

## The Crystal and Molecular Structure of 2-(2,6-Dimethylphenyl)imino-3-(2-methylbenzoyl)-thiazolidine

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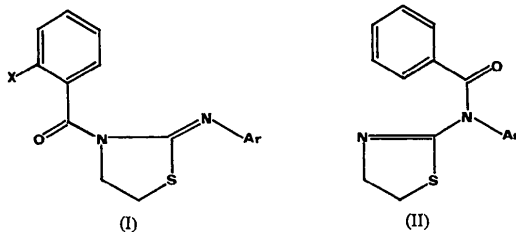
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2-(2,6-Dimethylphenyl)imino-3-(2-methylbenzoyl)thiazolidine,  $C_{19}H_{20}N_2OS$ , is monoclinic, space group  $P2_1/n$ , with  $a=9.430$ ,  $b=13.731$ ,  $c=14.439$  Å,  $\beta=105.06^\circ$ ,  $Z=4$ . The structure was refined by least-squares calculations to  $R=0.044$ . The structure (including the conformation) is similar to that of 2-(2,6-dimethylphenyl)imino-3-(2-chlorobenzoyl)thiazolidine. The arylimino group is linked to the thiazolidine ring by a strong localized C=N double bond of 1.250 Å; thus the N-C<sub>o</sub> bond (1.430 Å) has only weak  $\pi$ -bond character. Both C(sp<sup>3</sup>)-S<sup>II</sup> and C(sp<sup>2</sup>)-S<sup>II</sup> bond lengths (1.796 and 1.772 Å) indicate single bonds and agree well with expected values.

### Introduction

Argay, Kálmán, Tóth & Toldy (1972) described the structure of 2-(2,6-dimethylphenyl)imino-3-(2-chlorobenzoyl)thiazolidine (ATOCL) and showed that acylation of the 2-arylamino\*-2-thiazolines (and the analogous thiazines) with an *ortho*-substituted benzoyl group, in agreement with spectroscopic evidence, takes place only on the endocyclic N atom forming isomers of the type (I).



However, when X=H isomers of the type (II) are formed.

The refinement of the structure of ATOCL terminated at an  $R$  of 0.095 (Argay & Kálmán, 1975). Thus the bond lengths (especially S-C) and angles were of limited accuracy. In order to obtain more accurate atomic parameters for the five-membered ring and its environment, and to give further proof of the predominant formation of isomer (I) in these reactions, the structure of the title compound (X=Me, hereinafter: ATOME) has been determined.

### Experimental

Infrared and melting-point data showed that the product crystallized pure from ethyl alcohol. The lattice parameters were determined from oscillation and We-

issenberg photographs and refined by single-crystal diffractometry. The density was measured by flotation.

### Crystal data

$C_{19}H_{20}N_2OS$ ,  $M=324.45$ . Monoclinic;  $a=9.430(3)$ ,  $b=13.731(4)$ ,  $c=14.439(5)$  Å;  $\beta=105.06^\circ$ ;  $V=1805.48$  Å<sup>3</sup>,  $Z=4$ ,  $D_x=1.193$ ,  $D_m=1.18$  g cm<sup>-3</sup>.  $F(000)=688$ ; space group  $P2_1/n$  (No. 14);  $\mu$  (Mo  $K\alpha$ ,  $\lambda=0.7107$  Å) = 1.85 cm<sup>-1</sup>.

Intensities of 1154 independent reflexions were collected on a Syntex  $P1$  computer-controlled four-circle diffractometer with Mo  $K\alpha$  radiation from a graphite monochromator. The data were corrected for Lorentz and polarization effects, but not for absorption. After data reduction 248 reflexions with  $|F_o| - 5\sigma(F) < 0$  were taken as unobserved.

### Structure determination and refinement

The coordinates of the S atom were obtained by the Patterson method. Five successive cycles of structure-factor and Fourier calculations with the 250 strongest reflexions gave the positions of all non-hydrogen atoms. At this stage  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  was 0.34 for the observed reflexions.

The structure was refined by block-diagonal least-squares calculations (Albano, Domenicano & Vacigo, 1966). The function minimized was

$$\sum w(|F_o| - 1/G|F_c|)^2,$$

where  $G$  is the scaling factor and  $w$  the weight (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961),  $w = (6.0 + 1.0F_o + 0.06F_o^2)^{-1}$ . Six cycles of isotropic refinement reduced  $R$  to 0.140. In order to increase the ratio between the number of reflexions and the atomic parameters refined in an anisotropic cycle, the atoms were arranged in three overlapping groups with nine atoms in each. Two cycles of refinement with anisotropic thermal parameters for each group reduced  $R$

\* The aryl groups in these reactions are given by Tóth & Toldy (1972).

to 0.080. At this stage 17 of the 20 H atoms were located from a difference map. Their contributions improved  $R$  to 0.069. The three missing H atoms [belonging to C(19)] were located from a difference map computed after another cycle of anisotropic refinement for each group. Two further cycles of anisotropic refinement of the heavy atoms with the H atoms treated isotropically gave a final  $R$  of 0.044 for the observed and 0.068 for all reflexions.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30983 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

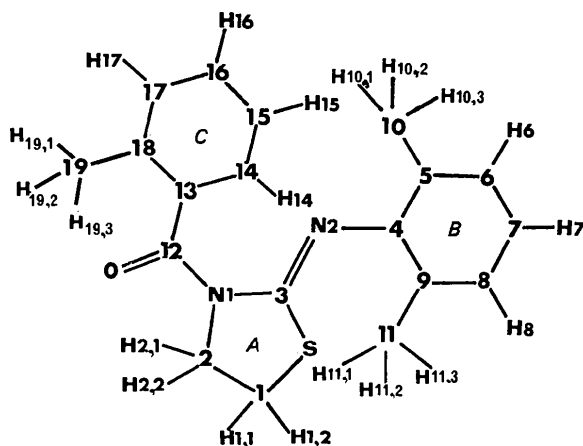


Fig. 1. Atomic numbering of the title compound. The bare numbers are for carbon atoms. Rings are labelled A, B and C.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). All calculations were carried out on a Varian 73 computer at Novi Sad. The final coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1, the parameters of the H atoms and the C-H distances in Table 2, the bond distances and angles in Table 3, and the atomic numbering in Fig. 1. A description of the structure of ATOCL appears in this issue (Argay & Kálmán, 1975).

Table 2. Fractional coordinates ( $\times 10^3$ ), isotropic temperature parameters ( $\text{\AA}^2$ ) and bond distances ( $\text{\AA}$ ) for the hydrogen atoms

Estimated standard deviations are given in parentheses.

	$x/a$	$y/b$	$z/c$	$B_i$ ( $\text{\AA}^2$ )	C-H ( $\text{\AA}$ )
H(1,1)	457 (6)	354 (4)	872 (4)	3.7 (15)	1.03 (6)
H(1,2)	375 (6)	451 (4)	820 (4)	3.0 (16)	0.99 (6)
H(2,1)	233 (6)	293 (5)	799 (4)	5.2 (17)	0.95 (6)
H(2,2)	215 (7)	369 (5)	705 (5)	5.3 (19)	1.05 (7)
H(6)	945 (8)	250 (6)	583 (5)	6.9 (23)	0.83 (8)
H(7)	902 (10)	362 (7)	465 (7)	10.5 (30)	0.91 (10)
H(8)	652 (9)	418 (7)	402 (6)	8.8 (26)	0.93 (9)
H(10,1)	726 (7)	119 (5)	672 (5)	6.6 (21)	1.04 (7)
H(10,2)	792 (8)	198 (6)	752 (6)	9.4 (24)	1.04 (8)
H(10,3)	875 (7)	143 (5)	695 (5)	6.3 (20)	0.86 (7)
H(11,1)	379 (8)	416 (6)	501 (5)	6.5 (22)	1.05 (8)
H(11,2)	344 (8)	330 (6)	427 (6)	7.7 (22)	0.92 (8)
H(11,3)	399 (10)	423 (7)	406 (6)	10.8 (30)	0.96 (9)
H(14)	517 (7)	80 (5)	815 (5)	6.7 (18)	0.97 (7)
H(15)	665 (7)	-60 (5)	810 (5)	6.9 (19)	1.04 (7)
H(16)	605 (6)	-151 (4)	671 (4)	4.9 (15)	0.99 (6)
H(17)	411 (6)	-92 (4)	535 (4)	4.4 (16)	0.85 (6)
H(19,1)	123 (8)	47 (6)	523 (5)	8.3 (23)	1.01 (8)
H(19,2)	201 (10)	17 (7)	464 (7)	11.4 (32)	0.81 (10)
H(19,3)	227 (9)	114 (6)	487 (6)	10.9 (27)	0.96 (8)

Table 1. Fractional coordinates and anisotropic thermal parameters ( $\times 10^4$ )

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are given in the form:  $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ .

	$x/a$	$y/b$	$z/c$	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
S	5304 (2)	3880 (1)	7279 (1)	195 (2)	58 (1)	84 (1)	-39 (3)	101 (2)	-46 (2)
O	1653 (4)	1386 (3)	7085 (4)	139 (5)	84 (3)	143 (3)	-20 (7)	149 (6)	-32 (6)
N(1)	3474 (5)	2441 (3)	7106 (4)	128 (6)	48 (3)	91 (3)	30 (7)	93 (7)	-11 (5)
N(2)	4978 (5)	2356 (3)	6052 (3)	144 (6)	49 (3)	64 (3)	-4 (8)	74 (7)	-6 (5)
C(1)	4103 (8)	3856 (5)	8061 (5)	248 (10)	59 (4)	98 (4)	15 (11)	146 (10)	-62 (7)
C(2)	2809 (7)	3214 (5)	7548 (5)	222 (10)	62 (4)	100 (4)	63 (11)	141 (10)	-26 (7)
C(3)	4604 (6)	2766 (4)	6725 (4)	129 (7)	36 (3)	50 (3)	14 (8)	58 (7)	6 (5)
C(4)	6124 (7)	2744 (4)	5680 (4)	205 (9)	38 (3)	54 (3)	-20 (10)	88 (9)	-31 (6)
C(5)	7547 (7)	2415 (5)	6041 (5)	168 (9)	58 (4)	64 (4)	-16 (11)	85 (9)	-19 (7)
C(6)	8614 (8)	2742 (6)	5596 (5)	212 (10)	93 (6)	107 (5)	-29 (13)	169 (11)	-28 (9)
C(7)	8260 (9)	3392 (6)	4866 (6)	330 (13)	96 (6)	119 (5)	-98 (16)	245 (11)	-30 (10)
C(8)	6845 (10)	3729 (6)	4509 (6)	401 (16)	73 (5)	85 (5)	-38 (16)	191 (13)	4 (8)
C(9)	5732 (8)	3406 (5)	4921 (5)	265 (11)	52 (4)	63 (4)	15 (12)	126 (10)	-7 (7)
C(10)	7908 (8)	1706 (5)	6847 (5)	173 (10)	88 (5)	70 (4)	14 (13)	60 (10)	15 (8)
C(11)	4192 (10)	3730 (6)	4537 (6)	316 (16)	80 (5)	82 (5)	92 (16)	26 (15)	27 (9)
C(12)	2871 (5)	1514 (4)	6990 (4)	98 (7)	53 (3)	71 (4)	15 (9)	64 (8)	7 (6)
C(13)	3803 (6)	695 (4)	6815 (4)	118 (7)	47 (3)	63 (3)	2 (8)	74 (7)	15 (6)
C(14)	4943 (6)	402 (5)	7577 (4)	156 (8)	69 (4)	68 (4)	32 (10)	85 (8)	23 (6)
C(15)	5774 (7)	-420 (5)	7516 (5)	170 (9)	78 (4)	101 (5)	6 (11)	90 (10)	23 (8)
C(16)	5429 (7)	-920 (4)	6682 (6)	188 (9)	48 (4)	148 (6)	44 (10)	158 (11)	47 (8)
C(17)	4308 (7)	-654 (5)	5903 (5)	240 (10)	63 (4)	110 (5)	-54 (11)	176 (10)	-54 (7)
C(18)	3446 (6)	186 (4)	5960 (4)	170 (9)	65 (4)	61 (3)	-53 (10)	76 (8)	-17 (7)
C(19)	2252 (8)	499 (7)	5127 (5)	198 (12)	143 (7)	78 (5)	-46 (16)	46 (12)	-32 (10)

Table 3. *Interatomic distances (Å) and bond angles (°) with their e.s.d.'s*

The estimated standard deviations are in parentheses.

S—C(1)	1.796 (7)	C(3)—N(1)—C(12)	125.4 (5)
S—C(3)	1.772 (5)	C(2)—N(1)—C(12)	120.7 (5)
C(3)—N(1)	1.392 (7)	N(1)—C(2)—C(1)	104.6 (5)
N(1)—C(2)	1.462 (8)	C(2)—C(1)—S	105.1 (5)
C(1)—C(2)	1.531 (10)		
		C(3)—N(2)—C(4)	121.2 (5)
C(3)—N(2)	1.250 (7)	N(2)—C(4)—C(5)	119.4 (5)
N(2)—C(4)	1.430 (8)	N(2)—C(4)—C(9)	117.7 (5)
C(4)—C(5)	1.382 (9)	C(5)—C(4)—C(9)	122.7 (6)
C(5)—C(6)	1.402 (10)	C(4)—C(5)—C(6)	117.7 (6)
C(6)—C(7)	1.355 (12)	C(4)—C(5)—C(10)	120.7 (6)
C(7)—C(8)	1.379 (12)	C(6)—C(5)—C(10)	121.5 (6)
C(8)—C(9)	1.405 (11)	C(5)—C(6)—C(7)	120.4 (7)
C(4)—C(9)	1.389 (9)	C(6)—C(7)—C(8)	122.0 (8)
C(5)—C(10)	1.487 (10)	C(7)—C(8)—C(9)	119.5 (8)
C(9)—C(11)	1.482 (11)	C(8)—C(9)—C(4)	117.5 (6)
		C(8)—C(9)—C(11)	120.9 (7)
N(1)—C(12)	1.386 (7)	C(4)—C(9)—C(11)	121.5 (6)
C(12)—O	1.204 (7)		
C(12)—C(13)	1.488 (8)	N(1)—C(12)—O	119.6 (5)
C(13)—C(14)	1.383 (8)	N(1)—C(12)—C(13)	118.2 (5)
C(14)—C(15)	1.390 (9)	C(13)—C(12)—O	122.1 (5)
C(15)—C(16)	1.350 (10)		

Table 3 (cont.)

C(16)—C(17)	1.377 (10)	C(12)—C(13)—C(14)	117.2 (5)
C(17)—C(18)	1.425 (9)	C(12)—C(13)—C(18)	121.1 (5)
C(13)—C(18)	1.383 (8)	C(14)—C(13)—C(18)	121.4 (5)
C(18)—C(19)	1.481 (10)	C(13)—C(14)—C(15)	121.4 (6)
		C(14)—C(15)—C(16)	117.4 (6)
C(1)—S—C(3)	92.6 (3)	C(15)—C(16)—C(17)	123.3 (6)
S—C(3)—N(1)	109.4 (4)	C(16)—C(17)—C(18)	119.7 (6)
S—C(3)—N(2)	126.3 (4)	C(17)—C(18)—C(13)	116.8 (5)
N(1)—C(3)—N(2)	124.2 (5)	C(17)—C(18)—C(19)	120.9 (6)
C(3)—N(1)—C(2)	113.5 (5)	C(13)—C(18)—C(19)	122.3 (6)

## Description and discussion of the structure

The structure determination of ATOME gave further proof of the conclusions (Tóth & Toldy, 1972) drawn from mass spectra (Tóth, Tamás & Toldy, 1971) and from the preliminary X-ray study of ATOCL (Argay, Kálmán, Tóth & Toldy, 1972). The conformation of ATOME (Fig. 2) is similar to that of ATOCL, as is shown by the angles (Table 4) between planes in the molecules. The plane *P*(4) of the phenyl ring (*B*) is almost perpendicular to the planes *P*(1) and *P*(2), in

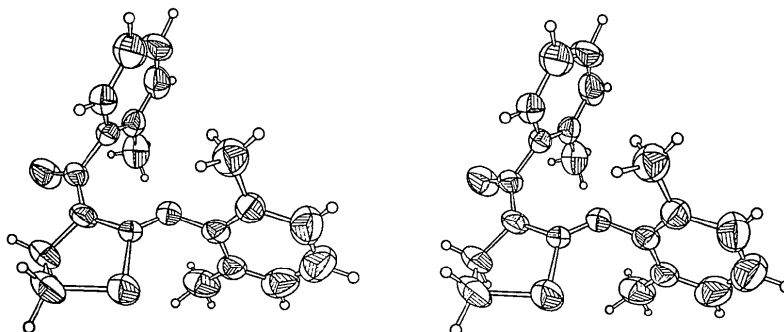


Fig. 2. An ORTEP stereo drawing of the title compound. The thermal ellipsoids are drawn at the 50% probability level.

Table 4. *Equations of the atomic planes of the ATOME and ATOCL molecules and atomic deviations*

*X, Y and Z are in Å and related to orthogonal axes a, b, c.*

ATOME ( <i>P</i> )	ATOCL ( <i>P'</i> )
Plane <i>P</i> (1) for S, N(1), C(1) and C(3) atoms: (Ring <i>A</i> ) 0.5165 <i>X</i> - 0.5177 <i>Y</i> + 0.6821 <i>Z</i> = 5.3506	0.8514 <i>X</i> + 0.5245 <i>Y</i> + 0.0036 <i>Z</i> = 3.5853
Plane <i>P</i> (2) for S, N(1), N(2), C(3) and C(12) atoms 0.5693 <i>X</i> - 0.4772 <i>Y</i> + 0.6694 <i>Z</i> = 5.4973	0.9021 <i>X</i> + 0.4289 <i>Y</i> + 0.0486 <i>Z</i> = 3.6377
Plane <i>P</i> (3) for N(1), C(12), C(13) and O atoms 0.1073 <i>X</i> - 0.1472 <i>Y</i> + 0.9833 <i>Z</i> = 9.3067	0.9434 <i>X</i> + 0.3255 <i>Y</i> + 0.0638 <i>Z</i> = 3.6034
Plane <i>P</i> (4) for C(4)→C(9) atoms: (Ring <i>B</i> ) 0.0300 <i>X</i> + 0.7616 <i>Y</i> + 0.6474 <i>Z</i> = 8.1110	0.5400 <i>X</i> - 0.8363 <i>Y</i> - 0.0951 <i>Z</i> = 0.6678
Plane <i>P</i> (5) for C(13)→C(18) atoms: (Ring <i>C</i> ) 0.7513 <i>X</i> + 0.5650 <i>Y</i> - 0.3412 <i>Z</i> = -1.9289	-0.2949 <i>X</i> + 0.0601 <i>Y</i> + 0.9537 <i>Z</i> = 0.1176

Dihedral angles (°) formed by the least-squares planes given above

	ATOME	ATOCL	<i>Δ</i>		ATOME	ATOCL	<i>Δ</i>
<i>P</i> (1)/ <i>P</i> (2)	3.9	6.7	2.8	<i>P</i> (2)/ <i>P</i> (4)	85.0	82.9	2.1
<i>P</i> (1)/ <i>P</i> (3)	36.7	13.1	23.6	<i>P</i> (2)/ <i>P</i> (5)	86.0	78.8	8.3
<i>P</i> (1)/ <i>P</i> (4)	86.4	88.8	2.4	<i>P</i> (3)/ <i>P</i> (4)	58.2	76.6	18.4
<i>P</i> (1)/ <i>P</i> (5)	82.1	77.5	4.6	<i>P</i> (3)/ <i>P</i> (5)	70.3	78.6	8.8
<i>P</i> (2)/ <i>P</i> (3)	37.9	6.4	31.4	<i>P</i> (4)/ <i>P</i> (5)	76.6	72.5	4.1

Table 4 (cont.)  
 Atoms defining the planes are marked with an asterisk.  
 Atomic deviations (Å) from the planes

P(1)	ATOME	ATOCL	P(2)	ATOME	ATOCL	P(3)	ATOME	ATOCL	P(4)	ATOME	ATOCL	P(5)	ATOME	ATOCL
S	-0.014	0.057*	S	0.046	-0.008*	O	0.008	-0.010*	C(4)	-0.005	-0.005*	C(13)	-0.001	0.024*
N(1)	-0.014	0.053*	N(1)	-0.118	0.030*	N(1)	0.007	-0.010*	C(5)	0.012	0.018*	C(14)	0.002	-0.021*
C(1)	0.010	-0.039*	N(2)	-0.013	0.006*	C(12)	-0.021	-0.028*	C(6)	-0.013	-0.010*	C(15)	-0.001	0.005*
C(3)	0.018	-0.072*	C(3)	0.002	-0.008*	C(13)	0.006	-0.008*	C(7)	0.006	-0.012*	C(16)	-0.001	0.009*
C(2)	-0.552	0.457	C(12)	0.082	-0.019*	C(1)	1.056	-0.564	C(8)	0.001	0.026*	C(17)	0.002	-0.007*
			O	-0.419	-0.003	C(2)	0.372	0.056	C(9)	-0.001	-0.017*	C(18)	-0.001	-0.010*
			C(13)	0.993	0.223	C(3)	-0.451	-0.002	C(10)	-0.001	0.136	C(19)	0.027	-0.090
			C(1)	-0.020	-0.281				C(11)	-0.048	-0.055	O	-1.193	-1.129
			C(2)	-0.663	0.262				N(2)	-0.111	0.069	C(12)	-0.159	-0.052
			C(4)	0.081	-0.087									

agreement with the weak  $\pi$ -character of N(2)-C(4)=1.430(8) Å. A similar arrangement (*cf.* dihedral angles  $P'(1)/P'(4)$  and  $P'(2)/P'(4)$  in Table 4) was also found in ATOCL. The O and C(13) atoms of the benzoyl moiety are turned considerably out of the plane  $P(2)$  about N(1)-C(12), which results in a weakened multiple bond ( $\pi p$ ) character of this bond (1.386 Å) compared with the corresponding one in ATOCL (1.337 Å). In ATOCL the O and C(13) atoms of the benzoyl group lie almost in the plane  $P'(2)$ .

The thiazolidine ring in ATOME has an almost perfect envelope shape. Only C(2) is significantly out ( $\Delta=0.55$  Å) of the plane  $P(1)$ . The envelope shape of the thiazolidine ring in ATOCL is somewhat more distorted [*cf.* planes  $P(1)$  and  $P'(1)$  in Table 4]. However, the torsion angles C-S-C are similar (24.9 and 23.6°, respectively).

The bond distances and angles in the thiazolidine ring (*A*) can be discussed in terms of data obtained for thiazole rings (Form, Raper & Downie, 1974). Additional results with the corresponding ones of ATOME and ATOCL, are given in Table 5. The thiazolidine rings (two molecules in the asymmetric unit) found in 2PI-3M-5PTO (Bally & Mornon, 1973*b*), apart from N(1)-C(2), show a strong resemblance to that in ATOME. In these structures there are strong localized C(3)-N(2) exocyclic double bonds (mean 1.260 Å) accompanied by low S-C(3)-N(1) angles (mean 110.1°) and long S<sup>II</sup>-C(*sp*<sup>2</sup>) bonds [mean S-C(3)=1.767 Å]. A similar phenomenon can also be seen in the less accurate ATOCL structure.

Recently Kálmán (1973) pointed out that the atomic radii and electronegativities suggested by Truter (1962) for S in different valence states (II, IV and VI) can still be regarded as valid for the estimation of S-C single-bond lengths. On the basis of various sorts of S<sup>II</sup>-C(*sp*<sup>2</sup>) bonds (Table 6) Kálmán (1974) agreed that 1.77 Å, in accordance with Truter's suggestion, is the upper limit of the S<sup>II</sup>-C(*sp*<sup>2</sup>) bond which could be formed only when the presence of strong multiple bonds {as in ATOME, 2PI-3M-5PTO and sodium-[5-phenylthiazolidine-2,4-dione] (Matthews, 1964)} prevent the S-C bonds gaining any  $\pi$ -bond character. It might, of course, be somewhat longer if thermal correction is performed as in rhodan hydrate (Hordvik, 1970). S=C double bonds (expected value: 1.61 Å, *cf.* Abrahams, 1956) are generally polarized so that they can be described by a mean value of 1.69 Å (Palenik, Rendle & Carter, 1974); S<sup>II</sup>-C(*sp*<sup>2</sup>) single bonds, on the other hand, seek to gain a partial  $\pi$ -character and have a mean value of about 1.74 Å. This phenomenon suggests that one of the S<sup>II</sup>-C(*sp*<sup>2</sup>) bonds [1.739(3) Å] in 2-methylamino-benzothiazole (Fehlman, 1970) cannot be regarded as a single bond. The other is, however a true single bond of 1.763(3) Å.

The length of the S<sup>II</sup>-C(*sp*<sup>3</sup>) bond [S-C(1)=1.796 Å] in ATOME is the shortest among those given in Table 5, but agrees with the value given by Truter (1962). Comparison of the S<sup>II</sup>-C(*sp*<sup>3</sup>) lengths (Table 5)

Table 5. *A comparison of some thiazoline ring dimensions*

Distances in Å, angles in degrees. Further data can be obtained from Form, Raper & Downie (1974).

Molecule	S-C(3)	S-C(1)	C(1)-C(2)	C(2)-N(1)	N(1)-C(3)	C(3)-N(2)*	S-C(3)-N(1)
2A-5PTO I <sup>a</sup>	1.756 (12)	1.841 (12)	1.535 (16)	1.349 (16)	1.336 (16)	1.303 (16)	119.0 (2.5)
	1.771 (12)	1.839 (12)	1.527 (16)	1.357 (16)	1.338 (16)	1.301 (16)	118.1 (2.5)
2A-5PTO II <sup>a</sup>	1.755	1.812	1.542	1.357	1.337	1.323	118.0
	1.737	1.813	1.531	1.354	1.342	1.316	118.9
2PMA-5PTO <sup>b</sup>	1.753 (8)	1.807 (8)	1.540 (11)	1.354 (11)	1.312 (10)	1.324 (10)	118.6 (1.3)
2PA-5PTO <sup>c</sup>	1.748 (9)	1.813 (11)	1.531 (15)	1.392 (13)	1.321 (13)	1.334 (13)	118.5 (1.5)
	1.753 (10)	1.826 (11)	1.549 (14)	1.364 (13)	1.316 (13)	1.344 (13)	119.0 (1.5)
2PI-3M-5PTO <sup>d</sup>	1.764 (8)	1.808 (8)	1.537 (11)	1.357 (10)	1.388 (10)	1.257 (11)	110.1 (1.0)
	1.764 (9)	1.814 (8)	1.520 (11)	1.368 (11)	1.377 (11)	1.273 (11)	110.8 (1.2)
ATOME <sup>e</sup>	1.772 (5)	1.796 (7)	1.531 (10)	1.462 (8)	1.392 (7)	1.250 (7)	109.4 (0.4)
ATOCL <sup>f</sup>	1.746 (10)	1.837 (12)	1.530 (18)	1.504 (17)	1.437 (14)	1.286 (13)	109.8 (0.7)

\* Exocyclic.

*a.* 2-Amino-5-phenylthiazolin-4-one (Mornon & Raveau, 1971; Mornon & Bally, 1972). *b.* 2-Phenylmethylamino-5-phenylthiazolin-4-one (Bally, 1973). *c.* 2-Phenylamino-5-phenylthiazolin-4-one (Bally & Mornon, 1973*a*). *d.* 2-Phenylimino-3-methyl-5-phenylthiazolidin-4-one (Bally & Mornon, 1973*b*). *e.* Present work. *f.* 2-(2,6-Dimethylphenyl)imino-3-(2-chlorobenzoyl)thiazolidine (Argay & Kálmán, 1975).

Table 6. *A comparison of S<sup>II</sup>-C(sp<sup>2</sup>) multiple bonds (Å)*

Further data may be obtained from Form, Raper & Downie (1974), Hordvik (1970), Johnson & Paul (1970), Kruger & Gafner (1972), Palenik, Rendle & Carter (1974).

	S <sup>II</sup> -C(sp <sup>2</sup> )
<i>N</i> -(3-Phenyl-2-benzo[ <i>b</i> ]thienyl)thiobenzamide <sup>a</sup>	1.739 (3)
	1.742 (3)
2-Methylthio-5,5-diphenyl-2-imidazolin-4-one <sup>b</sup>	1.732 (5)
2-Methylthio-4,4-diphenyl-2-imidazolin-5-one <sup>b</sup>	1.740 (4)
6-6-Dimethyl-3-methylthio-6,7-dihydro- <i>as</i> -triazino[1,6- <i>c</i> ]quinazolin-5-ium-1-olate <sup>c</sup>	1.750 (4)
1-Phenylthiosemicarbazide <sup>d</sup>	1.696 (2)
4-Phenylthiosemicarbazide <sup>e</sup>	1.685 (5)
<i>N</i> -(3-Phenyl-2-benzo[ <i>b</i> ]thienyl)thiobenzamide <sup>f</sup>	1.643 (3)

*a.* Argay & Kálmán (1973). *b.* Lempert, Nyitrai, Zauer, Kálmán, Argay, Duisenberg & Sohár (1973). *c.* Duisenberg, Kálmán, Doleschall & Lempert (1975). *d.* Czugler, Kálmán & Argay (1973). *e.* Kálmán, Argay & Czugler (1972). *f.* Argay & Kálmán (1973).

with those listed by Jones, Bernal, Frey & Koetzle (1974) shows that S<sup>II</sup>-C(sp<sup>3</sup>) single bonds, unlike S<sup>II</sup>-C(sp<sup>2</sup>) single bonds, are generally longer than the expected value of 1.80–1.81 Å. Jones *et al.* (1974) tried to find a correlation between S–C distances and C–S–S–C dihedral angles characteristic of the disulphides investigated. No convincing result could be obtained, however, presumably because of the different reliability of the experimental data.

### Conclusion

S<sup>II</sup>-C(sp<sup>3</sup>) and S<sup>II</sup>-C(sp<sup>2</sup>) single bonds are influenced by various effects. S<sup>II</sup>-C(sp<sup>3</sup>) bonds are mostly longer while S<sup>II</sup>-C(sp<sup>2</sup>) bonds are shorter than the expected values given by Truter (1962). ATOME displays the phenomenon of two S<sup>II</sup>-C single bonds (1.772 and 1.796 Å) in the same structure. Perhaps these remarks might help to improve the tentative bond-order/bond-length curve for S<sup>II</sup>-C(sp<sup>2</sup>) bonds suggested by Hordvik & Sletten (1970).

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### References

- ABRAHAMS, S. C. (1956). *Quart. Rev.* **10**, 407–436.
- ALBANO, V., DOMENICANO, A. & VACIAGO, A. (1966). Full- and Block-Diagonal Matrix Least-Squares Refinement Program for the IBM 7040 Computer (adapted to the Varian 73 computer by ARGAY, G.), Centro di Studio per la Strutturistica Chimica del C.N.R., Roma.
- ARGAY, G. & KÁLMÁN, A. (1973). *Cryst. Struct. Commun.* **2**, 19–22.
- ARGAY, G. & KÁLMÁN, A. (1975). *Acta Cryst.* **B31**, 1961–1962.
- ARGAY, G., KÁLMÁN, A., TÓTH, G. & TOLDY, L. (1972). *Tetrahedron Lett.* pp. 3179–3182.
- BALLY, R. (1973). *Acta Cryst.* **B29**, 2635–2637.
- BALLY, R. & MORNON, J. P. (1973*a*). *Acta Cryst.* **B29**, 1157–1159.
- BALLY, R. & MORNON, J. P. (1973*b*). *Acta Cryst.* **B29**, 1160–1162.
- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. Oxford: Pergamon Press.
- CZUGLER, M., KÁLMÁN, A. & ARGAY, G. (1973). *Cryst. Struct. Commun.* **2**, 655–658.
- DUISENBERG, A. J. M., KÁLMÁN, A., DOLESCHALL, G. & LEMPert, K. (1975). *Cryst. Struct. Commun.* **4**, 295–298.
- FEHLMAN, M. (1970). *Acta Cryst.* **B26**, 1736–1741.
- FORM, G. R., RAPER, E. S. & DOWNIE, T. C. (1974). *Acta Cryst.* **B30**, 342–348.
- HORDVIK, A. (1970). *Quart. Rep. Sulfur. Chem.* **5**, 21–43.
- HORDVIK, A. & SLETTEN, E. (1966). *Acta Chem. Scand.* **20**, 1938–1942.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, P. L. & PAUL, I. C. (1970). *J. Chem. Soc. (B)*, pp. 1296–1303.
- JONES, D. D., BERNAL, I., FREY, M. N. & KOETZLE, T. F. (1974). *Acta Cryst.* **B30**, 1220–1227.

- KÁLMÁN, A. (1973). *Proc. Yugoslav Centre Cryst. (Zagreb)*, **8**, 5–19.
- KÁLMÁN, A. (1974). Thesis for Degree of Doctor in Chemical Sciences. MTA, Budapest.
- KÁLMÁN, A., ARGAY, G. & CZUGLER, M. (1972). *Cryst. Struct. Commun.* **1**, 375–378.
- KRUGER, G. J. & GAFNER, G. (1972). *Acta Cryst.* **B28**, 272–283.
- LEMPERT, K., NYITRAI, J., ZAUER, K., KÁLMÁN, A., ARGAY, G., DUSENBERG, A. J. M. & SOHÁR, P. (1973). *Tetrahedron*, **29**, 3565–3569.
- MATTHEWS, B. W. (1964). *Acta Cryst.* **17**, 1413–1420.
- MORNON, J. P. & BALLY, R. (1972). *Acta Cryst.* **B28**, 2074–2079.
- MORNON, J. P. & RAVEAU, B. (1971). *Acta Cryst.* **B27**, 95–108.
- PALENIK, G. J., RENDLE, D. F. & CARTER, W. S. (1974). *Acta Cryst.* **B30**, 2390–2395.
- TÓTH, G., TAMÁS, J. & TOLDY, L. (1971). *Magyar Kém. Lapja*, pp. 561–570.
- TÓTH, G. & TOLDY, L. (1972). *Acta Chim. (Budapest)*, **77**, 103–107.
- TRUTER, M. R. (1962). *J. Chem. Soc.* pp. 3400–3406.

## SHORT STRUCTURAL PAPERS

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### 2-(2,6-Dimethyl-phenyl)imino-3-(2-chloro-benzoyl) thiazolidine

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(Received 3 March 1975; accepted 7 March 1975)

**Abstract.**  $C_{18}H_{17}N_2OSCl$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.518(3)$ ,  $b = 13.547(6)$ ,  $c = 19.314(8)$  Å;  $V = 1705.4$  Å<sup>3</sup>;  $Z = 4$ ;  $D_x = 1.335$ ,  $D_c = 1.323$  g cm<sup>-3</sup>. The structure was solved by direct methods and Fourier techniques. An  $R$  of 0.095 was obtained for 1207 observed reflexions after least-squares refinement.

**Introduction.** The structure of the title compound (hereinafter ATOCL) was determined in order to find out whether the *o*-chlorobenzoyl group is bound to the endocyclic N(1) (Fig. 1) or to the exocyclic N(2) of the 2-iminothiazoline moiety. A preliminary communication (Argay, Kálmán, Tóth & Toldy, 1972) revealed

that the *o*-chlorobenzoyl group is linked to the endocyclic N(1). This paper reports the complete structure analysis and gives the final atomic parameters.

The crystals are colourless. Cell constants were determined from Weissenberg and precession photographs with  $Cu K\alpha$  ( $\lambda = 1.5418$  Å) radiation. The density was measured by flotation.

Intensities were collected on a Stoe semi-automatic two-circle diffractometer (for details see Kálmán, Simon, Schawartz & Horváth, 1974). Because of the small size of the crystal 970 (out of 1750) independent reflexions had  $I - 1.5\sigma(I) < 0$  and were taken as unobserved, with values of  $I_o = \frac{1}{2}\sigma(I)$ . The phase problem for 236 reflexions with  $E > 1.50$  was solved with *MULTAN* (Main, Woolfson & Germain, 1971). The  $E$  map computed from the solution with the best ABSFOM = 1.11 revealed the positions of the Cl, S and a further six non-hydrogen atoms. Three cycles of structure-factor and Fourier calculations revealed the missing 15 non-hydrogen atoms ( $R = 0.245$ ). Block-diagonal refinement of the atomic coordinates with isotropic and anisotropic thermal parameters resulted in a final  $R$  of 0.112 for the observed reflexions. The anisotropic refinement was then continued with new experimental data (1358 independent reflexions of which only 143 were unobserved) collected from a larger crystal on the same instrument.

The H atoms were located geometrically by comparison with a related compound, 2-(2,6-dimethyl-phenyl)imino-3-(2-methylbenzoyl)thiazolidine (hereinafter ATOME), the structure of which has recently been solved (Argay, Kálmán, Nahlovski & Ribár, 1975). The closing stage of the refinement, which was carried out for two separate groups of atoms (12 non-hydrogen

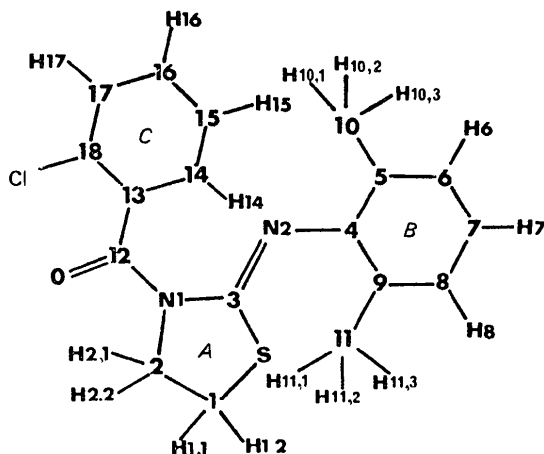


Fig. 1. Atomic numbering of the title compound. Unaccompanied numbers indicate carbon atoms. Rings are labelled A, B and C.