Acta Cryst. (1980). B**36**, 1709–1710

3-(*p*-Bromobenzoyl)-1,3-thiazolidine-2-thione

By R. F. Bryan, P. Hartley and S. Peckler

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, *USA*

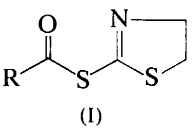
and E. Fujita, Y. Nagao and K. Seno

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, *Japan*

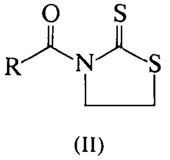
(*Received* 14 *September* 1979; *accepted* 8 *January* 1980)

Abstract. $C_{10}H_8BrNOS_2$, orthorhombic, *Pbca*, $a = 7{\cdot}166\,(4)$, $b = 14{\cdot}716\,(9)$, $c = 21{\cdot}507\,(12)$ Å ($\lambda = 1{\cdot}5418$ Å), $U = 2268$ Å^3, $Z = 8$, $D_x = 1{\cdot}77$ Mg m^{-3} = D_m (flotation in C_2H_5I/toluene), $F(000) = 1200$, μ(Cu $K\alpha$) = 8·5 mm^{-1}. The structure was solved by the heavy-atom method. Refinement led to $R = 0{\cdot}037$ for 1366 independent significant [$I > 3\sigma(I)$] reflections. The chemical identity of the title compound was established by the analysis, distinguishing it from the isomeric thioester. The thiazolidine ring has a C(4) envelope conformation. With respect to the planar amide unit, the phenyl-ring plane is inclined at 32° and the four-atom planar unit of the thiazolidine ring at 49°. This non-planar conformation is attributed to potential intramolecular interactions between lone pairs of electrons on the thio and carbonyl groups.

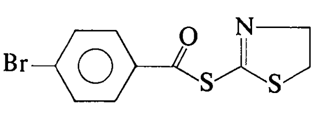
Introduction. Nagao, Kawabata & Fujita (1978) have published a procedure for the reduction of carboxylic acids to alcohols or aldehydes by sodium borohydride or diisobutylaluminium hydride *via* Δ^2-1,3-thiazoline-2-thiol esters (I). Izawa & Mukaiyama (1977) have reported a similar reduction, but *via* the isomeric 3-acyl-1,3-thiazolidine-2-thione (II) prepared by a different method. For identical *R* groups, the intermediates in both procedures are the same. To solve the problem of chemical identity, a single-crystal X-ray analysis was carried out on the *p*-bromobenzoyl derivative (III), which was prepared by treatment of the thallium salt of Δ^2-1,3-thiazoline-2-thiol (1,3-thiazolidine-2-thione) with *p*-bromobenzoyl chloride. The material was obtained by recrystallizaton from chloroform as yellow prisms of m.p. 391·5–392·5 K. The correct structure is (III*b*).



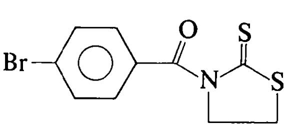
(I)



(II)



(III*a*)



(III*b*)

Systematic absences in 0*kl* with *k* odd, *h*0*l* with *l* odd, and *hk*0 with *h* odd, define the space group as *Pbca*. Intensity measurements were made from a crystal 0·12 × 0·12 × 0·12 mm. A Picker diffractometer was used with graphite-monochromated Cu $K\alpha$ radiation. The $\theta/2\theta$ scan method was used with a scan range between 3 and 4° in 2θ, and a scan speed of 2° min^{-1}. The reflections in a single octant of reciprocal space ($2\theta < 120°$) were measured, yielding intensities significantly above background at 1366 of the 1663 locations (82·1%) accessible to the instrument. No absorption corrections were made.

The structure was solved by the heavy-atom method. Block-diagonal least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, gave $R = 0{\cdot}037$ and $R_w = 0{\cdot}040$ at convergence for the 1366 reflections used. For the full set of 1663 data, $R = 0{\cdot}049$.*

The maximum shift-to-error ratio in the final cycle of refinement was 0·23 and the average ratio was 0·07. Despite the very large absorption coefficient, and probably because of the equidimensional crystal used, there was no evidence of systematic errors caused by absorption. Anisotropic thermal parameters were used for all atoms except H, for which individual isotropic *B* values were refined. A final difference electron-density map was devoid of structurally significant density. The scattering functions used were those of Cromer & Waber (1974) for the non-hydrogen atoms, and of Stewart, Davidson & Simpson (1965) for H.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34961 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/80/071709-02$01.00

Discussion. A projection of the molecule in the conformation found in the crystal on the plane of the amide group is shown in Fig. 1 with the numbering scheme adopted. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. The X-ray study has identified the molecule as 3-(*p*-bromobenzoyl)-1,3-thiazolidine-2-thione – thus resolving the problem in favor of the proposal of Izawa & Mukaiyama (1977). Bond lengths and angles are shown in Fig. 2. Atoms C(1), N, C(8), S(1), and S(2) are coplanar within the limits of error, and the shortening of the bond lengths S(2)—C(8), S(1)—C(8), and C(8)—N indicates substantial conjugation with the amide residue.

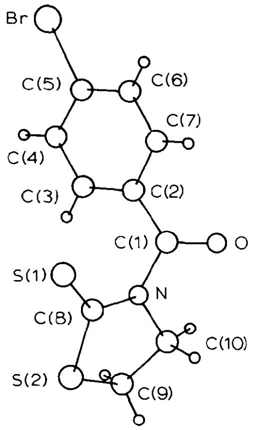


Fig. 1. Projection of the molecule on the amide plane.

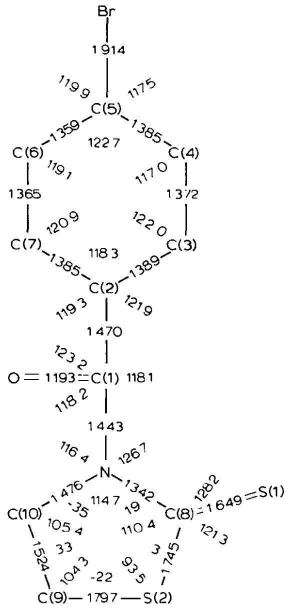


Fig. 2. Bond lengths (Å), bond angles (°), and endocyclic torsion angles (°). E.s.d.'s are: Br—C, 0·004; S—C, 0·006; C—N, 0·005; C—O, 0·006; C—C, 0·007 Å; bond angles, 0·4°; torsion angles 1·5°.

Table 1. *Fractional coordinates* ($\times 10^4$, H $\times 10^3$) *and equivalent isotropic B values* (Å^2)

Hydrogen atoms have been labelled to correspond to the atom of attachment.

	x	*y*	*z*	*B*
Br	812 (1)	549·5 (4)	3004·0 (3)	3·45
S(1)	−1781 (2)	3690 (1)	874·3 (7)	2·74
S(2)	76 (2)	3772 (1)	−353·1 (6)	3·08
O	3738 (6)	4266 (3)	1453 (2)	3·83
N	1918 (5)	3780 (3)	659 (2)	2·06
C(1)	2541 (8)	3751 (3)	1297 (2)	2·33
C(2)	1849 (7)	3013 (3)	1695 (2)	1·91
C(3)	1400 (7)	2163 (3)	1457 (2)	2·11
C(4)	1047 (7)	1432 (3)	1836 (2)	2·30
C(5)	1139 (7)	1579 (3)	2471 (2)	2·36
C(6)	1483 (8)	2410 (3)	2721 (2)	2·52
C(7)	1876 (8)	3121 (3)	2335 (2)	2·68
C(8)	149 (7)	3726 (3)	458 (2)	2·06
C(9)	2572 (9)	3805 (4)	−428 (2)	3·57
C(10)	3252 (8)	4148 (4)	201 (2)	3·11
H(3)	134 (6)	209 (3)	106 (2)	1·6 (9)
H(4)	84 (6)	89 (3)	164 (2)	2·1 (10)
H(6)	133 (7)	250 (4)	311 (2)	5·0 (14)
H(7)	216 (7)	363 (3)	245 (2)	3·1 (11)
H(9*a*)	302 (7)	423 (3)	−73 (2)	3·2 (11)
H(9*b*)	311 (7)	319 (3)	−52 (2)	4·3 (13)
H(10*a*)	326 (7)	480 (3)	23 (2)	3·7 (12)
H(10*b*)	459 (8)	394 (4)	30 (2)	5·6 (15)

Presumably because of potential lone-pair repulsions between S(1) and the amide oxygen, the observed conformation has these two atoms *trans* to one another. Steric interactions between the thio sulfur, S(1), and the ring atoms C(3) and H(3), however, prevent a *trans* conformer from being planar. Steric strain is relieved in two ways. With respect to the nearly planar four-atom amide group centered on C(1), the phenyl ring is rotated about C(1)—C(2) by 32°, and the coplanar ring grouping, N, S(2), C(8), and C(9), is rotated about N—C(1) by 49°. The contact C(3)··· S(1) is then 3·44 Å, a limiting value.

The thiazolidine ring has an envelope conformation with C(10) displaced from the plane of the remaining four atoms by 0·67 Å. Endocyclic torsion angles are given in Fig. 2.

Crystal cohesion arises mainly from parallel overlap of phenyl rings of neighboring molecules related by the symmetry operation $\frac{1}{2}+x, y, \frac{1}{2}-z$. The Br atom of the reference molecule makes van der Waals contacts with S(1) and S(2) in two neighbors at separations of 3·71 Å.

References

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

IZAWA, T. & MUKAIYAMA, T. (1977). *Chem. Lett.* pp. 1443–1446.

NAGAO, Y., KAWABATA, K. & FUJITA, E. (1978). *Chem. Commun.* p. 330.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.