

$= 0.97$ (2), $O(3)\cdots O(4)^* = 3.124$ (8), $HO(3)\cdots O(4)^* = 2.19$ (3) Å, $O(3)-HO(3)\cdots O(4)^* = 160.2$ (6)°.

References

- ABADI, B. E. A., MOSS, D. S. & PALMER, R. A. (1984). *J. Crystallogr. Spectrosc. Res.* **14**, 269–281.
- LIN, H. S., LEVY, R. H., BLEHAUT, H. & TOR, J. (1984). *Metabolism of Antiepileptic Drugs*, p. 199. New York: Raven Press.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
- ROLLETT, J. S. (1965). *Computing Methods in Crystallography*, p. 22. Oxford: Pergamon Press.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of 5,5-Dimethyl-4-(2-methylallyl)-2-tolyl-1,2,4-triazolidine-3-thione

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Abstract. $C_{15}H_{21}N_3S$, $M_r = 275.4$, monoclinic, $P2_1/c$, $a = 11.047$ (2), $b = 14.050$ (4), $c = 11.608$ (3) Å, $\beta = 119.27$ (2)°, $V = 1572$ (1) Å³, $Z = 4$, $D_x = 1.16$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 0.197$ mm⁻¹, $F(000) = 592$, $T = 295$ K, $R = 0.053$ for 2682 unique observed reflections. The 1,2,4-triazolidine ring is in a near envelope conformation, the flap of which is N(1). There are two kinds of C–N bond lengths: two single-bond lengths [1.484 (2) and 1.472 (2) Å] and two intermediate single–double-bond lengths [1.352 (2) and 1.364 (2) Å], indicating considerable conjugation with the thione. The C–S bond length [1.677 (2) Å] is similar to that found in other 1,2,4-triazoline-3-thiones.

Introduction. Triazolidine-3-thiones and thiazolidine-3-imines are isomeric compounds. They can be synthesized by cyclization reactions with thiosemicarbazides and thiosemicarbazones (Willems, 1965; Malbec, Milcent & Barbier, 1984). Depending on the reaction conditions, triazolidines or thiazolidines (Malbec *et al.*, 1984) or mixtures of both heterocycles (Valters & Flitsch, 1985; Jensen, 1969) are formed. Also, one of these heterocyclic compounds can be rearranged to the other by Dimroth rearrangement (L'Abbé, 1984). Sometimes, the determination of the structure is difficult (Jensen, 1969; Buccheri, Cusmano, Noto, Rainieri & Werber, 1987).

In connection with our investigations of 1,4- and 2,4-disubstituted thiosemicarbazides, we have found a

new cyclization reaction between 2,4-disubstituted thiosemicarbazides and ketones (Schulze & Richter, 1988), and we are interested in the structure determination of the cyclization product. We report here the molecular structure of the title compound. To the best of our knowledge, no structural investigations have been carried out for such substituted triazolidine-3-thiones. Only mercapto-1,2,4-triazoles (Senko & Templeton, 1958) and triazoline-3-thiones have been investigated (Gors, Devos, Baert, Henichart & Houssin, 1977; Isaacs & Kennard, 1970).

Experimental. The title compound was synthesized by condensation between 4-(2-methylallyl)-2-tolylthiosemicarbazide and acetone in ethanol with some drops of concentrated H₂SO₄. A white precipitate was formed on diluting with water and cooling. Transparent crystal from ethanol, 0.3 × 0.3 × 0.4 mm. Nonius CAD-4 diffractometer, graphite monochromator, Mo K α radiation, ω - $\frac{1}{2}\theta$ scan, $2 \leq 2\theta \leq 60^\circ$. Unit-cell parameters refined from setting angles of 25 selected reflections ($24.20 < 2\theta < 41.54$). 4532 independent reflections, only 2682 observed [$I > 1.4\sigma(I)$ and $I > 1.3 \times I_{\text{background}}$]. $-15 \leq h \leq 13$, $0 \leq k \leq 19$, $0 \leq l \leq 16$. Standard reflection, 656, showed 2.9% intensity variation. Lp corrections, no absorption correction. Direct methods: program *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix refinements based on F with $w = (a + b|F_o|)^{-2}$

calculated from $|\Delta\bar{F}|$ vs $|\bar{F}_o|$ curves. H atoms located from ΔF syntheses, with isotropic B equal to the B_{eq} of bearing C or N atoms. Final refinement involving the x , y , z , β_{ij} parameters for the non-H atoms and x , y , z for the H atoms. $R = 0.053$, $wR = 0.071$, $S = 0.72$, $(\Delta/\sigma)_{max} = 0.40$ (non-H atoms), $|\Delta\rho| \leq 0.16 \text{ e } \text{\AA}^{-3}$. f from *International Tables for X-ray Crystallography* (1974). Computing by means of our library of classical crystallographic programs (Quaglieri, Loiseleur & Thomas, 1972), IBM 3090/200 computer, Centre Inter Regional de Calcul Electronique (CIRCE), Orsay.

Discussion. The refined atomic parameters are given in Table 1.* Main bond lengths and angles are in Table 2.

The drawing of the molecule in Fig. 1 was obtained by means of *ORTEP* (Johnson, 1965). This shows that the cyclization reaction leads to a 1,2,4-triazolidine-3-thione.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, C—H and N—H distances, torsion angles and mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51119 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

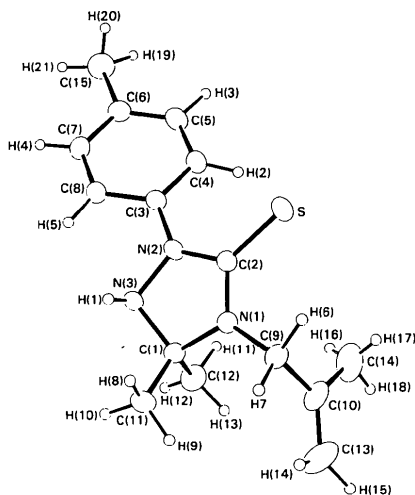


Fig. 1. *ORTEP* view of the molecule with 25% probability thermal ellipsoids. The H atoms are arbitrarily scaled.

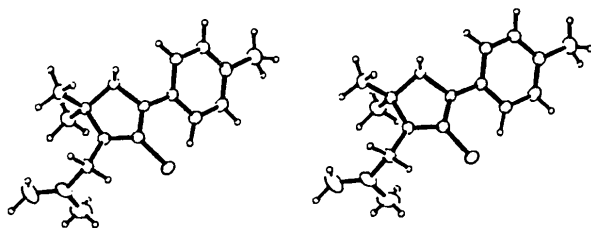


Fig. 2. *ORTEP* stereoscopic view.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \frac{4}{3} \sum_i \beta_i a_i \cdot a_i$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
S	0.33139 (6)	0.52669 (4)	0.12961 (5)	4.7 (1)
N(1)	0.2785 (1)	0.6089 (1)	-0.1006 (1)	3.4 (1)
C(1)	0.2532 (2)	0.5838 (1)	-0.2348 (2)	3.7 (1)
N(2)	0.3163 (2)	0.4559 (1)	-0.0957 (2)	4.1 (1)
C(2)	0.3071 (2)	0.5301 (1)	-0.0247 (2)	3.6 (1)
N(3)	0.3186 (2)	0.4893 (1)	-0.2123 (2)	3.9 (1)
C(3)	0.3176 (2)	0.3562 (1)	-0.0769 (2)	3.5 (1)
C(4)	0.2619 (2)	0.3149 (2)	-0.0040 (2)	4.4 (1)
C(5)	0.2623 (2)	0.2166 (2)	0.0075 (2)	4.6 (1)
C(6)	0.3158 (2)	0.1575 (1)	-0.0521 (2)	4.2 (1)
C(7)	0.3703 (2)	0.2002 (1)	-0.1244 (2)	4.2 (1)
C(8)	0.3716 (2)	0.2980 (1)	-0.1378 (2)	3.8 (1)
C(9)	0.2684 (2)	0.7047 (1)	-0.0593 (2)	4.1 (1)
C(10)	0.1234 (2)	0.7438 (2)	-0.1229 (2)	5.5 (1)
C(11)	0.0991 (2)	0.5748 (2)	-0.3311 (2)	5.2 (1)
C(12)	0.3247 (3)	0.6524 (2)	-0.2821 (2)	4.9 (1)
C(13)	0.0931 (4)	0.8231 (3)	-0.1945 (4)	8.6 (3)
C(14)	0.0218 (4)	0.6920 (4)	-0.0966 (5)	8.0 (3)
C(15)	0.3133 (4)	0.0510 (2)	-0.0401 (4)	6.4 (2)

Table 2. *Main bond lengths (Å) and angles (°)*

C(1)—N(1)	1.484 (2)	C(7)—C(6)	1.387 (3)
C(2)—S	1.677 (2)	C(8)—C(3)	1.392 (2)
C(2)—N(1)	1.352 (2)	C(8)—C(7)	1.384 (3)
C(2)—N(2)	1.364 (2)	C(9)—N(1)	1.452 (2)
N(3)—C(1)	1.472 (2)	C(10)—C(9)	1.502 (3)
N(3)—N(2)	1.444 (2)	C(11)—C(1)	1.517 (3)
C(3)—N(2)	1.417 (2)	C(12)—C(1)	1.510 (3)
C(4)—C(3)	1.394 (2)	C(13)—C(10)	1.331 (5)
C(5)—C(4)	1.386 (3)	C(14)—C(10)	1.489 (5)
C(6)—C(5)	1.385 (3)	C(15)—C(6)	1.504 (3)
C(1)—N(1)—C(2)	110.7 (1)	C(1)—N(3)—N(2)	103.1 (1)
C(1)—N(1)—C(9)	124.2 (1)	N(2)—C(3)—C(4)	122.2 (2)
C(2)—N(1)—C(9)	125.1 (2)	N(2)—C(3)—C(8)	118.5 (2)
N(1)—C(1)—N(3)	101.8 (1)	C(4)—C(3)—C(8)	119.3 (2)
N(1)—C(1)—C(11)	111.2 (2)	C(3)—C(4)—C(5)	119.5 (2)
N(1)—C(1)—C(12)	111.5 (2)	C(4)—C(5)—C(6)	122.1 (2)
N(3)—C(1)—C(11)	109.4 (2)	C(5)—C(6)—C(7)	117.4 (2)
N(3)—C(1)—C(12)	109.9 (2)	C(5)—C(6)—C(15)	121.2 (2)
C(11)—C(1)—C(12)	112.5 (2)	C(7)—C(6)—C(15)	121.3 (2)
C(2)—N(2)—N(3)	111.0 (1)	C(6)—C(7)—C(8)	122.0 (2)
C(2)—N(2)—C(3)	131.4 (1)	C(3)—C(8)—C(7)	119.7 (2)
N(3)—N(2)—C(3)	117.5 (1)	N(1)—C(9)—C(10)	114.3 (2)
S—C(2)—N(1)	125.7 (1)	C(9)—C(10)—C(13)	119.7 (3)
S—C(2)—N(2)	127.1 (1)	C(9)—C(10)—C(14)	116.8 (3)
N(1)—C(2)—N(2)	107.1 (1)	C(13)—C(10)—C(14)	123.5 (3)

The molecular conformation can be discussed by means of the torsion angles and the least-squares planes. An *ORTEP* stereoscopic view (Fig. 2) (Johnson, 1965) shows this conformation. The triazolidine ring can be described as having a near-envelope conformation, the flap of which is N(3). The dihedral angles are 37.0° between the triazolidine and the tolyl, 77.9° between the triazolidine and the methallyl. There is no intramolecular interaction between thione and tolyl: $S \cdots H(2) = 2.63 (3) \text{ \AA}$ and $C(4)-H(2) \cdots S = 122 (2)^\circ$.

The C—S bond length [$1.677 (2) \text{ \AA}$] is considerably shorter than the single bond, for example, in 2,5-diphenylthiadiazole (Zvonkova & Khvatkina, 1965)

(1.769 Å) and in a 1,3,4-thiadiazolidine-5-thione (Karle & Karle, 1965) (1.777 and 1.842 Å) but similar to that found in the morpholinoethyl-1,2,4-triazoline-3-thione (Gors *et al.*, 1977) (1.67 Å) and other 1,2,4-triazoline-3-thiones (Secombe & Kennard, 1973*a,b,c*) (1.668, 1.673, 1.675 Å).

There are two kinds of C–N bond lengths within the triazolidine ring. Two [C(1)–N(1) = 1.484 (2) and C(1)–N(3) = 1.472 (2) Å] are single-bond lengths. The other two [C(2)–N(1) = 1.352 (2) and C(2)–N(2) = 1.364 (2) Å] are intermediate between single-bond and double-bond length, indicating considerable conjugation with the C–S bond.

The exocyclic angles at N(2) show considerable asymmetry, C(2)–N(2)–C(3) [131.4 (1)°] being significantly larger than N(3)–N(2)–C(3) [117.5 (1)°]. As previously noted (Branch & Nowell, 1985, 1986), this asymmetry appears to be characteristic of the triazolyl ring itself rather than due to the influence of any intra- or intermolecular interactions.

References

- BRANCH, S. K. & NOWELL, I. W. (1985). *Acta Cryst.* **C41**, 594–597, and references therein.
 BRANCH, S. K. & NOWELL, I. W. (1986). *Acta Cryst.* **C42**, 440–442.
 BUCCHERI, F., CUSMANO, G., NOTO, R., RAINIERI, R. & WERBER, G. (1987). *J. Heterocycl. Chem.* **24**, 521–523.

- GORS, C., DEVOS, L., BAERT, F., HENICHART, J. P. & HOUSSIN, R. (1977). *Cryst. Struct. Commun.* **6**, 565–570.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 99. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 ISAACS, N. W. & KENNARD, C. H. L. (1970). *J. Chem. Soc. Chem. Commun.* p. 631.
 JENSEN, K. A. (1969). *Z. Chem.* **9**, 121–128.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 KARLE, I. L. & KARLE, J. (1965). *Acta Cryst.* **19**, 92–99.
 L'ABBÉ, G. (1984). *J. Heterocycl. Chem.* **21**, 627–638.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 MALBEC, F., MILCENT, R. & BARBIER, G. (1984). *J. Heterocycl. Chem.* **21**, 1689–1698.
 QUAGLIERI, P., LOISELEUR, H. & THOMAS, G. (1972). *Acta Cryst.* **B28**, 2583–2590.
 SCHULZE, K. & RICHTER, C. (1988). *Z. Chem.* In the press.
 SECCOMBE, R. C. & KENNARD, C. H. L. (1973*a*). *J. Chem. Soc. Perkin Trans. 2*, pp. 4–6.
 SECCOMBE, R. C. & KENNARD, C. H. L. (1973*b*). *J. Chem. Soc. Perkin Trans. 2*, pp. 9–11.
 SECCOMBE, R. C. & KENNARD, C. H. L. (1973*c*). *J. Chem. Soc. Perkin Trans. 2*, pp. 11–14.
 SENKO, M. E. & TEMPLETON, D. H. (1958). *Acta Cryst.* **11**, 808–812.
 VALTERS, R. E. & FLITSCH, W. (1985). *Ring-Chain Tautomerism*, pp. 199–203. New York: Plenum.
 WILLEMS, J. F. (1965). *Fortschr. Chem. Forsch.* **5**, 147–211.
 ZVONKOVA, Z. V. & KHVATKINA, A. V. (1965). *Kristallografiya*, **10**, 734–737.

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Structure of Mangostin Acetate

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Abstract. 1,3,6-Triacetoxy-7-methoxy-2,8-bis(3-methyl-2-butenyl)-9*H*-xanthen-9-one, C₃₀H₃₂O₉, *M_r* = 536.6, triclinic, *P* $\bar{1}$, *a* = 11.400 (4), *b* = 11.464 (3), *c* = 13.403 (1) Å, α = 70.03 (1), β = 106.57 (2), γ = 118.53 (3)°, *V* = 1430.5 (7) Å³, *Z* = 2, *D_m* =

1.241 (3) (floatation), *D_x* = 1.246 Mg m⁻³, Cu *K* α radiation, λ = 1.5418 Å, μ = 0.725 mm⁻¹, *F*(000) = 568, *T* = 294 K, final *R* = 0.063 for 3022 reflections [*I* > 3 σ (*I*)]. The tricyclic xanthone system is not planar. The mean planes of the two isoprenyl side chains are inclined at an angle of 159.8 (2)°.

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Introduction. Xanthenes are a class of compounds which have been shown to possess anti-inflammatory and CNS depressant activities (Gopalakrishnan,