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Structure of 3-(2-Pyridyl)-2-(2-tolyl)-1,3-thiazolidin-4-one, C₁₅H₁₄N₂OS

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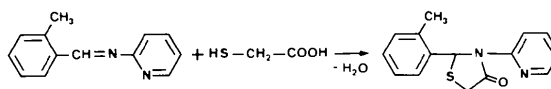
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Abstract. $M_r = 270.36$, space group $P\bar{1}$, $a = 10.304$ (1), $b = 13.845$ (2), $c = 19.852$ (3) Å, $\alpha = 80.87$ (1), $\beta = 78.19$ (1), $\gamma = 89.25$ (1)°, $Z = 8$ (four molecules in the asymmetric unit), $V = 2736.4$ Å³, $D_m = 1.30$ (1), $D_x = 1.313$ Mg m⁻³, $F(000) = 1136$, and $\mu(\text{Cu } K\alpha) = 2.0$ mm⁻¹. The structure of this antibacterial drug was solved by direct methods and refined by least-squares calculations to $R = 0.066$ for 10713 observed reflections. Two different conformations appeared, differing mainly in torsional angles, the four molecules being related in pairs through a pseudoglide plane. In one conformation the thiazolidine ring was found to be in an envelope conformation, whereas in the other it was found to be significantly more twisted.

Introduction. The synthesis of the thiazolidinone investigated has been described elsewhere (Fenech,

1960). It is obtained from the reaction of thioglycolic acid with the corresponding Schiff base:



This molecule is a member of the substituted 2-aryl-1,3-thiazolidin-4-one family, which have great and diverse therapeutical interest (some have antibacterial, antifungal, anti-tubercular, myorelaxant, or antiviral properties) (Newkome & Nayak, 1979; Fenech, 1972–73). The title compound shows antibacterial activity (Fenech, 1962).

Furthermore, from a theoretical point of view, very few reports have appeared concerning the 1,3-thiazolidin-4-one conformation (Anantha-Murthy & Murthy, 1975).

For this reason, investigations were undertaken (Vigorita, Chimirri, Grasso & Fenech, 1979) to determine its preferred conformations in solution from IR and ^1H NMR studies; the IR solid-phase analysis was temporarily set aside since the carbonyl absorption showed a strange splitting into two bands. This suggested the possibility of other conformations which are not present in the liquid phase. At this stage, it became obvious that crystallography could afford otherwise unattainable information about these compounds and permit a valuable comparison with IR and ^1H NMR results.

Experimental. Samples of the title compound were synthesized at the Istituto di Chimica Farmaceutica dell'Università di Messina by the above procedure, they were then dissolved in ethanol and allowed to evaporate slowly at room temperature. Colourless prismatic crystals suitable for X-ray diffraction studies grew. Weissenberg and precession photographs indicated that the crystals were triclinic. No systematic absence could be seen, but it was noticeable that, in the $h0l$ plane, the intensities of the rows with h odd were considerably weaker than those with h even. This phenomenon was explained later. The unit-cell dimensions were refined during the alignment process along with the determination of an accurate orientation matrix for the crystal on an Enraf-Nonius CAD-4 diffractometer. 23 well centred randomly spread reflections were used for this purpose.

At this stage, the number of eight molecules per unit cell, determined as a function of the observed density, was somewhat disturbing in view of the crystal's triclinic symmetry. In fact, the asymmetric unit proved to contain four molecules in space group $P\bar{1}$.

Data collection on a crystal $0.4 \times 0.2 \times 0.15$ mm was performed on the automatic diffractometer according to the parameters given in Table 1. 11271 independent reflections were measured, 10713 of which were considered as observed [$I > 3\sigma(I)$]. No absorption correction was applied; the data were corrected for Lorentz and polarization effects.

Table 1. *Data-collection parameters*

Temperature: 291 K		
$\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$		
Monochromator: graphite crystal		
Crystal-detection-aperture distance: 173 mm		
Detector aperture: height 4 mm, width $(1.3^* + 1.0^* \text{tg } \theta) \text{ mm}$		
θ limits: 1 to 78°		
Scan angle: $\Delta\theta = 0.80^* + (0.14 \text{tg } \theta)^\circ$		
Scan mode: ω - θ with speed ratio 1:1* (ω/θ)		
Intensity-measurement parameters:† $\sigma_{\text{pre}} = 0.35$; $\sigma = 0.005$; scan speed		
pre-scan: $20^\circ \text{ min}^{-1}$; $T_{\text{max}} = 80 \text{ s}$		
Take-off angle: 5° *		
Attenuation factor: 16.8		
	Intensity control	Orientation control
Standard reflections	111, 123	6, 0, 16, 7, 5, 15
Periodicity	3600 s	100 reflections

* Experimentally determined parameters.

† Enraf-Nonius (1977).

The distribution of the E values calculated during the data reduction confirmed that the space group was centrosymmetric, with a close fit between the experimental and theoretical values.

The structure was solved with the *MULTAN* program (Germain, Main & Woolfson, 1970), after estimation of the triplet invariant phases from the corresponding estimation for quartets (Busetta, 1976). The choice of $E > 1.95$ led to 1975 relationships. Three origin-defining reflections (548; 0, 6, 11; $\bar{3}$, 5, 20) were used. One sign was determined by the \sum_1 method and six symbols were necessary. The solution was given by the tangent formula.

The E map calculated from this solution revealed the positions of 39 of the 76 non-hydrogen atoms. Three more cycles of sign determination and subsequent Fourier synthesis were necessary to locate the remaining 37. At this stage the R value dropped to 0.128. Two further refinement cycles with all non-hydrogen atoms treated anisotropically resulted in a reduction of R to 0.097. 40 of the 56 H atoms were then positioned theoretically and the remaining 16 were located distinctly from difference Fourier maps.

To this stage, the only reflections used were located within a 45° (θ) sphere in order to save computing time. After completion of the refinement using all the measured reflections considered as observed, the final R value was 0.066.*

Discussion. The final positional parameters and their standard deviations are presented in Table 2. The stereochemistry of the molecules is illustrated and the numbering of the atoms depicted in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters, parameters concerning the H atoms, and Tables 5, 8, 9 and 10 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38142 (75 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

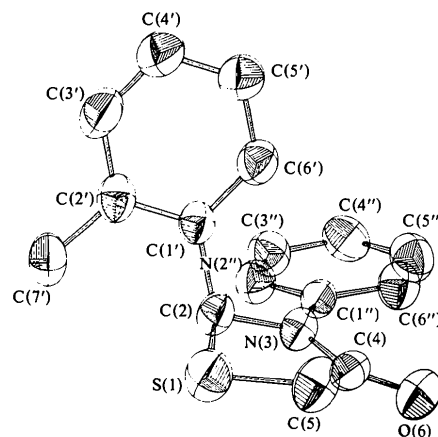


Fig. 1. ORTEP drawing (Johnson, 1965) and numbering scheme.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for the non-hydrogen atoms

	x	y	z	B_{eq} (Å ²)	x	y	z	B_{eq} (Å ²)
Molecule (1)					Molecule (2)			
S(1)	-16 (1)	4587 (1)	3914 (1)	5.6	3647 (1)	2384 (1)	1418 (1)	3.8
C(2)	1775 (2)	4465 (2)	3733 (1)	3.8	5019 (2)	1606 (2)	1095 (1)	3.3
N(3)	2324 (2)	5459 (2)	3446 (1)	3.5	6112 (2)	1884 (2)	1388 (1)	3.4
C(4)	1441 (3)	6208 (2)	3482 (1)	4.0	5788 (3)	2342 (2)	1969 (1)	3.5
C(5)	83 (4)	5874 (3)	3883 (2)	5.6	4327 (3)	2496 (2)	2170 (2)	4.4
O(6)	1708 (2)	7059 (2)	3210 (1)	5.1	6590 (2)	2585 (2)	2291 (1)	4.5
C(1')	2313 (3)	4001 (2)	4364 (1)	3.5	4665 (3)	525 (2)	1292 (1)	3.4
C(2')	2199 (3)	2994 (2)	4560 (1)	4.1	3905 (3)	98 (2)	910 (2)	4.1
C(3')	2702 (4)	2586 (2)	5150 (2)	5.2	3562 (4)	-892 (3)	1103 (2)	5.5
C(4')	3275 (4)	3142 (3)	5522 (2)	5.5	3995 (4)	-1456 (3)	1661 (2)	6.1
C(5')	3377 (4)	4147 (2)	5328 (2)	4.9	4764 (4)	-1031 (3)	2027 (2)	5.7
C(6')	2879 (3)	4567 (2)	4751 (1)	4.3	5109 (3)	-42 (2)	1839 (2)	4.3
C(7')	1590 (5)	2349 (3)	4164 (2)	6.3	3392 (4)	678 (3)	318 (2)	5.5
C(1'')	3700 (3)	5574 (2)	3171 (1)	3.3	7422 (2)	1631 (2)	1085 (1)	3.3
N(2'')	4289 (3)	4768 (2)	2991 (1)	4.1	7604 (2)	1632 (2)	408 (1)	4.8
C(3'')	5605 (3)	4807 (2)	2744 (2)	4.6	8826 (4)	1389 (4)	81 (2)	6.1
C(4'')	6390 (3)	5662 (3)	2665 (2)	4.9	9838 (4)	1141 (4)	412 (2)	6.2
C(5'')	5714 (3)	6495 (2)	2868 (2)	4.7	9612 (4)	1157 (4)	1123 (2)	6.5
C(6'')	4391 (3)	6457 (2)	3123 (2)	4.2	8384 (3)	1404 (3)	1475 (2)	4.9
Molecule (3)					Molecule (4)			
S(1)	-1356 (1)	4244 (1)	1355 (1)	4.1	5030 (1)	904 (1)	3927 (1)	5.4
C(2)	-55 (3)	5194 (2)	1048 (1)	3.5	6832 (3)	1111 (2)	3748 (1)	3.6
N(3)	1069 (2)	4799 (2)	1329 (1)	3.4	7390 (2)	227 (2)	3467 (1)	3.6
C(4)	798 (3)	4078 (2)	1903 (1)	3.5	6522 (3)	-520 (2)	3502 (1)	3.6
C(5)	-674 (3)	3800 (3)	2104 (2)	4.5	5183 (4)	-380 (3)	3901 (2)	5.4
O(6)	1608 (2)	3692 (2)	2223 (1)	4.3	6829 (2)	-1256 (2)	3229 (1)	5.0
C(1')	-490 (2)	6170 (2)	1277 (1)	3.2	7329 (3)	1279 (2)	4384 (1)	3.5
C(2')	-1308 (3)	6757 (2)	919 (1)	4.0	7206 (3)	2203 (2)	4579 (1)	4.1
C(3')	-1788 (3)	7625 (2)	1165 (2)	4.9	7674 (4)	2342 (3)	5172 (2)	5.7
C(4')	-1390 (4)	7911 (3)	1732 (2)	5.3	8243 (4)	1617 (3)	5559 (2)	5.5
C(5')	-513 (4)	7337 (3)	2063 (2)	5.4	8362 (4)	681 (2)	5373 (2)	4.9
C(6')	-76 (3)	6465 (2)	1840 (2)	4.6	7907 (3)	534 (2)	4786 (2)	4.2
C(7')	-1708 (4)	6499 (3)	284 (2)	5.5	6610 (4)	3031 (2)	4167 (2)	5.7
C(1'')	2347 (3)	5226 (2)	1028 (1)	3.3	8778 (3)	235 (2)	3189 (1)	3.2
N(2'')	2451 (3)	5626 (2)	368 (1)	4.4	9349 (2)	1119 (2)	3032 (1)	4.0
C(3'')	3605 (4)	6070 (3)	44 (2)	5.5	10647 (3)	1187 (2)	2772 (2)	4.4
C(4'')	4654 (4)	6121 (3)	347 (2)	6.7	11452 (3)	385 (2)	2663 (2)	5.7
C(5'')	4510 (4)	5711 (4)	1056 (2)	6.6	10807 (4)	-531 (2)	2830 (2)	4.9
C(6'')	3335 (3)	5244 (3)	1399 (2)	4.8	9483 (3)	-615 (2)	3105 (2)	4.2

Bond distances and angles. The bond distances and their e.s.d.'s are provided in Table 3, the bond angles and their e.s.d.'s in Table 4. As there are four independent molecules in the asymmetric unit, the corresponding bond lengths and angles of the four molecules are compared. The largest bond-length differences are calculated in Table 5.* From this comparison it appears that the bond distances and angles agree very well in the two pairs of molecules (1) and (4) (largest bond-length difference 0.029 Å) and (2) and (3) (0.027 Å), whereas the agreement is much poorer in the other sets of two molecules.

From this stage on, the two molecules (1) and (4) on the one hand, and (2) and (3) on the other appear very similar.

Our results have also been compared to those obtained by other authors on related compounds.

This comparison was made only between the distances and angles of the thiazolidine ring since there were no unusual values concerning the pyridyl and tolyl rings.

Table 6 gives the bond distances and the hybridization nature of the C(2), N(3), C(4) and C(5)

atoms in several thiazoli(di)nes, while Table 7 gives the intracyclic bond angles of the thiazoli(di)ne rings and their sums.

Of all these compounds, molecule *F* (1,3-thiazolidine-4-carboxylic acid) is the only one to

Table 3. Bond distances (Å) and their e.s.d.'s

	Molecule (1)	Molecule (2)	Molecule (3)	Molecule (4)
C(1') C(2')	1.386 (4)	1.391 (4)	1.384 (4)	1.391 (4)
C(2') C(7')	1.501 (6)	1.500 (5)	1.498 (5)	1.499 (5)
C(2') C(3')	1.410 (5)	1.395 (5)	1.414 (5)	1.400 (5)
C(3') C(4')	1.363 (6)	1.396 (6)	1.389 (6)	1.367 (6)
C(4') C(5')	1.383 (6)	1.373 (6)	1.391 (6)	1.401 (6)
C(5') C(6')	1.391 (5)	1.392 (6)	1.390 (5)	1.386 (5)
C(6') C(1'')	1.390 (4)	1.388 (4)	1.393 (4)	1.404 (4)
C(1'') C(2)	1.519 (4)	1.515 (4)	1.528 (4)	1.508 (4)
S(1) C(2)	1.818 (3)	1.839 (3)	1.831 (3)	1.836 (3)
C(2) N(3)	1.476 (4)	1.451 (4)	1.450 (4)	1.485 (4)
N(3) C(4)	1.372 (4)	1.383 (4)	1.374 (4)	1.361 (4)
C(4) O(6)	1.225 (4)	1.222 (4)	1.219 (4)	1.235 (4)
C(4) C(5)	1.500 (5)	1.498 (5)	1.525 (5)	1.471 (5)
C(5) S(1)	1.777 (4)	1.801 (4)	1.793 (4)	1.792 (4)
N(3) C(1''')	1.411 (4)	1.425 (4)	1.423 (4)	1.424 (4)
C(1''') N(2'')	1.327 (4)	1.317 (4)	1.322 (4)	1.328 (4)
N(2'') C(3'')	1.343 (5)	1.358 (5)	1.337 (5)	1.330 (4)
C(3'') C(4'')	1.412 (5)	1.356 (7)	1.347 (7)	1.395 (5)
C(4'') C(5'')	1.410 (5)	1.386 (7)	1.411 (7)	1.400 (5)
C(5'') C(6'')	1.352 (5)	1.381 (6)	1.375 (6)	1.360 (5)
C(6'') C(1''')	1.403 (4)	1.381 (5)	1.377 (5)	1.390 (4)

* This table has been deposited. See deposition footnote.

Table 4. Bond angles ($^{\circ}$) and their e.s.d.'s

	Molecule (1)	Molecule (2)	Molecule (3)	Molecule (4)
C(2')-C(1')-C(6')	120.1 (3)	120.0 (3)	120.5 (3)	119.2 (3)
C(2')-C(1')-C(2)	118.6 (3)	119.1 (3)	119.0 (2)	118.7 (3)
C(6')-C(1')-C(2)	121.3 (3)	120.8 (3)	120.5 (3)	122.1 (3)
C(1')-C(2')-C(3')	117.2 (3)	118.8 (3)	118.8 (3)	117.7 (3)
C(1')-C(2')-C(7')	122.3 (3)	122.2 (3)	122.3 (3)	121.6 (3)
C(3')-C(2')-C(7')	120.5 (3)	119.0 (3)	118.9 (3)	120.7 (3)
C(2')-C(3')-C(4')	122.5 (4)	120.9 (4)	120.6 (3)	123.1 (4)
C(3')-C(4')-C(5')	120.1 (4)	119.8 (4)	119.7 (4)	119.8 (4)
C(4')-C(5')-C(6')	118.4 (3)	119.7 (4)	120.0 (4)	117.8 (3)
C(1')-C(6')-C(5')	121.6 (3)	120.7 (3)	120.3 (3)	122.5 (3)
C(2)-S(1)-C(5)	93.2 (2)	91.3 (1)	91.4 (2)	93.0 (2)
C(1')-C(2)-S(1)	113.5 (2)	112.6 (2)	112.3 (2)	112.6 (2)
C(1')-C(2)-N(3)	112.8 (2)	112.8 (2)	112.3 (2)	113.1 (2)
S(1)-C(2)-N(3)	105.8 (2)	104.6 (2)	104.9 (2)	104.4 (2)
C(2)-N(3)-C(4)	116.3 (2)	116.7 (2)	116.7 (2)	116.7 (2)
C(2)-N(3)-C(1'')	118.6 (2)	118.6 (2)	118.4 (2)	117.4 (2)
C(4)-N(3)-C(1'')	125.1 (2)	124.6 (2)	124.8 (2)	125.9 (2)
N(3)-C(4)-C(5)	112.7 (3)	112.1 (3)	111.7 (3)	114.0 (3)
N(3)-C(4)-O(6)	124.5 (3)	124.5 (3)	125.7 (3)	123.2 (3)
C(5)-C(4)-O(6)	122.8 (3)	123.4 (3)	122.5 (3)	122.8 (3)
S(1)-C(5)-C(4)	107.1 (3)	106.6 (2)	106.1 (2)	106.7 (3)
N(3)-C(1'')-N(2'')	114.4 (2)	113.2 (3)	112.5 (2)	114.5 (2)
N(3)-C(1'')-C(6'')	122.6 (3)	122.3 (3)	122.8 (3)	122.7 (3)
N(2'')-C(1'')-C(6'')	123.0 (3)	124.5 (3)	124.6 (3)	122.8 (3)
C(1'')-N(2'')-C(3'')	118.2 (3)	116.9 (3)	117.0 (3)	118.1 (3)
N(2'')-C(3'')-C(4'')	123.3 (3)	123.7 (4)	124.1 (4)	124.0 (3)
C(3'')-C(4'')-C(5'')	116.1 (3)	117.7 (4)	118.0 (4)	115.9 (3)
C(4'')-C(5'')-C(6'')	120.8 (3)	120.3 (4)	119.0 (4)	120.8 (3)
C(1'')-C(6'')-C(5'')	118.6 (3)	116.9 (4)	117.3 (4)	118.3 (3)

include four sp^3 -hybridized atoms in the thiazolidine ring, to form a zwitterionic structure. This results in both $N(sp^3)-C(sp^3)$ distances (1.521 and 1.486 Å) being longer than all other corresponding ones in Table 6, distance N(3)-C(4) in compound *Q* (1.493 Å) excepted [due to the binding of N(3) to a mesyl group]; this also results in a decrease of the ring angle at N(3) (110.3°).

The compound studied is the only one in which atoms C(2) to C(5) are in the sequence $sp^3-sp^2-sp^2-sp^3$, so that the ring angles at C(2) and C(5) are smaller (average 105 and 106.5, respectively) than those at N(3) and C(4) (respectively 116.6 and 112.6°). Also, the bond distances from C(2) to C(5) agree well with this sequence, as compared to the published values.

Moreover, there are four compounds in which C(2) and C(5) are both sp^3 hybridized: *F*, *L*, *M* and *U*, and we have compared the S(1)-C(2) distance to the S(1)-C(5) distance in these molecules. In the title compound *U*, the mean value of the S(1)-C(5) bond, 1.791 Å, is smaller than the mean of S(1)-C(2) (1.831 Å). The same situation is encountered in

Table 6. Comparison of the bond distances (Å) in various thiazoli(di)non(es)

Compound	S(1)-C(2)	C(2)-N(3)	N(3)-C(4)	C(4)-C(5)	C(5)-S(1)	C(2)-X	N(3)-X'	C(4)-X''	C(2)	N(3)	C(4)	C(5)	sp^3
<i>A</i>	1.754 (6)	1.323 (5)	1.353 (6)	1.542 (8)	1.818 (5)	1.309 (6)		1.225 (4)	sp^2	sp^2	sp^2	sp^3	1
<i>B</i>	1.755	1.337	1.357	1.542	1.812	1.323		1.224	sp^2	sp^2	sp^2	sp^3	1
	1.737	1.342	1.354	1.531	1.813	1.316		1.223					
<i>C</i>	1.748 (9)	1.321 (13)	1.393 (13)	1.531 (15)	1.813 (11)	1.334 (13)		1.207 (13)	sp^2	sp^2	sp^2	sp^3	1
	1.753 (10)	1.316 (13)	1.364 (13)	1.549 (14)	1.826 (11)	1.344 (13)		1.213 (12)					
<i>D</i>	1.764 (8)	1.388 (10)	1.357 (10)	1.537 (11)	1.808 (8)	1.257 (11)	1.462 (12)	1.207 (10)	sp^2	sp^2	sp^2	sp^3	1
	1.764 (8)	1.377 (11)	1.368 (11)	1.520 (11)	1.814 (8)	1.273 (11)	1.472 (13)	1.202 (10)					
<i>E</i>	1.753 (8)	1.312 (10)	1.364 (11)	1.540 (11)	1.807 (8)	1.324 (10)		1.212 (10)	sp^2	sp^2	sp^2	sp^3	1
<i>F</i>	1.770 (8)	1.521 (8)	1.486 (8)	1.525 (8)	1.828 (8)			1.569 (8)	sp^3	sp^3	sp^3	sp^3	4
<i>G</i>	1.774 (3)	1.396 (5)	1.377 (5)	1.492 (4)	1.737 (3)	1.258 (5)	1.465 (5)	1.214 (4)	sp^2	sp^2	sp^2	sp^3	0
	1.777 (3)	1.383 (5)	1.381 (5)	1.489 (4)	1.737 (3)	1.272 (5)	1.466 (5)	1.220 (4)	sp^2	sp^2	sp^2	sp^3	0
<i>H</i>	1.772 (5)	1.392 (7)	1.462 (8)	1.531 (10)	1.796 (7)	1.250 (7)	1.386 (7)		sp^2	sp^2	sp^3	sp^3	2
<i>I</i>	1.751 (7)	1.372 (8)	1.373 (8)	1.547 (8)	1.845 (5)	1.209 (8)	0.9 (1)	1.219 (8)	sp^2	sp^2	sp^2	sp^3	1
<i>J</i>	1.727 (1)	1.361 (2)	1.404 (2)	1.346 (2)	1.723 (1)	1.678 (1)	1.489 (2)	1.512 (2)	sp^2	sp^2	sp^2	sp^2	0
<i>K</i>	1.739 (2)	1.366 (3)	1.423 (3)	1.377 (3)	1.740 (2)	1.688 (2)	1.542 (3)	1.516 (3)	sp^2	sp^2	sp^2	sp^2	0
<i>L</i>	1.800 (4)	1.467 (4)	1.448 (4)	1.515 (4)	1.809 (4)		1.339 (4)	1.535 (4)	sp^3	sp^2	sp^3	sp^3	3
<i>M</i>	1.818 (4)	1.476 (4)	1.466 (5)	1.519 (5)	1.813 (4)	1.519 (5)	1.329 (5)	1.507 (5)	sp^3	sp^2	sp^3	sp^3	2
	1.836 (4)	1.470 (4)	1.469 (5)	1.526 (5)	1.806 (5)	1.519 (5)	1.333 (4)	1.513 (5)	sp^3	sp^2	sp^3	sp^3	3
<i>N</i>	1.765 (4)	1.365 (5)	1.400 (7)	1.480 (8)	1.791 (6)	1.264 (5)	0.92 (5)		sp^2	sp^2	sp^3	sp^3	2
	1.770 (4)	1.358 (5)	1.442 (6)	1.484 (7)	1.800 (5)	1.276 (5)	0.86 (5)						
<i>O</i>	1.771 (4)	1.328 (5)	1.423 (6)	1.470 (7)	1.778 (5)	1.284 (5)	0.81 (4)		sp^2	sp^2	sp^3	sp^3	2
<i>P</i>	1.756 (5)	1.297 (5)	1.460 (5)	1.497 (5)	1.817 (5)	1.346 (5)			sp^2	sp^2	sp^3	sp^3	2
<i>Q</i>	1.773 (6)	1.403 (7)	1.493 (7)	1.505 (9)	1.828 (6)	1.279 (6)	1.663 (5)		sp^2	sp^2	sp^3	sp^2	2
<i>R</i>	1.763 (4)	1.293 (5)	1.463 (6)	1.528 (7)	1.818 (5)	1.354 (5)			sp^2	sp^2	sp^3	sp^2	2
<i>S</i>	1.742 (4)	1.346 (5)	1.340 (5)	1.531 (5)	1.844 (4)	1.662 (4)		1.322 (4)	sp^2	sp^2	sp^2	sp^3	1
<i>T</i>	1.759 (2)	1.389 (2)	1.389 (2)	1.521 (3)	1.797 (2)	1.207 (2)	1.439 (2)	1.201 (2)	sp^2	sp^2	sp^2	sp^3	1
<i>U</i>	1.818 (3)	1.476 (4)	1.372 (4)	1.500 (5)	1.777 (4)	1.519 (4)	1.411 (4)	1.225 (4)					
	1.839 (3)	1.451 (4)	1.383 (4)	1.498 (5)	1.801 (4)	1.515 (4)	1.425 (4)	1.222 (4)	sp^3	sp^2	sp^2	sp^3	2
	1.831 (3)	1.450 (4)	1.374 (4)	1.525 (5)	1.793 (4)	1.528 (4)	1.423 (4)	1.219 (4)					
	1.836 (3)	1.485 (4)	1.361 (4)	1.471 (5)	1.792 (4)	1.508 (4)	1.424 (4)	1.235 (4)					

Compounds: *A*: 2-Amino-5-phenyl-1,3-thiazolin-4-one (Plastas & Stewart, 1969; Mornon & Raveau, 1971). *B*: 2-Amino-5-phenyl-1,3-thiazolin-4-one, second form (Mornon & Bally, 1972). *C*: 5-Phenyl-2-phenylamino-1,3-thiazolin-4-one (Bally & Mornon, 1973a). *D*: 3-Methyl-5-phenyl-2-phenylamino-1,3-thiazolidin-4-one (Bally & Mornon, 1973b). *E*: 5-Phenyl-2-phenylmethylamino-1,3-thiazolin-4-one (Bally, 1973). *F*: 1,3-Thiazolidine-4-carboxylic acid (Loscalzo, Kallen & Voet, 1973). *G*: Methyl (2-imino-3-methyl-4-oxo-1,3-thiazolidin-5-ylidene)acetate (Adman, Jensen & Warren, 1975). *H*: 2-(2,6-Dimethylphenyl)imino-3-(2-methylbenzoyl)thiazolidine (Argay, Kálmán, Nahlovski & Ribár, 1975). *I*: 1,3-Thiazolidine-2,4-dione (Form, Raper & Downie, 1975). *J*: 3,4-Diisopropyl-1,3-thiazoline-2-thione (Pépe & Pierrot, 1976a). *K*: 3,4-Diisopropyl-5-methyl-1,3-thiazoline-2-thione (Pépe & Pierrot, 1976b). *L*: *N*-*tert*-Butoxycarbonyl-L-1,3-thiazolidine-4-carboxylic acid (Robert, 1976). *M*: *N*-Acetyl-2-(*p*-tolyl)-1,3-thiazolidine-4-carboxylic acid (Parthasarathy, Paul & Korytnyk, 1976). *N*: 2-[(2,6-Dimethylphenyl)imino]-1,3-thiazolidine (Argay, Kálmán, Lazar, Ribár & Tóth, 1977). *O*: 2-Phenylimino-1,3-thiazolidine (Petrović, Ribár, Argay, Kálmán & Nowacki, 1977). *P*: 2-(2-Chlorobenzoylamino)-1,3-thiazoline (Cohen Addad & Viallet, 1978). *Q*: 2-[(2,6-Dimethylphenyl)imino]-3-mesyl-1,3-thiazolidine (Kálmán & Argay, 1978). *R*: 2-(2-Methylbenzoylamino)-1,3-thiazoline (Cohen-Addad, Viallet & Boucherle, 1979; Viallet, 1979). *S*: 4-Dimethylamino-5-ethyl-5-phenyl-1,3-thiazoline-2-thione (Germain, Declercq, Touillaux, Van Meerssche & Henriët, 1979). *T*: 3-Phenyl-1,3-thiazolidine-2,4-dione (Stanković & Andreotti, 1979). *U*: Title compound.

molecule (2) of compound *M* (1.806 versus 1.836 Å) whereas it is the opposite in *F* (1.828 versus 1.770 Å); in the other molecules [(1) of *M* and *L*], both values are nearly equal.

These results seem consistent with the fact that in molecule *L* the S(1) ring atom is symmetrically bound to two methylene C atoms, while in *F* the carboxylic acid group bound to C(4) and engaged in several hydrogen bonds weakens the C(5)–S(1) bond. On the contrary, in molecule *U*, the O(6) ketonic O atom bound to C(4) induces a strengthening of the C(5)–S(1) bond.

The ring angle at S(1) undergoes small variations throughout all the compounds of Table 7 (89.4 to 94.2°).

Conformation of the five-membered ring. In order to determine this conformation, we have first calculated the torsion angles around the ring. These angles are presented in Table 8.* It is again readily seen that molecules (1) and (4) on the one hand, and (2) and (3) on the other are very similar, but differ from one to the other. In molecules (1) and (4) no such torsion angle is very near to 0° and these angles range from 6 to only 21°. In molecules (2) and (3), however, C(2)–N(3)–C(4)–C(5) is near 0° and the torsion-angle range is wider, from 2 to 27°, so atoms C(2) through C(5) are almost in the same plane.

This indicates that the thiazolidine ring is in an envelope conformation in molecules (2) and (3), whereas it is more twisted in molecules (1) and (4).

For both pairs of molecules, the best plane through four of the five ring atoms omits the S atom (Table 9a* gives the equations of these planes and the distances from the five atoms to these planes). The deviations are smaller for the four atoms defining the plane, and greater for the S in the pair of molecules (2) and (3). Moreover, in molecules (1) and (4) another plane through S(1) to C(4) omits C(5) (Table 9b). Therefore, it seemed interesting to determine the equations of the planes through the three atoms C(2), N(3) and C(4). The distances of the two remaining atoms S(1) and C(5) to this plane are given in Table 9(b). In the pair of molecules (1) and (4), S(1) and C(5) are each on opposite sides of this plane, whereas in molecules (2) and (3), C(5) is close to this plane and on the same side as S(1) which lies farther away.

Stereochemistry of the molecule. Some torsion angles involving atoms either inside or outside the thiazolidine ring are given in Table 8(b). We also calculated the angles between the mean planes through the atoms of the three different rings of the molecules (Table 10).* In both types, the angle between the thiazolidine and the pyridyl rings is small (18 to 28°), while the thiazolidine and the tolyl group are not far from perpendicular (73

* This table has been deposited. See deposition footnote.

* This table has been deposited. See deposition footnote.

Table 7. Comparison of the bond angles (°) in various thiazoli(di)n(on)es

Compound*	C(5)–S(1)–C(2)	S(1)–C(2)–N(3)	C(2)–N(3)–C(4)	N(3)–C(4)–C(5)	C(4)–C(5)–S(1)	Σ
<i>A</i>	{ 87.8	119.0	111.8	114.5	106.2	539.3 } 539.5 }
	{ 88.4	118.1	111.5	115.7	105.8	
<i>B</i>	{ 90.0	118.0	110.8	116.4	104.5	539.7 } 539.8 } ¹
	{ 89.7	118.9	109.7	117.1	104.4	
<i>C</i>	{ 90.1 (0.7)	118.5 (1.5)	110.8 (1.6)	115.2 (1.7)	105.1 (1.3)	539.7 } 539.6 } ¹
	{ 89.5 (0.7)	119.0 (1.5)	111.1 (1.6)	115.7 (1.6)	104.3 (1.2)	
<i>D</i>	{ 93.4 (0.6)	110.1 (1.0)	118.2 (1.4)	112.1 (1.3)	106.0 (1.0)	539.8 } 539.7 } ¹
	{ 92.5 (0.6)	110.8 (1.2)	117.9 (1.5)	111.7 (1.4)	106.8 (1.0)	
<i>E</i>	89.7 (0.6)	118.6 (1.3)	111.3 (1.4)	115.5 (1.4)	104.9 (1.0)	540.0 ¹
<i>F</i>	89.4 (0.4)	107.0 (0.4)	110.3 (0.4)	109.2 (0.4)	102.8 (0.4)	518.7 ⁴
<i>G</i>	{ 91.6 (0.15)	110.9 (0.25)	116.0 (0.25)	110.5 (0.25)	111.1 (0.25)	540.1 } 539.9 } ⁰
	{ 91.3 (0.15)	110.8 (0.25)	116.5 (0.25)	110.0 (0.25)	111.3 (0.25)	
<i>H</i>	92.6 (0.3)	109.4 (0.4)	113.5 (0.5)	104.6 (0.5)	105.1 (0.5)	525.2 ²
<i>I</i>	94.2 (0.3)	111.2 (0.5)	117.5 (0.5)	113.6 (0.5)	103.6 (0.4)	540.1 ¹
<i>J</i>	92.1 (0.1)	109.4 (0.1)	114.8 (0.1)	112.2 (0.1)	111.6 (0.1)	540.1 ⁰
<i>K</i>	92.3 (0.1)	109.9 (0.2)	115.0 (0.2)	111.7 (0.2)	111.2 (0.2)	540.1 ⁰
<i>L</i>	91.1 (0.3)	105.5 (0.3)	115.9 (0.3)	105.7 (0.3)	103.5 (0.3)	521.7 ³
	{ 89.5 (0.4)	103.8 (0.4)	115.8 (0.4)	106.4 (0.4)	104.0 (0.4)	519.5 } 523.7 } ³
<i>M</i>	{ 90.8 (0.4)	103.9 (0.4)	117.5 (0.4)	106.0 (0.4)	105.5 (0.4)	
	{ 92.9 (0.2)	109.6 (0.3)	118.4 (0.4)	110.5 (0.5)	108.4 (0.4)	539.8 } 535.1 } ²
<i>N</i>	{ 92.1 (0.2)	110.6 (0.3)	116.2 (0.4)	108.4 (0.4)	107.8 (0.4)	
	92.5 (0.2)	110.0 (0.3)	118.7 (0.4)	109.6 (0.4)	109.0 (0.4)	539.8 ²
<i>P</i>	90.5 (0.3)	113.9 (0.3)	116.3 (0.3)	107.6 (0.3)	107.5 (0.3)	535.8 ²
<i>Q</i>	92.7 (0.3)	109.2 (0.4)	115.1 (0.4)	105.1 (0.5)	105.9 (0.4)	528.0 ²
<i>R</i>	90.5 (0.2)	116.3 (0.3)	114.3 (0.3)	109.8 (0.3)	106.7 (0.3)	537.6 ²
<i>S</i>	92.6 (0.2)	114.6 (0.3)	112.7 (0.3)	118.6 (0.3)	101.0 (0.2)	539.5 ¹
<i>T</i>	93.2 (0.1)	110.3 (0.1)	117.6 (0.2)	110.9 (0.2)	107.3 (0.1)	539.3 ¹
	{ 93.2 (0.2)	105.8 (0.2)	116.3 (0.2)	112.7 (0.3)	107.1 (0.3)	535.1 } 531.3 } ²
<i>U</i>	{ 91.3 (0.1)	104.6 (0.2)	116.7 (0.2)	112.1 (0.3)	106.6 (0.2)	531.3 } 530.8 } 534.8 }
	{ 91.4 (0.2)	104.9 (0.2)	116.7 (0.2)	111.7 (0.3)	106.1 (0.2)	
	{ 93.0 (0.2)	104.4 (0.2)	116.7 (0.2)	114.0 (0.3)	106.7 (0.3)	

* See Table 6 for compounds.

to 80°). In contrast, another important difference appears when considering the tolyl-pyridyl angle: the values are almost identical in each pair of molecules: 77° for (1) and (4), against 90° for (2) and (3).

On the other hand, the range of allowed rotation of the tolyl group around the C(2)-C(1') bond is very small for reasons of steric overcrowding.

Packing of the molecule. The packing is governed by van der Waals contacts, either inside or outside the asymmetric unit. Fig. 2 is a projection of the structure along *x*. Molecules (1) and (4) and (2) and (3) are respectively related by the approximate relations: $x_4 = \frac{1}{2} + x_1$; $z_4 = z_1$ and $x_3 = -\frac{1}{2} + x_2$; $z_3 = z_2$ which correspond to a pseudoglide plane nearly perpendicular to the *y* axis with translation *a*/2. This explains the phenomenon already mentioned: in the *h0l* plane, the rows with *h* odd are almost, but not completely absent.

Comparison between IR, ¹H NMR and X-ray results. The two different conformations of the title compound, evidenced by X-ray crystallography, clarify the above-mentioned clear-cut splitting of the carbonyl absorption into two bands with similar intensities at 1692 and 1680 cm⁻¹ in the IR spectrum recorded as Nujol mull.

In an earlier study (Vigorita, Chimirri, Grasso & Fenech, 1979) the IR and ¹H NMR spectra were consistent with the presence of one conformer in solution. In fact, the carbonyl band became single and ¹H NMR signals did not show any multiplicity. Furthermore, the presence of a long-range coupling, through S(1), between H(2) and H_{eq}(5) atoms suggested that the C(2) proton and one of the methylene

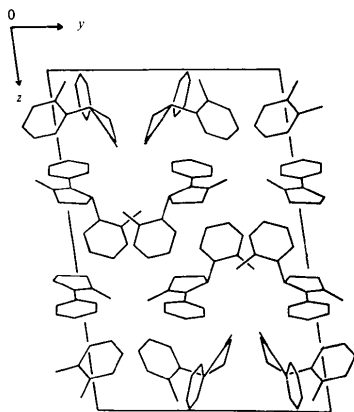


Fig. 2. Projection down *a*.

protons are in a *cis*-1,3 pseudo-diequatorial relationship and consequently that the 2-tolyl is in a pseudo-axial orientation, as the X-ray results confirm.

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