structure of the title compound was determined as a part of a continuing study of the α-substituted β-propiothiolactones.[1–4] These optically active compounds polymerized in solution and in bulk giving the polymers[5–7] which represent a new class of nonamide-bonded polycysteins. The rate of polymerization is dependent on the nature of the substituent in the *p*-position on the benzene ring[8,9], which is, however, quite far from the atoms involved in polymerization.

This X-ray study was undertaken in order to establish the possible effect of the *p*-substituent on the geometry of β-propiothiolactone ring and of intermolecular contacts on bulk polimerization[10].

EXPERIMENTAL

The crystals are colourless prisms elongated along [010]. Preliminary cell dimensions and space group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were refined by least-squares using 15 reflections taken on a Siemens AED single-crystal diffractometer.

Crystal Data. — $C_{10}H_8N_2O_3S_2$, $M = 268.31$, monoclinic, space group $P2_1$, $a = 1.0018(2)$, $b = 0.9722(2)$, $c = 0.6262(1)$ nm, $\beta = 102.32(1)^\circ$, $V = 0.5958(2)$ nm^3, $Z = 2$, $D_c = 1.496$ Mgm^{-3}, $F(000) = 276$, Cu$K\alpha$ radiation; $\lambda = 154.18$ pm, μ(Cu$K\alpha$) = 3.998 mm^{-1}.

Intensity Data, Structure Determination and Refinement. — Intensity data were collected on a Siemens AED diffractometer up to Θ 70° by the $\omega - 2\Theta$ scan method (Ni-filtered Cu$K\alpha$ radiation). 1262 reflections were measured, of which 1113, having intensities $I \geq 2\sigma(I)$ were used in the crystal analysis. The size of the crystal specimen was 0.07 × 0.15 × 0.49 mm. No absorption correction was applied.

The structure was solved by direct methods using SHELX-76[11]. An E-map computed by the use of phase set for 151 normalized structure factors having $E \geq 1.4$ revealed the positions of six atoms. A subsequent Fourier synthesis located the remaining non-hydrogen atoms. The refinement was carried out with isotropic ($R = 0.119$) and anisotropic thermal parameters, reducing R factor to 0.072. A difference Fourier synthesis revealed the positions of the hydrogen atoms, except H(5) and H(9). Including the hydrogen atoms with isotropic thermal parameters the refinement resulted in the final R factor of 0.051.

TABLE I

Fractional Atomic Coordinates (× 10^4, for H Atoms × 10^3) and Equivalent or Isotropic Thermal Parameters (pm^2) with Estimated Standard Deviations.
$U_{eq} = 1/3\ \Sigma_i\Sigma_j\ U_{ij}a_i^*a_j^*a_i \cdot a_j$

	x	y	z	U_{eq}/U_{iso}
S(1)	2680(4)	560(4)	6902(4)	8.5(1)
S(2)	—648(2)	1986	—13(3)	4.6(1)
O(1)	3345(9)	2478(11)	4195(15)	11.6(4)
O(2)	—674(6)	1732(8)	—2278(9)	5.7(2)
O(3)	—625(7)	3378(6)	821(9)	5.6(2)
N(1)	703(8)	1244(8)	1353(11)	5.0(3)
N(2)	—6411(11)	—1319(14)	2596(16)	10.6(5)
C(1)	2520(12)	1724(12)	4669(16)	6.5(4)
C(2)	1091(10)	1348(10)	3710(13)	5.3(3)
C(3)	1119(13)	53(11)	5085(15)	6.8(4)
C(4)	—2065(8)	1148(9)	662(13)	4.6(3)
C(5)	—2622(11)	12(12)	—524(17)	6.6(4)
C(6)	—3719(10)	—642(12)	17(19)	7.2(4)
C(7)	—4288(9)	—172(10)	1703(15)	6.1(3)
C(8)	—3713(9)	962(11)	2907(16)	6.3(4)
C(9)	—2615(11)	1611(10)	2401(16)	6.0(4)
C(10)	—5447(10)	—828(14)	2236(18)	7.3(4)
H(1)	71(9)	44(6)	60(13)	8(2)
H(2)	59(7)	215(7)	427(12)	9(2)
H(31)	128(9)	—63(7)	387(14)	8(3)
H(32)	12(7)	12(9)	550(13)	14(3)
H(5)	—202(9)	—41(9)	—154(12)	10(3)
H(6)	—415(10)	—126(11)	—125(15)	10(3)
H(8)	—428(9)	133(9)	379(14)	13(3)
H(9)	—202(8)	234(7)	346(12)	12(3)

The positional parameters and equivalent or isotropic thermal parameters are given in Table I. The atomic scattering factors for non-hydrogen atoms were from ref. 12 and those for hydrogen atoms from ref. 13. Correction for the anomalous dispersion was taken from ref. 14. All calculations were carried out on the CDC Cyber 76 computer using the SHELX-76 program. Lists of structure factors and anisotropic thermal parameters are available from the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The molecular conformation and the atomic numbering scheme are shown in Figure 1. Interatomic distances and angles 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(1) is shown in Figure 2. Molecular packing with hydrogen bonding scheme is illustrated in Figure 3. Details on the least-square planes calculated for various parts of molecule are given in Table V.

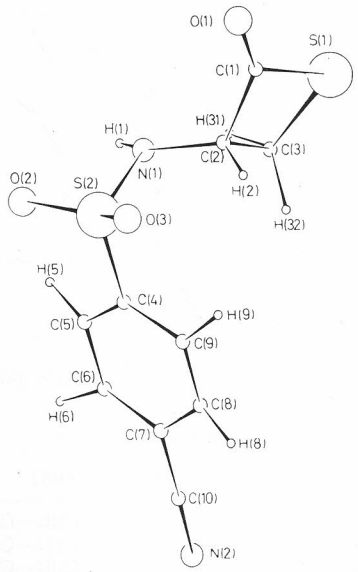

Figure 1. Perspective view of the molecule.

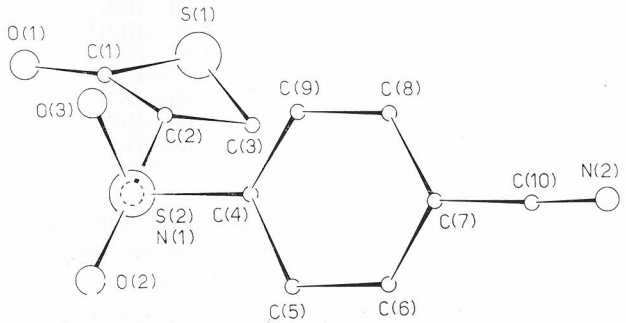

Figure 2. Projection of the molecule looking along *S*(2)—*N*(1) bond.

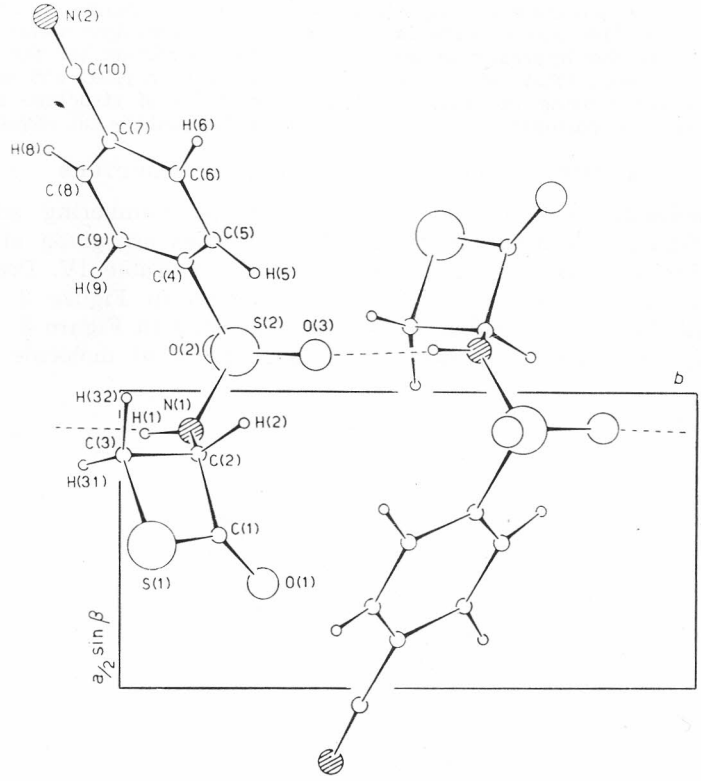

Figure 3. Molecular packing with hydrogen bonding scheme.

TABLE II

Interatomic Distances (pm)

S(1)—C(1)	177.8(9)	C(6)—C(7)	138.0(11)
S(1)—C(3)	180.4(10)	C(7)—C(8)	139.0(11)
C(1)—C(2)	147.5(12)	C(8)—C(9)	136.3(11)
C(1)—O(1)	118.9(10)	C(7)—C(10)	142.6(11)
C(2)—C(3)	152.2(10)	C(10)—N(2)	114.2(10)
N(1)—C(2)	144.8(8)	N(1)—H(1)	92(4)
N(1)—S(2)	160.9(6)	C(2)—H(2)	103(4)
S(2)—O(2)	143.4(4)	C(3)—H(31)	105(4)
S(2)—O(3)	144.9(5)	C(3)—H(32)	109(4)
S(2)—C(4)	176.5(7)	C(5)—H(5)	105(4)
C(4)—C(5)	138.0(10)	C(6)—H(6)	102(8)
C(4)—C(9)	139.6(9)	C(8)—H(8)	95(7)
C(5)—C(6)	137.3(12)	C(9)—H(9)	106(4)

The most important feature of this molecule is the conformation of the four-membered hetero ring. As expected the thietane ring is puckered. The puckering angle between planes S(1) C(1) C(2) and S(1) C(3) C(2) is 18.7(7) while that between planes C(1) C(2) C(3) and C(1) S(1) C(3) is 17.6(5)°. These angles in the present structure are significantly larger than those of the

TABLE III

Bond Angles (°)

C(1)—S(1)—C(3)	75.7(4)	O(3)—S(2)—C(4)	107.2(3)
S(1)—C(1)—C(2)	94.8(5)	N(1)—S(2)—C(4)	107.1(3)
S(1)—C(3)—C(2)	92.2(6)	S(2)—C(4)—C(5)	119.6(6)
C(1)—C(2)—C(3)	94.3(7)	S(2)—C(4)—C(9)	120.6(6)
O(1)—C(1)—S(1)	129.3(8)	C(9)—C(4)—C(5)	119.8(7)
O(1)—C(1)—C(2)	135.8(8)	C(4)—C(5)—C(6)	119.4(8)
C(1)—C(2)—N(1)	117.3(6)	C(5)—C(6)—C(7)	121.2(8)
C(3)—C(2)—N(1)	119.1(7)	C(6)—C(7)—C(8)	119.2(7)
C(2)—N(1)—S(2)	121.5(5)	C(7)—C(8)—C(9)	120.2(7)
O(2)—S(2)—O(3)	120.8(3)	C(8)—C(9)—C(4)	120.3(7)
O(2)—S(2)—N(1)	106.5(3)	C(6)—C(7)—C(10	121.4(8)
O(2)—S(2)—N(1)	106.3(3)	C(8)—C(7)—C(10)	119.4(8)
O(2)—S(2)—C(4)	108.2(3)	C(7)—C(10)—N(2)	177.1(11)

TABLE IV

Selected Torsion Angles (°)

S(1)—C(1)—C(2)—C(3)	—13.9(8)
C(1)—C(2)—C(3)—S(1)	13.7(8)
C(1)—S(1)—C(3)—C(2)	—11.7(7)
C(3)—S(1)—C(1)—C(2)	12.1(7)
C(3)—S(1)—C(1)—O(1)	—165.8(14)
O(1)—C(1)—C(2)—C(3)	163.7(15)
S(1)—C(1)—C(2)—N(1)	—140.8(8)
O(1)—(C1)—C(2)—N(1)	37.6(19)
N(1)—C(2)—C(3)—S(1)	138.4(8)
C(1)—C(2)—N(1)—S(2)	—131.1(8)
C(3)—C(2)—N(1)—S(2)	116.2(9)
C(2)—N(1)—S(2)—C(4)	—67.5(8)
C(2)—N(1)—S(2)—O(2)	176.9(7)
C(2)—N(1)—S(2)—O(3)	46.9(8)
O(2)—S(2)—C(4)—C(5)	25.8(8)
O(2)—S(2)—C(4)—C(9)	—155.1(7)
O(3)—S(2)—C(4)—C(5)	157.7(7)
O(3)—S(2)—C(4)—C(9)	—23.2(8)
N(1)—S(2)—C(4)—C(5)	—88.6(8)
N(1)—S(2)—C(4)—C(9)	90.5(8)

corresponding derivatives with Cl, Br and H in *p*-position on the benzene ring[1–3] (13, 8.9 and 11.2°, respectively) but they are comparable with the values reported for some thietane derivatives with bulky substituents on vicinal carbons[15,16] or for spiro compounds with thietane moiety[17].

The values for S—C(sp^3) and S—C(sp^2) bond lengths are 180.4(10) and 177·8(9) pm, in agreement with the corresponding values reported for Br--derivative[3] and those of Argay[18] and Bocelli[19]. The C(1)—C(2) of 147.5(12) pm is much shorter than the C(2)—C(3) [152.2(10) pm]. The values of bond angles inside the ring show clearly the strain the ring is submitted to. The C(1)—S(1)—C(3) angle of 75.7(4)° is the smallest value reported so far for the thietane derivatives[1-4,15-17,20-24].

Atoms around the sulphur atom S(2) are arranged in a distorted tetrahedral coordination with enlarged O—S—O angle like in other sulphonamido compounds.

Projection along the S(2)—N(1) bond is illustrated in Figure 2. There is a great difference in orientation of the heterocyclic and benzene rings according to the analogous Cl and Br derivatives[1,3]. These facts are also evident in the comparison of the corresponding torsion angles. The dihedral angle between the mean planes of two rings is 70.2(3)°.

The values of distances and angles in cyano group are in accordance with the known values in the literature[25-27]. The short C≡N distance is a typical problem in the X-ray structure analysis[28]. This effect is due to thermal motion of the atoms and to the high electron density between the triple-bonded atoms. From Table V it is evident that these two atoms deviate significantly from the mean plane of the benzene ring.

TABLE V

Least-Squares Planes and Atomic Distances from These Planes. The Plane Equtations 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)	—44.5	71.0	54.6	190.4
II	S(1), C(2), C(3)	—66.2	47.1	58.3	154.5
III	S(1), C(1), C(3)	—62.2	63.1	46.4	120.2
IV	C(1), C(2), C(3)	—46.7	53.0	70.7	202.2
V	S(1), C(1), C(2), O(1)	43.4	—71.8	—54.4	—191.9
VI	S(1), C(1), C(2), C(3), O(1)	51.4	—68.4	—51.7	—162.9
VII	C(4), C(5), C(6), C(7), C(8), C(9)	—49.5	59.9	—63.0	147.6

(*b*) Deviations in pm From Planes:

V		VI		VII	
S(1)	0.0	S(1)	—1.4	C(4)	0.6
C(1)	—1.3	C(1)	—1.6	C(5)	—0.1
C(2)	0.3	C(2)	—13.3	C(6)	—1.0
O(1)	0.5	C(3)	21.4	C(7)	0.8
		O(1)	9.0	C(8)	—0.2
				C(9)	—0.7
				C(10)	3.1
				S(2)	0.6
				N(2)	10.8

(*c*) Dihedral Angle Between Planes (°)

I, II	18.7(7)	II, V	19.5(5)
III, IV	17.6(5)	VI, VII	70.2(3)

Molecules are connected in an infinitive chain along the *b* axis by hydrogen bonds N(1)—H(1)···O(3) of 309.5(9) pm; the angle is 172.(8)°. It is worth mentioning that the O atom participating in this hydrogen bond is from sulphonamido and not from thiolactone group, as in Br derivative[3].

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SAŽETAK

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

I. Matijašić, G. D. Andreetti, P. Sgarabotto, A. Bezjak i D. Fleš

Spoj kristalizira u monoklinskom sustavu sa $a = 1{,}0018(2)$, $b = 0{,}9722(2)$, $c = 0{,}6262$ pm i $\beta = 102{,}32(1)^\circ$, $Z = 2$ u prostornoj grupi $P2_1$. Struktura je riješena direktnim metodama upotrebom 1113 refleksa sa $I \geq 2\sigma(I)$ i utočnjena do $R = 0{,}051$. Heterociklički četveročlani prsten ima kut izvijanja od $18{,}7(7)^\circ$. Diedarski kut između ravnina položenih β-propiotiolaktonskim i benzenskim prstenom iznosi $70{,}2(3)^\circ$. Struktura se sastoji od molekula povezanih duž osi *b* intermolekulskom vodikovom vezom N—H...O od 309,5(9) pm.