Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Methyl 2-methyl-7-oxo-1,2,4-triazolo-[3,2-*b*]-1,3-thiazine-5-carboxylate

Süheyla Özbey[a]* and Birsen Tozkoparan[b]

[a]Department of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and [b]Department of Pharmaceutical Chemistry, Hacettepe University, Sıhhiye 06100, Ankara, Turkey

Correspondence e-mail:
sozbey@hacettepe.edu.tr

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.125
Data-to-parameter ratio = 13.5

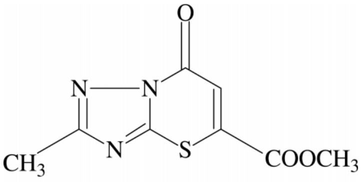
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 24 September 2002
Accepted 1 October 2002
Online 5 October 2002

In the title molecule, $C_8H_7N_3O_3S$, the triazole and thiazine rings are nearly coplanar, with a dihedral angle of 2.27 (9)°. The methyl carboxylate moiety is also planar and makes a dihedral angle of 7.31 (13)° with the thiazine–triazole mean plane.

Comment

Recently, we have been interested in the chemistry and biological activity of heterocyclic compounds derived from 3-substituted-1,2,4-triazole-5-thiones (Tozkoparan *et al.*, 1999, 2000, 2001). Because of the thiourea moiety in the ring, these are convenient materials for the synthesis of fused derivatives. As a result of tautomerism of the triazoline–thione ring, cyclization can occur at either N1 or N4. In this study, we clarify the molecular structure of the adduct, (I), produced by the addition of dimethyl acetylenedicarboxylate (DMAD) to 3-methyl-1,2,4-triazole-5-thione.



(I)

As reported before (Tozkoparan *et al.*, 2002), there are different possibilities in the formation of the adduct resulting from the reaction of DMAD with 3-substituted-1,2,4-triazole-5-thiones. Giammonia *et al.* (1991) have reported the reaction of 3-methyl-1,2,4-triazole-5-thione with DMAD in methanol and identified the end product as methyl 3-methyl-5-oxo-1,2,4-triazolo[3,4-*b*]-1,3-thiazine-7-carboxylate according to spectral data. We carried out the same reaction in toluene and characterized the product by spectral data. Although the end product has similar ^{1}H NMR assignments and melting point to those of the compound reported by Giammonia *et al.* (1991), we identified it as methyl 2-methyl-7-oxo-1,2,4-triazolo[3,2-*b*]-1,3-thiazine-5-carboxylate by X-ray analysis.

Compound (I) as a whole is not planar. The 1,2,4-triazole moiety is essentially planar, while the thiazine ring deviates slightly from planarity [maximum deviations of 0.003 (3) and 0.059 (2) Å for atoms C5 and C4, respectively], and the dihedral angle between the mean planes of these rings is 2.27 (9)°. Atom O1 lies −0.197 (2) Å from the least-squares plane defined by all the atoms of the two fused rings. The methoxycarbonyl group at C2 is also nearly planar [maximum deviation of −0.014 (3) Å for C7] and makes a dihedral angle of 7.31 (13)° with the thiazine–triazole mean plane. The C3—

DOI: 10.1107/S1600536802018056

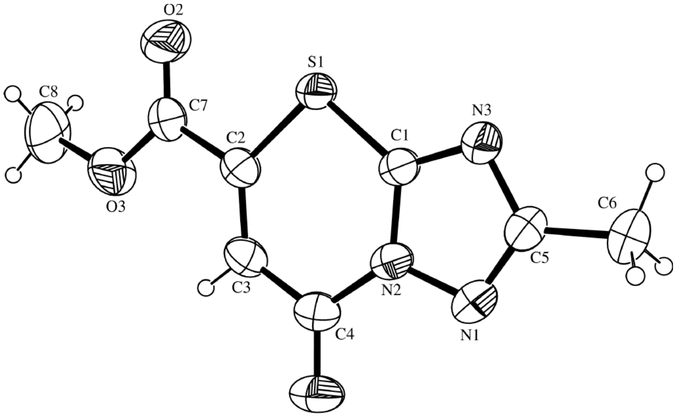


Figure 1
ORTEP-3 (Farrugia, 1999) drawing of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

C2—C7—O2 torsion angle is −178.0 (3)°. The interatomic distances O2···H8*C* (2.63 Å) and O3···H3 [2.45 (3) Å] indicate close contacts.

The bond distances and angles (Table 1) are within expected ranges. The N1—C5 and N3—C1 bond lengths have the same value [1.305 (3) Å] and are in good agreement with those found for structures containing a 1,2,4-triazole ring (Wang *et al.*, 1998; Özbey *et al.*, 1999, 2000). The slight lengthening of the S1—C2 bond [1.731 (2) Å] compared with S1—C1 [1.723 (2) Å] may be explained in terms of both the steric effect of the methoxycarbonyl group at C2 and strain.

Experimental

A solution of 3-methyl-5-mercapto-1,2,4-triazole (0.002 mol) and dimethyl acetylenedicarboxylate (0.0025 mol) in toluene (100 ml) was refluxed for 4 h. After cooling, the reaction mixture was filtered and the resulting solid was recrystallized from an ethyl acetate/*n*-hexane solution. Yield 32%; m.p. 427–428 K.

Crystal data

$C_8H_7N_3O_3S$
$M_r = 225.23$
Triclinic, $P\bar{1}$
$a = 4.0299\ (3)$ Å
$b = 10.2866\ (7)$ Å
$c = 11.9615\ (9)$ Å
$\alpha = 104.870\ (6)^\circ$
$\beta = 96.745\ (6)^\circ$
$\gamma = 95.831\ (6)^\circ$
$V = 471.42\ (6)$ Å^3

$Z = 2$
$D_x = 1.587$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.4$–18.4°
$\mu = 0.33$ mm^{-1}
$T = 295\ (2)$ K
Prism, colorless
$0.40 \times 0.32 \times 0.12$ mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled $\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.880$, $T_{\max} = 0.961$
2173 measured reflections
1893 independent reflections
1504 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.011$
$\theta_{\max} = 26.3^\circ$
$h = -5 \rightarrow 0$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.125$
$S = 1.09$
1891 reflections
140 parameters
H atoms treated by a mixture of constrained and independent refinement

$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 0.1626P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N3	1.305 (3)	C4—N2	1.409 (3)
C1—N2	1.373 (3)	C5—N1	1.305 (3)
C1—S1	1.723 (2)	C5—N3	1.374 (3)
C2—C3	1.339 (4)	C5—C6	1.489 (3)
C2—C7	1.498 (3)	C7—O2	1.191 (3)
C2—S1	1.731 (2)	C7—O3	1.307 (3)
C3—C4	1.452 (3)	N1—N2	1.380 (3)
C4—O1	1.208 (3)		
N2—C1—S1	124.57 (17)	C5—N1—N2	102.76 (19)
C3—C2—C7	123.2 (2)	C1—N2—N1	108.02 (19)
C3—C2—S1	127.09 (19)	C1—N2—C4	128.5 (2)
C2—C3—C4	126.0 (2)	C1—N3—C5	102.8 (2)
N2—C4—C3	114.5 (2)	C7—O3—C8	116.8 (2)
N1—C5—N3	115.6 (2)	C1—S1—C2	98.98 (11)
O2—C7—O3	126.1 (2)		

Methyl H atoms were positioned geometrically, with C—H distances of 0.96 Å, and refined riding on their parent atoms. The H atom on C3 was located from a difference map and freely refined.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1999); software used to prepare material for publication: *PARST* (Nardelli, 1995).

References

Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Giammonia, G., Neri, M., Carlisi, B., Palazzo, A. & Rosa, C. (1991). *J. Heterocycl. Chem.* **28**, 325–327.

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Özbey, S., Kendi, E., Tozkoparan, B. & Ertan, M. (1999). *Acta Cryst.* C**55**, 1939–1941.

Özbey, S., Ulusoy, N. & Kendi, E. (2000). *Acta Cryst.* C**56**, 222–224.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Tozkoparan, B., Aktay, G. & Yeşilada, E. (2002). Il Farmaco, **57**, 145–152.

Tozkoparan, B., Aktay, G., Yeşilada, E. & Ertan, M. (2001). *Arzneim. Forsch. (Drug Res.)*, **51**, 470–477.

Tozkoparan, B., Ayhan Kılcıgil, G., Ertan, R., Ertan, M., Kelicen, P. & Demirdamar, R. (1999). *Arzneim. Forsch. (Drug Res.)*, **49**, 1006–1011.

Tozkoparan, B., Gökhan, N., Aktay, G., Yeşilada, E. & Ertan, M. (2000). *Eur. J. Med. Chem.* **35**, 743–750.

Wang, Z., Bai, Z., Yang, J., Okamoto, K. & You, X. (1998). *Acta Cryst.* C**54**, 438–439.