

## Crystal Structure of Methyl-3-(5-chloro-2-oxo-1,3-benzothiazol-3(2H)-yl)-propanoate

Abdullah AYDIN,\*<sup>1</sup> Cengiz ARICI,\*<sup>2</sup> Mehmet AKKURT,\*<sup>3</sup> Yasemin AKKOÇ,\*<sup>4</sup> and M. Fethi ŞAHİN\*<sup>4</sup>

\*<sup>1</sup> Department of Physics Education, Kastamonu Education Faculty, Gazi University, Kastamonu-37200, Turkey

\*<sup>2</sup> Department of Physics Engineering, Faculty of Engineering, Hacettepe University, Beytepe, Ankara-06532, Turkey

\*<sup>3</sup> Department of Physics, Faculty of Arts and Sciences, Erciyes University, Kayseri-38039, Turkey

\*<sup>4</sup> Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Gazi University, Hipodrom, Ankara-06330, Turkey

(Received November 30, 2001; Accepted February 12, 2002)

As part of our research programs, we synthesized the title compound from the reaction of 5-chloro-2-benzothiazolinone (0.1 mol) with methyl acrylate (0.012 mol). Both of them were dissolved in 30 ml of water in the presence of 0.012 mol triethylamine. The mixture was stirred for 8 h on water bath (50 - 60°C) and then stirred for 18 h at room temperature. The precipitated solid material was subsequently filtered and crystallized from ethanol. In the present study, with the aim of further clarifying the molecular structure of the title compound, a single-crystal X-ray analysis of C<sub>11</sub>H<sub>10</sub>ClNO<sub>3</sub>S was carried out.

The benzothiazole unit is similar to those found in other derivatives, *e.g.* bis(1,3-benzothiazol-2-yl)disulfide<sup>1</sup> or 2-methylthio-1,3-benzothiazole.<sup>2</sup> The adopted molecular

conformation and the labeling scheme are shown in Fig. 2. Crystal and experimental data are given in Table 1. The final positional and equivalent isotropic thermal parameters are reported in Table 2; Table 3 lists selected bond lengths and bond angles. The lengthening of the S1-C7 bond distance [1.776(3)Å] versus the S1-C6 bond distance [1.742(3)Å] may be described in term of the steric interaction, whereas in the structures of 4-benzoyl-5-phenylthiophene-2,3-dione<sup>3</sup> and 2-(*o*-hydroxyphenyl)-Δ<sup>2</sup>-1,3-benzo[4,5]thiazoline<sup>4</sup> the S-C distances range between 1.74(3) and 1.78(9)Å.

The C3-C11 distance [1.744(3)Å] is in agreement with those

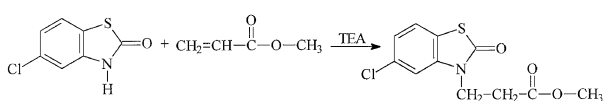


Fig. 1 Synthesis the pathway of the title compound.

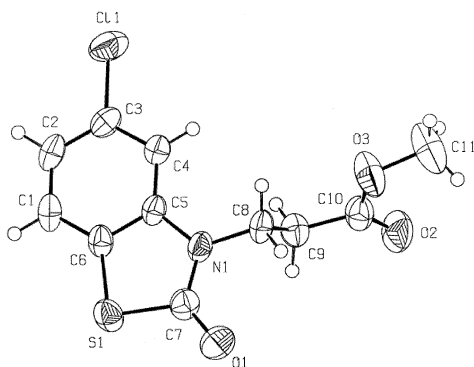


Fig. 2 ORTEP view of the title compound showing the labeling of the non-H atoms. Thermal ellipsoids are shown at the 50% probability level.

Table 1 Crystal and experimental data

Formula: C <sub>11</sub> H <sub>10</sub> ClNO <sub>3</sub> S
Formula weight = 271.7
Crystal system: monoclinic
Space group: P2 <sub>1</sub> /a (No. 14); Z = 4
a = 9.3429(13)Å
b = 14.0844(14)Å β = 94.878(3)°
c = 9.3662(12)Å
V = 1228.0(3)Å <sup>3</sup>
D <sub>x</sub> = 1.470 g/cm <sup>3</sup>
μ(Mo Kα) = 0.476 mm <sup>-1</sup>
T = 295 K
F(0 0 0) = 560
Crystal size = 0.40 × 0.35 × 0.30 mm
Radiation: Mo Kα
R = 0.060
Rw = 0.1792
w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> ) + (0.1194P) <sup>2</sup> + 0.5329P] where P = (F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3
No. of unique data measured = 2256
No. of observed data with [I ≥ 2σ(I)] = 1871
No. of parameters = 155
Goodness-of-fit = 1.06
(Δρ) <sub>max</sub> = 1.13 eÅ <sup>-3</sup>
(Δρ) <sub>min</sub> = -0.33 eÅ <sup>-3</sup>
Measurements: Enraf Nonius CAD-4 diffractometer
Structure determination: SHELXS97
Treatment of hydrogen atoms: geometric calculation
Refinement: full matrix least-squares SHELXL97

Table 2 Final atomic coordinates and equivalent isotropic thermal displacement parameters for non-hydrogen atoms

Atom	x	y	z	$U_{eq}$
C11	-0.2076(1)	0.5478(1)	0.8559(1)	0.070(1)
S1	0.2319(1)	0.3390(1)	0.5068(1)	0.054(1)
O1	0.4920(3)	0.3984(2)	0.6047(3)	0.068(1)
O2	0.5451(3)	0.7610(2)	0.7702(3)	0.074(1)
O3	0.4861(4)	0.6788(2)	0.9586(3)	0.080(1)
N1	0.2976(2)	0.4635(2)	0.7037(3)	0.044(1)
C1	-0.0518(3)	0.3746(2)	0.5691(3)	0.051(1)
C2	-0.1453(3)	0.4227(2)	0.6498(3)	0.052(1)
C3	-0.0900(3)	0.4874(2)	0.7529(3)	0.047(1)
C4	0.0558(3)	0.5060(2)	0.7778(3)	0.041(1)
C5	0.1475(3)	0.4570(2)	0.6956(3)	0.038(1)
C6	0.0940(3)	0.3913(2)	0.5934(3)	0.042(1)
C7	0.3631(3)	0.4051(2)	0.6133(3)	0.049(1)
C8	0.3825(3)	0.5284(2)	0.7999(3)	0.045(1)
C9	0.3922(3)	0.6255(2)	0.7313(3)	0.051(1)
C10	0.4836(3)	0.6960(2)	0.8192(3)	0.053(1)
C11	0.5558(8)	0.7475(3)	1.0574(5)	0.097(2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$$

Table 3 Bond lengths (Å) and bond angles (°)

C1 - C2	1.380(5)	C7 - O1	1.218(4)
C1 - C6	1.382(5)	C7 - N1	1.362(4)
C2 - C3	1.394(5)	C7 - S1	1.776(3)
C3 - C4	1.387(4)	C8 - N1	1.469(3)
C3 - C11	1.744(3)	C8 - C9	1.516(4)
C4 - C5	1.384(4)	C9 - C10	1.508(4)
C5 - C6	1.393(4)	C10 - O2	1.193(4)
C5 - N1	1.401(4)	C10 - O3	1.326(4)
C6 - S1	1.742(3)	C11 - O3	1.454(4)
C2 - C1 - C6	119.2(3)	O1 - C7 - S1	124.1(2)
C1 - C2 - C3	119.0(2)	N1 - C7 - S1	109.9(2)
C4 - C3 - C2	122.7(3)	C9 - C8 - N1	110.5(3)
C4 - C3 - C11	118.1(2)	C10 - C9 - C8	114.4(2)
C2 - C3 - C11	119.2(2)	O2 - C10 - O3	123.4(3)
C5 - C4 - C3	117.2(3)	O2 - C10 - C9	124.3(3)
C4 - C5 - C6	120.7(2)	O3 - C10 - C9	112.3(3)
C4 - C5 - N1	127.0(2)	C7 - N1 - C5	115.3(3)
C6 - C5 - N1	112.3(2)	C7 - N1 - C8	120.7(2)
C1 - C6 - C5	121.1(3)	C5 - N1 - C8	124.0(2)
C1 - C6 - S1	127.6(2)	C10 - O3 - C11	118.3(3)
C5 - C6 - S1	111.3(2)	C6 - S1 - C7	91.1(1)
O1 - C7 - N1	126.0(3)		

of other compounds, such as 2-[(2-chlorophenyl)iminomethyl]-4,6-dimethyl-quinoline<sup>5</sup> [1.738(4)Å] and *N*-(3-chloro-4-methylphenyl)aminoglycine<sup>6</sup> [1.743(3)Å], and also with the theoretical length of a  $Csp^2$ -Cl bond, given as 1.734 Å by Allen *et al.* (1987).<sup>7</sup> The carbonyl O3 atom and the Cl atom are close to coplanar with the 5-chloro-1,3-benzothiazol-2-(3*H*)-one moiety [torsion angles C1-C2-C3-C11 -179.6(2)° and O1-C7-N1-C5 -178.8(3)°]. The angle between the least-squares planes which pass through the 5-chloro-1,3-benzothiazol-2-(3*H*)-one moiety and the methyl propionate moiety is 73.3(1)°.

The MNDO molecular dipole moment, calculated using the Mopac 6.0 program package, is 2.308 debyes ( $1D \approx 3.33564 \times 10^{-30}$  cm) for the title compound. The calculated overall conformation of the compound, except for atoms O2, O3 and C11, are planar. The intermolecular Madelung (charge-charge) energy, based on the point charges, is found to be -17873.4 eV. The final heat of formation is -94.3 kcal.

There are two C-H...O-type intermolecular hydrogen bonds between the C2 and C9 atoms, and the carbonyl atom (O1) in the structure where the donor-acceptor distances of C2-H2...O1<sup>i</sup> and C9-H9A...O1<sup>ii</sup> are 3.396(4) and 3.430(4)Å, respectively

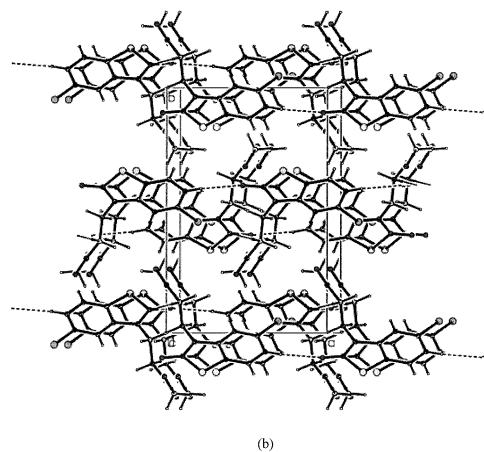
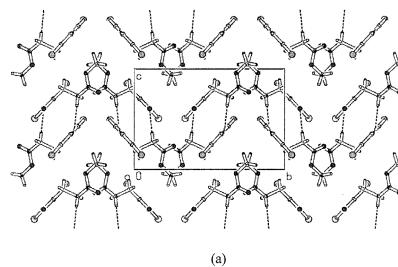


Fig. 3 View of the crystal packing and hydrogen bonds; (a) along the *a*-axis, and (b) along the *c*-axis.

[symmetry codes: (i)  $1+x, y, z$ ; (ii)  $-x, -y, 1-z$ ]. These intermolecular distances conform to normal van der Waals interactions. A packing diagram of the unit cell is given in Fig. 3 and the hydrogen bonds are shown by the dotted lines.

## Acknowledgements

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

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