Crystal structure of ethyl 4-methylthio-3-phenyl-2-thioxo-2,3dihydro-1,3-oxazole-5-carboxylate

Frank W. Heinemann,⁽¹⁾ Wolfgang Dölling,⁽²⁾ Thomas Gildenast,⁽²⁾ and Helmut Hartung^(1,*)

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The title compound $C_{13}H_{13}NO_3S_2$ crystallizes in the triclinic space group P1 (Z = 2) with lattice constants a = 8.382(2), b = 10.042(2), c = 10.134(2) Å, $\alpha = 119.35(1)^\circ$, $\beta = 101.40(1)^\circ$ and $\gamma = 90.54(1)^\circ$. The interplanar angle between the least squares planes of the 1,3-oxazoline ring and the phenyl ring amounts to 90.2°, thus hindering conjugation between the benzene and heterocyclic system. The observed bond parameters of the five-membered heterocycle suggest a significant contribution from a zwitterionic dipolar limiting structure [38.7(5)%] to the description of this ring system. The particular contributions of the resonance structures were estimated by calculations using the HOSE model on the base of the observed bond lengths.

KEY WORDS: Crystal structure, 1,3-oxazoline-2-thione, resonance structures.

Introduction

Recently it has been shown that CH-acidic thioand dithiocarbonates react with heterocumulenes giving the products of heterocyclization.¹ In the case of the reaction of thiocarbonates with phenyl isothiocyanate, two cyclization directions might be possible leading to either 1,3-dithiole (ring closure on sulfur) or 1,3-thiazole de-



⁽¹⁾Institut f. Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, D-06108 Halle (Saale), Germany.

*To whom correspondence should be addressed.

rivatives (ring closure on nitrogen). Recent studies concerning this particular problem showed the ring closure on nitrogen to be more favourable.^{2,3} In the thiocarbamoylation reaction of S-ethyl O-(ethoxy-carbonylmethyl) dithiocarbonate 1 with phenyl isothiocyanate and subsequent methylation again the two cyclization directions might be possible. In order to exclude the cyclization by the sulfur atom of the isothiocyanate an X-ray analysis of the reaction product has been performed.

Experimental

The title compound ethyl 4-methylthio-3-phenyl-2-thioxo-2,3-dihydro-1,3-oxazole-5-carboxylate was formed by thiocarbamoylation of S-ethyl O-(ethoxycarbonylmethyl) dithiocarbonate with phenyl isothiocyanate in dry THF in the presence of potassium *tert*-butoxide at -78 °C followed by a methylation reaction with methyl iodide.⁴ S-ethyl O-(ethoxycarbonylmethyl) dithiocarbonate was prepared according to a procedure described by Gotthardt *et al.*⁵

Colorless needles, suitable for the X-ray investigation were obtained by recrystallization from ethanol. The unit cell dimensions were determined from a least-

⁽²⁾Institut f. Organische Chemie, Martin-Luther-Universität Halle-Wittenberg, Weinbergweg 16, D-06120 Halle (Saale), Germany.

Compound	$C_{13}H_{13}NO_3S_3$	Radiation, graphite monochromator	$M_0 K_{\alpha} (\lambda = 0.71073 \text{ Å})$
Color/shape	colorless/needles	Max. crystal dimensions, mm	$0.34 \times 0.30 \times 0.23$
Formula weight	295.38	Scan width	1.05 - 1.20 variable
Space group	PĪ	Standard reflections	500;005;042
Temp., °C	20	Decay of standards	±5%
Cell constants		Reflections measured	3217
a, Å	8.382(2)	2θ range, deg	$3.0 \leq 2\theta \leq 53.0$
b, Å	10.042(2)	Range of h, k, l	$\pm 10, \pm 12, -12$
c, Å	10.134(2)	Refl. observed $[F_0 \ge 4.0\sigma(F_0)]$	2328
α, deg	119.35(1)	Computer programs	SHELX-76 ¹³ , SHELXS-86 ¹⁴
β, deg	101.40(1)	Structure solution	Direct methods
γ, deg	90.54(1)	No. of parameters varied	225
Cell volume, Å ³	723.1	Weights	$1.47/[\sigma(F_0)^2 + 0.0004 F_0^2]$
Formula units/unit cell	2	GOF	1.813
$D_{\rm calc}$, g cm ⁻³	1.356	$\mathbf{R} = \boldsymbol{\Sigma} \mathbf{F}_{\mathbf{o}} - \mathbf{F}_{\mathbf{c}} / \boldsymbol{\Sigma} \mathbf{F}_{\mathbf{o}} $	0.031
$\mu_{\rm calc}, {\rm cm}^{-1}$	3.50	R _w	0.042
Diffractometer/scan	Stoe STADI-4/ $\omega - \theta$	Largest feature final diff. map	0.22 e Å $^{-3}$

Table 1. Crystal data and summary of intensity data collection and structure refinement

squares refinement of the 2θ -angles of 84 reflections in the range of $23^{\circ} \le 2\theta \le 35^{\circ}$. The intensity data were corrected for Lorentz and polarization effects while absorption effects were ignored ($\mu = 3.5 \text{ cm}^{-1}$). The crystal data and further details of the intensity data collection and structure refinement are summarized in Table 1.

Results and discussion

The reaction product has been identified as the title compound 2a, i.e., ring closure after C-C bond formation has occurred on the nitrogen atom of the isothiocyanate. The molecular structure including the atomic numbering scheme of 2a is shown in Fig. 1. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Selected bond lengths, bond angles and torsion angles are presented in Table 3.

The 1,3-oxazoline ring is planar, only slight but significant deviations from the least-squares plane through the five ring atoms are observed for C1 and C3 amounting to 0.014(1) Å for both atoms. The four exocyclic bonded atoms S1, S2, C4, and C6 deviate by no more than 0.095 Å from this plane. The interplanar angle formed by the 1,3-oxazoline ring and the exactly planar phenyl ring amounts to 90.2°. This value is in good agreement with the corresponding interplanar angles of 99.4° and 94.7° observed in the closely related compounds methyl 4-methylthio-3-phenyl-2-thioxo-2,3dihydro-1,3-thiazole-5-carboxylate² (CSD-Code: JUD-WEK) and methyl 4-methylthio-2-oxo-3-phenyl-2,3dihydro-1,3-thiazole-5-carboxylate³ (CSD-Code: VOM-



Fig. 1. Molecular structure and atomic numbering of 2a. (ORTEP-II drawing,¹⁵ the thermal ellipsoids are drawn at the 50% level and the H atoms are represented by spheres of arbitrary radius.)

ZAY), respectively. The almost perpendicular orientation of the two rings determined for all three compounds is hindering conjugation between the benzene and heterocyclic system and is responsible for a significant lengthening of the C-N(phenyl) bonds. The observed C-N(phenyl) bond distances of 1.442(3) in **2a**, 1.443(3) in VOMZAY and 1.444(4) Å in JUDWEK, respectively, are significantly longer than the standard value of 1.40 Å given for a $C(sp^2)$ -N(sp²) bond.⁶ The value of 1.371 Å for a C(aromatic)-N(sp²) bond distance derived by Allen *et al.*⁷ is even shorter. The only slight deviations of the N-atom from the l.s. plane defined by the three adjacent atoms C2, C3 and C6 (0.015(1) Å for **2a**, 0.036(2) Å for VOMZAY and 0.012(3) Å for **Table 2.** Final fractional coordinates and equivalent isotropic displacement parameters $(Å^2)$ with esd's in parentheses

$$U_{eq} = \frac{1}{3} \sum_{i} \sum_{j} U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	у	z	U_{eq}
S 1	0.05216(6)	0.40229(6)	0.10756(5)	0.050(6)
S2	0.46962(5)	0.72088(5)	0.67929(5)	0.046(6)
01	0.2412(1)	0.4812(1)	0.5317(1)	0.037(7)
O2	0.0495(2)	0.2308(1)	0.4724(1)	0.061(7)
O3	-0.0431(1)	0.1698(1)	0.2240(1)	0.049(7)
N1	0.2705(1)	0.5809(1)	0.3882(1)	0.036(7)
C1	0.1356(2)	0.3921(2)	0.3872(2)	0.035(7)
C2	0.1492(2)	0.4529(2)	0.2970(2)	0.036(7)
C3	0.3271(2)	0.5953(2)	0.5299(2)	0.035(7)
C4	0.0434(2)	0.2569(2)	0.3683(2)	0.039(7)
C5	-0.1552(2)	0.4296(2)	0.1248(2)	0.071(8)
C6	0.3319(2)	0.6803(2)	0.3396(2)	0.040(7)
C7	0.4640(2)	0.6448(2)	0.2729(2)	0.059(8)
C8	0.5251(2)	0.7421(2)	0.2295(2)	0.071(8)
C9	0.4563(2)	0.8726(2)	0.2549(2)	0.065(8)
C10	0.3238(2)	0.9075(2)	0.3223(2)	0.064(8)
C11 -	0.2597(2)	0.8104(2)	0.3645(2)	0.054(8)
C12	-0.1379(2)	0.0294(2)	0.1897(2)	0.054(8)

 Table 3. Selected bond lengths (Å), bond angles (°) and torsion angles (°) with esd's in parentheses

1			
S1-C2	1.739(2)	C2-S1-C5	101.2(1)
\$1-C5	1.792(2)	C1-O1-C3	108.6(1)
S2-C3	1.642(1)	C2-N1-C3	109.7(1)
01-C1	1.384(1)	C2-N1-C6	126.2(1)
O1-C3	1.357(2)	C3-N1-C6	124.0(1)
N1-C2	1.407(2)	01-C1-C2	109.1(1)
N1-C3	1.354(2)	O1-C1-C4	114.6(1)
N1-C6	1.442(3)	C2-C1-C4	136.2(1)
C1-C2	1.344(3)	S1-C2-N1	121.1(1)
C1-C4	1.465(2)	S1-C2-C1	133.2(1)
		N1-C2-C1	105.6(1)
		S2-C3-O1	122.8(1)
		S2-C3-N1	130.4(1)
		01-C3-N1	106.8(1)
C5-S1-C2-N1	-116.2(1)	C6-N1-C3-O1	-179.4(1)
C5-S1-C2-C1	64.3(2)	C2-N1-C6-C7	-90.0(2)
C3-N1-C2-S1	-179.7(1)	C2-N1-C6-C11	91.6(2)
C6-N1-C2-S1	-1.8(2)	C3-N1-C6-C7	87.7(2)
C3-N1-C2-C1	-0.1(2)	C3-N1-C6-C11	-90.7(2)
C6-N1-C2-C1	177.8(2)	01-C1-C4-02	5.0(2)
C2-N1-C3-S2	178.8(1)	01-C1-C4-O3	-174.2(1)
C2-N1-C3-O1	-1.4(2)	C2-C1-C4-O2	-177.4(2)
C6-N1-C3-S2	0.8(2)	C2-C1-C4-O3	3.4(3)

JUDWEK) indicate the predominant sp^2 hybridization state of the N-atom in these three compounds.

The considerable difference between the bond dis-



tances C2-N1 = 1.407(2) Å and C3-N1 = 1.354(2) Å suggests a significant contribution of the zwitterionic oxazolium resonance structure (b) (cf. scheme 2) to the description of the 1,3-oxazoline ring in **2a**. A similar situation has been observed in thiamine thiazolone⁸ where the contribution of the zwitterionic thiazolium resonance structure has been estimated to about 25%. In contrast to these results, in VOMZAY the corresponding C-N distances [1.391(2) and 1.389(2) Å] agree very well with each other while the relevant C-N distances observed in JUDWEK [1.395(4) and 1.374(5) Å] are in between.

For a quantitative estimation of the contribution of the two resonance structures (a) and (b) (cf. scheme 2) to the 1,3-oxazoline ring of **2a**, HOSE calculations^{9,10} have been performed. The five endocyclic and the exocyclic C=S bond have been included in the calculations. The relevant atomic positions were corrected for libration according to the method proposed by Schomaker and Trueblood.¹¹ Thus obtained corrected bond lengths were used in the calculations. The results are summarized in Table 4. While for compound VOMZAY there is only a minor contribution of the zwitterionic resonance structure (about 12%) this contribution in **2a** is much higher and amounts to almost 39%.

There is one intramolecular contact distance in **2a** $[S1 \cdot \cdot \cdot O3 = 3.244(1) \text{ Å}]$ shorter than the sum of the

Table 4. HOSE values (kJ mol⁻¹) and contribution C_i (%) of the resonance structures **a** and **b** given in scheme 2 with esd's in parentheses

Compound	HOSE _a	Ca	HOSE	C _b	HOSE
2a	55(2)	61.3(9)	87(2)	38.7(5)	67(2)
VOMZAY ³	30(2)	88.3(7)	226(6)	11.7(3)	53(3)

corresponding van der Waals-radii of 3.32 Å¹² while there are no short intermolecular contacts observed.

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