

The crystal packing and the hydrogen-bonding scheme are shown in Fig. 2. Hydrogen-bonding parameters are listed in Table 2. The anions form pairs related by a centre of inversion and linked through hydrogen bonds between phosphate O atoms. These pairs are linked by hydrogen bonds between amide N and terminal phosphate oxygen O(3) into infinite chains parallel to *b*. The O(3) atom also participates in a hydrogen bond with the N atom of the triethylammonium cation. The exterior surfaces of the chains are defined by the hydrophobic phenyl and ethyl groups whereas the hydrophilic groups occupy the interiors of the chains.

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Structure of Methyl 4-Methylthio-2-oxo-3-phenyl-2,3-dihydro-1,3-thiazole-5-carboxylate

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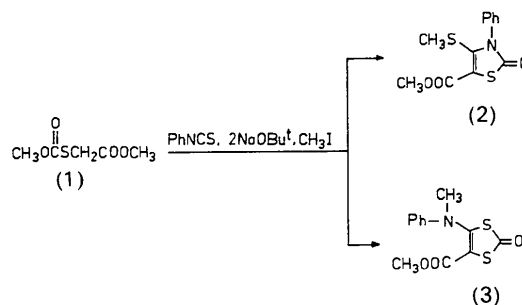
Abstract. $C_{12}H_{11}NO_3S_2$, $M_r = 281.4$, triclinic, $P\bar{1}$, $a = 9.492$ (2), $b = 11.110$ (3), $c = 6.854$ (2) Å, $\alpha = 75.68$ (1), $\beta = 79.54$ (1), $\gamma = 68.43$ (1)°, $V = 648.0$ (3) Å³, $Z = 2$, $D_m = 1.42$, $D_x = 1.44$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.354$ mm⁻¹, $F(000) = 292$, room temperature, final $R = 0.038$, $wR = 0.032$ for 2186 reflections. The structure was solved by the heavy-atom method. Bond distances and angles are within the expected ranges. The thiazoline ring is almost exactly planar and twisted to the benzene ring by 99.4°.

Introduction. Recently we have been able to show that CH-acidic thio- and dithiocarbonates react with heterocumulenes giving the products of heterocyclization (Augustin & Dölling, 1990). In the case of the reaction of the thiocarbonate (1) with phenyl isothiocyanate, two cyclization directions might be possible. The products expected according to the two pathways should be the 1,3-thiazolin-2-one (2) or the 1,3-dithiol-2-one (3). In order to come to a decision between these two alternatives an X-ray analysis of the reaction product has been performed. As a result the reaction product has been identified as the title compound (2).

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References

- ALLEN, C. M., RICHELSON, E. & JONES, M. E. (1966). *Biochemical Energetics*, pp. 401–412. New York: Academic Press.
 BERGMAYER, H. U. (1970). *Methoden Der Enzymatischen Analyze*, p. 490. Berlin: Akademie-Verlag.
 CRAMER, F. & WINTER, M. (1959). *Chem. Ber.* **92**, 2761–2768.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
 SOUTHERLAND, W. M. (1990). *Biochemistry*, pp. 236–237, 299–300. London: Churchill Livingstone.
 STARYNOWICZ, P. (1986). *Collected Abstracts of Tenth European Crystallographic Meeting, Wrocław*, p. 174.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
 WEICHSEL, A. & LIS, T. (1990). *Acta Cryst.* **C46**, 962–965.



Experimental. The title compound (2) was prepared by treatment of methyl methoxycarbonylthioglycolate (1) with phenyl isothiocyanate and sodium *tert*-butoxylate followed by alkylation according to a recently published procedure (Augustin, Dölling & Rudolf, 1989). Pale-yellow clear crystals (m.p. 396–397 K) were obtained by recrystallization from methanol. The density was measured by flotation in aqueous KI solution. All X-ray data were collected on a Stoe STADI-4 diffractometer for a crystal with dimensions 0.4 × 0.3 × 0.1 mm using graphite-monochromated Mo *K*α radiation. The unit-cell dimensions were obtained from least-squares refinement of the setting angles of 25 reflections in the 2θ range 12–25°. Intensity data measurement: ω–2θ scan, 2θ_{max} = 50°, *hkl* range from –10, –12, 0

to 11, 13, 8; 2186 unique reflections (all considered observed and used in the structure solution and refinement). Three check reflections (620, 451 and $\bar{3}51$) varied in intensity by 5.5, 4.1 and 2.9%, respectively. Lp correction was carried out but absorption effects were ignored. The structure was solved by Patterson methods and subsequent Fourier syntheses and refined on F by full-matrix least-squares procedures with anisotropic displacement parameters for the non-H atoms. All H-atom positions were located in a difference Fourier map and isotropically refined. The final weighting scheme was $w = 0.611/\sigma^2(F)$, an empirical extinction correction was applied with $F_{\text{corr}} = F_c(1 - \chi F_c^2/\sin\theta)$ with $\chi = 4.6(2) \times 10^{-7}$. The final agreement factors were $R = 0.038$, $wR = 0.032$, $S = 2.200$ for 10.51 reflections per refined parameter. The maximum Δ/σ in the last refinement cycle was 0.016. The final difference map showed maximum and minimum heights of 0.25 and $-0.23 \text{ e } \text{\AA}^{-3}$, respectively. Atomic scattering factors were from *SHELX76* (Sheldrick, 1976). All calculations and plots were performed with program packages *SHELX76*, *SHELXS86* (Sheldrick, 1986), *EDIT* (Jaskólski, 1982) and *ORTEPII* (Johnson, 1976).

Discussion. Final fractional coordinates and equivalent isotropic displacement parameters for (2) are listed in Table 1.* The molecular structure is shown in Fig. 1, selected bond lengths and angles are given in Table 2.

The thiazoline ring, as the central part of the molecule, is planar, the only significant deviation from the best plane through its five atoms is 0.018(2) Å for C3. None of the four exocyclic bonded atoms deviates by more than 0.065 Å from this plane. The benzene ring is exactly planar and has standard dimensions [C—C = 1.374(8) Å, C—C—C = 120.0(7)°]; the interplanar angle formed by the two rings amounts to 99.4°. This value is similar to that of 113.8° in 3-phenyl-1,3-thiazolidine-2,4-dione, the only suitable structure found in the literature for an appropriate comparison (Stanković & Andreotti, 1979). All atoms of the methyl acetate group (C1, C4, O2, O3, C12) lie in a plane (only C12 deviates significantly by 0.028 Å from the plane) which is tilted to the thiazoline ring plane by only 7.6°. Surprisingly, known structures containing a 1,3-thiazoline-2-one fragment are rare and confined to thiamine thiazolone (Shin & Kim, 1986) and, with some restrictions, to benzyl 2-oxo-2,3-dihydro-1,3-benzothiazoleacetate (Vrábel, Lokaj, Kellő,

Table 1. Final fractional coordinates and equivalent isotropic displacement parameters (Å²) with e.s.d.'s in parentheses

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
S1	0.09996 (6)	0.43881 (5)	0.24211 (8)	0.052 (6)
S2	0.42272 (6)	0.52530 (5)	-0.24880 (7)	0.047 (5)
O1	0.3214 (2)	0.7735 (1)	-0.2004 (2)	0.068 (10)
O2	0.3407 (2)	0.2027 (1)	0.0448 (2)	0.064 (10)
O3	0.4816 (2)	0.2587 (1)	-0.2409 (2)	0.058 (9)
N1	0.2098 (2)	0.6282 (2)	0.0104 (2)	0.040 (9)
C1	0.3327 (2)	0.4254 (2)	-0.0753 (3)	0.04 (1)
C2	0.2236 (2)	0.4956 (2)	0.0497 (3)	0.04 (1)
C3	0.3110 (2)	0.6651 (2)	-0.1452 (3)	0.05 (1)
C4	0.3810 (2)	0.2845 (2)	-0.0775 (3)	0.05 (1)
C5	0.2283 (4)	0.3496 (4)	0.4323 (4)	0.08 (1)
C6	0.1093 (2)	0.7242 (2)	0.1272 (3)	0.04 (1)
C7	0.1509 (3)	0.7278 (2)	0.3068 (3)	0.05 (1)
C8	0.0564 (3)	0.8227 (3)	0.4155 (4)	0.06 (1)
C9	-0.0750 (3)	0.9128 (2)	0.3420 (4)	0.06 (1)
C10	-0.1152 (3)	0.9081 (2)	0.1631 (4)	0.06 (1)
C11	-0.0232 (2)	0.8129 (2)	0.0542 (3)	0.05 (1)
C12	0.5450 (5)	0.1214 (3)	-0.2624 (6)	0.08 (1)

Table 2. Selected bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

S1—C2	1.757 (2)	N1—C2	1.391 (2)
S1—C5	1.793 (3)	N1—C3	1.389 (2)
S2—C1	1.747 (2)	N1—C6	1.443 (2)
S2—C3	1.762 (2)	C1—C2	1.352 (2)
O1—C3	1.205 (2)	C1—C4	1.464 (3)
C2—S1—C5	100.0 (1)	C2—C1—C4	128.9 (2)
C1—S2—C3	91.9 (1)	S1—C2—N1	119.1 (1)
C2—N1—C3	115.4 (2)	S1—C2—C1	127.5 (2)
C2—N1—C6	125.3 (2)	N1—C2—C1	113.4 (2)
C3—N1—C6	119.1 (2)	S2—C3—O1	125.6 (2)
S2—C1—C2	111.2 (1)	S2—C3—N1	108.1 (1)
S2—C1—C4	119.9 (1)	O1—C3—N1	126.4 (2)

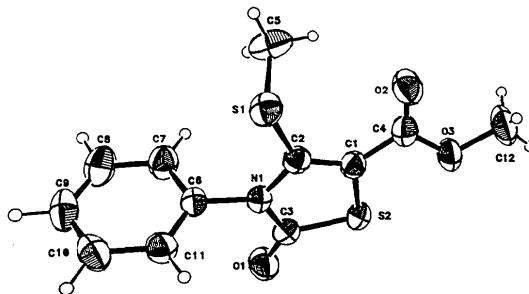


Fig. 1. Molecular structure and atomic numbering. The thermal ellipsoids are drawn at the 50% level and the H atoms are shown as spheres of arbitrary radius.

Konečný, Batsanov & Struchkov, 1990). For the former compound the authors discuss, on the basis of the observed bond distances [especially the C3—O1 keto bond length of 1.238(6) Å and the considerable difference between the bond lengths N1—C3 = 1.348(6) and N1—C2 = 1.420(6) Å], a significant contribution (about 25%) from the

* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54534 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

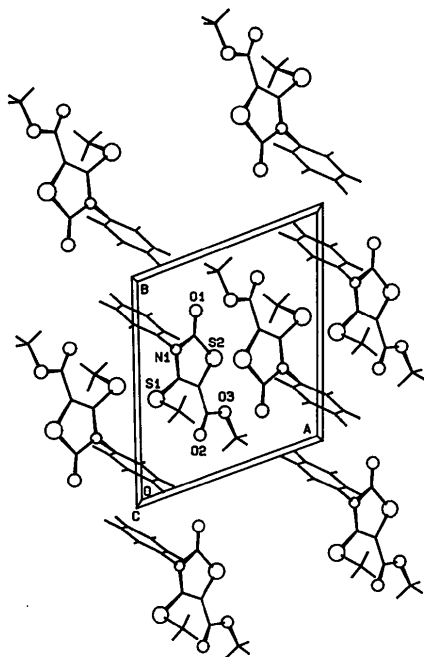


Fig. 2. Molecular packing.

zwitterionic thiazolium resonance structure. In contrast to these bond distances, in (2) the C3—O1 bond length of 1.205 (2) Å has double-bond character and the two endocyclic N—C distances [N1—C2 = 1.391 (2), N1—C3 = 1.389 (2) Å] agree with each other and are typical for N—C single bonds (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). All geometric bonding parameters of the 2-oxo-thiazoline moiety in the latter above-mentioned com-

pound agree well with those in (2), except the C1—C2 bond length of 1.401 (10) Å. This bond belongs to both the aromatic benzene and the thiazolone rings and is elongated by 0.049 Å compared with the C1—C2 distance of 1.352 (2) Å in (2), which corresponds to an isolated double bond.

All other geometrical parameters in (2) are in agreement with expectation. Intermolecular contacts are consistent with van der Waals radii. The molecular packing is shown in Fig. 2.

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References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- AUGUSTIN, M. & DÖLLING, W. (1990). *Z. Chem.* **30**, 395–403.
- AUGUSTIN, M., DÖLLING, W. & RUDORF, W.-D. (1989). *Z. Chem.* **29**, 445–446.
- JASKÓLSKI, M. (1982). *EDIT*. Program to edit atomic information from atom data files. Univ. of Poznań, Poland.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination, Univ. of Cambridge, England.
- SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- SHIN, W. & KIM, Y. C. (1986). *J. Am. Chem. Soc.* **108**, 7078–7082.
- STANKOVIĆ, S. & ANDRETTI, G. D. (1979). *Acta Cryst.* **B35**, 3078–3080.
- VRÁBEL, V., LOKAJ, J., KELLÖ, E., KONEČNÝ, V., BATSANOV, A. C. & STRUCHKOV, YU. T. (1990). *Acta Cryst.* **C46**, 470–472.

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Structures of 3-Methoxypyrazine 1-Oxide (1a) and 3-Methoxy-5-methylpyrazine 1-Oxide (1b)

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Abstract. (1a), C₅H₆N₂O₂, *M_r* = 126.1, triclinic, *P* $\bar{1}$, *a* = 12.094 (1), *b* = 14.689 (1), *c* = 7.0228 (4) Å, α = 96.991 (6), β = 101.856 (4), γ = 101.361 (7)°, *V* = 1179.8 (4) Å³, *Z* = 8, *D_x* = 1.420 g cm⁻³, λ (Cu *K*α) = 1.54178 Å, μ = 9.11 cm⁻¹, *F*(000) = 528, *T* =

293 K, *R* = 0.061 for 1544 observed [*I*/ σ (*I*) ≥ 3] reflexions. (1b), C₆H₈N₂O₂, *M_r* = 140.1, orthorhombic, *Pna*2₁, *a* = 8.0056 (5), *b* = 12.7140 (6), *c* = 6.6861 (9) Å, *V* = 680.5 (2) Å³, *Z* = 4, *D_x* = 1.368 g cm⁻³, λ (Mo *K*α) = 0.71069 Å, μ = 0.98 cm⁻¹, *F*(000) = 296, *T* = 294 K, *R* = 0.032 for 877 observed [*I*/ σ (*I*) ≥ 3] reflexions. Each *N*-oxide,

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