

## Molecular and Crystal Structures of Two Derivatives of 1-Oxo-1- $\lambda^4$ -1,2,4-thiadiazolidin-3-one

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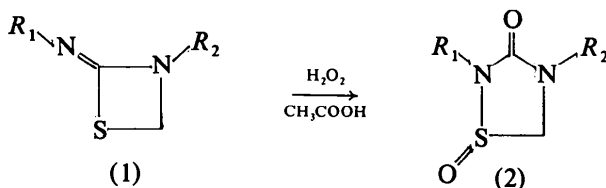
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1-Oxo-1- $\lambda^4$ -1,2,4-thiadiazolidin-3-ones are obtained by the oxidation of 2-imino-1,3-thiazetidines with  $\text{H}_2\text{O}_2$ /glacial acetic acid. The molecular and crystal structure of this system was solved by X-ray structure analysis of the 2-methyl-4-phenyl and 2-benzyl-4-phenyl derivatives. 2-Methyl-1-oxo-4-phenyl-1- $\lambda^4$ -1,2,4-thiadiazolidin-3-one ( $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ ) is orthorhombic, space group  $Pbca$ ,  $a = 38.540$  (10),  $b = 6.537$  (2),  $c = 7.778$  (2) Å; the 2-benzyl-4-phenyl derivative ( $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ ) is monoclinic, space group  $P2_1/c$ ,  $a = 8.515$  (3),  $b = 6.251$  (2),  $c = 25.775$  (9) Å,  $\beta = 97.59$  (5)°. The thiadiazolidine rings are very similar in both compounds and show pronounced deviations from planarity with the S atom out of the plane of the other four atoms.

The heterocyclic ring of 1,2,4-thiadiazolidine is known to be a possible oxidation product of monoarylthioureas. The molecular structures of this class of compounds have been reviewed by Kurzer (1965). The *S*-oxide of this heterocycle has been reported by Kinoshita, Sato, Furukawa & Tamura (1975) without any experimental detail. Ried, Möisinger & Schuckmann (1976) have shown that the *S*-oxide is obtained by the oxidation of 2-imino-1,3-thiazetidines (1) by a mixture of  $\text{H}_2\text{O}_2$ /glacial acetic acid. The 2-imino-1,3-thiazetidine system itself is obtained by the reaction of the thiourea system with diiodomethane



(Möisinger, 1977). The reaction comprises a rearrangement of the molecule and results in an extension of the heterocycle. The S and C of the original thiourea system, used to produce the thiazetidine, are oxidized. The structure of the diphenyl derivative of (1) has recently been described by us (Schuckmann, Fuess, Möisinger & Ried, 1978). The four-membered heterocycle of thiazetidine is considerably strained by a small

C—S—C angle of 74.3°. Spectroscopic (IR and NMR) data could not discriminate between three possible structures of the oxidation products. The X-ray structure investigation was therefore carried out on two derivatives: (2a)  $R_1 = \text{methyl}$ ,  $R_2 = \text{phenyl}$  and (2b)  $R_1 = \text{benzyl}$ ,  $R_2 = \text{phenyl}$ .

Two other structures of 1,2,4-thiadiazole systems have been reported. One (Kutoglu & Jepsen, 1972) on 5-benzoylimino-3-phenyl-2-(4-bromophenyl)-2,5-dihydro-1,2,4-thiadiazole showed a completely conjugated system. The other by Christophersen, Øttersen, Seff & Treppendahl (1975) on 2,4-dimethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine revealed only a small amount of conjugation in the central ring. Several studies of other thiadiazole derivatives are known. Arora (1974) and Mellini & Merlino (1976) studied derivatives of the 1,2,5-thiadiazole system. 1,3,4-Thiadiazole has been solved by La Cour (1974), and Bats (1976) described the structure and electron distribution in 2,5-dimercapto-1,3,4-thiadiazole.

### Experimental

Crystals of the two derivatives were obtained from a solution of the reaction product in chloroform. They were recrystallized from ethanol. Crystals of (2a) are colourless and platelike; crystals of (2b) are colourless needles. The compositions were confirmed by chemical analysis.

Space groups and cell dimensions were determined

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by precession photographs. The cell dimensions were subsequently refined from the setting angles of about 20 well centred reflections and are given in Table 1. Intensities were collected with a  $\theta/2\theta$  scan, a scintillation counter and Ni-filtered Cu  $K\alpha$  radiation on a computer-controlled four-circle Hilger & Watts diffractometer. A line profile analysis of the step-scan data

was applied for background corrections (Bartl & Schuckmann, 1966). Lorentz-polarization corrections were applied in the usual way and the structure amplitudes were derived.

### Structure determination and refinement

Both structures were solved by symbolic addition methods with the programs *SINGEN* and *PHASE* from the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), which was also used for all subsequent calculations. The form factors for C, S and N were taken from Cromer & Mann (1968); those for H were from Stewart, Davidson & Simpson (1965).

Table 1. *General information*

	(2a)	(2b)
Formula	C <sub>9</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	38.540 (10)	8.515 (3)
<i>b</i> (Å)	6.537 (2)	6.251 (2)
<i>c</i> (Å)	7.778 (2)	25.775 (9)
$\beta$ (°)	—	97.59 (5)
<i>Z</i>	8	4
<i>V</i> (Å <sup>3</sup> )	1960	1360
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.42	1.40
Unique reflections	1227	1102
Unique reflections with $I > 2\sigma(I)$	1065	973
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.53	0.46

Table 2. *Results of the refinement*

	(2a)	(2b)
$g \times 10^3$	4.69	0.3
Number of parameters	167	237
$R(F) = \Sigma ( F_o  -  F_c ) / \Sigma  F_o $	0.031	0.028
$R_w(F) = [\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o ^2]^{1/2}$	0.034	0.030

Table 3. *Positional parameters* ( $\times 10^4$ , for H  $\times 10^3$ ) *with standard deviations in parentheses*

	Compound (2a)			Compound (2b)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	1517 (1)	4784 (5)	4428 (3)	6895 (3)	6576 (5)	2122 (1)
C(2)	1719 (1)	6130 (4)	3506 (4)	6950 (4)	7945 (5)	2542 (1)
C(3)	2069 (1)	6318 (5)	3875 (4)	7860 (4)	7472 (6)	3009 (1)
C(4)	2218 (1)	5154 (5)	5122 (5)	8709 (4)	5607 (7)	3066 (1)
C(5)	2018 (1)	3833 (5)	6047 (4)	8654 (4)	4228 (5)	2655 (1)
C(6)	1669 (1)	3633 (4)	5719 (4)	7764 (4)	4699 (5)	2184 (1)
C(7)				1944 (3)	5023 (5)	580 (1)
C(8)				1061 (4)	6398 (5)	835 (1)
C(9)				-427 (4)	5822 (6)	950 (1)
C(10)				-1017 (3)	3837 (3)	813 (1)
C(11)				-155 (4)	2447 (4)	557 (1)
C(12)				1327 (4)	3045 (4)	440 (1)
C(13)	365 (1)	1618 (5)	4096 (5)	3523 (3)	5687 (3)	438 (1)
C(14)	970 (1)	2816 (4)	4239 (3)	5261 (3)	5716 (3)	1287 (1)
C(15)	961 (1)	6221 (4)	3288 (4)	5635 (3)	9344 (3)	1501 (1)
N(1)	1158 (1)	4593 (3)	4068 (3)	6009 (3)	7129 (3)	1640 (1)
N(2)	627 (1)	3194 (3)	3837 (3)	4500 (2)	6823 (3)	860 (1)
O(1)	448 (1)	6401 (3)	5559 (2)	6399 (2)	9604 (3)	535 (1)
O(2)	1081 (1)	1140 (2)	4643 (3)	5222 (2)	3791 (3)	1328 (1)
S	512 (1)	5667 (1)	3797 (1)	4989 (1)	9423 (1)	804 (1)
H(2)	162 (1)	686 (4)	265 (3)	635 (2)	916 (4)	248 (1)
H(3)	220 (1)	727 (5)	317 (4)	788 (3)	841 (4)	326 (1)
H(4)	244 (1)	525 (4)	542 (3)	937 (3)	528 (4)	339 (1)
H(5)	212 (1)	309 (4)	693 (4)	922 (3)	292 (4)	268 (1)
H(6)	153 (1)	280 (4)	636 (3)	773 (2)	382 (3)	189 (1)
H(8)				150 (2)	780 (3)	93 (1)
H(9)				-93 (3)	677 (4)	114 (1)
H(10)				-202 (2)	347 (3)	89 (1)
H(11)				-55 (2)	110 (3)	46 (1)
H(12)				189 (2)	207 (3)	24 (1)
H(131)	39 (1)	65 (5)	332 (5)	408 (2)	450 (3)	35 (1)
H(132)	39 (1)	103 (5)	512 (5)	339 (2)	658 (4)	13 (1)
H(133)	14 (1)	219 (5)	384 (3)			
H(151)	100 (1)	745 (4)	208 (4)	654 (2)	1021 (3)	157 (1)
H(152)	98 (1)	614 (4)	377 (3)	482 (3)	984 (4)	170 (1)

An anomalous-dispersion correction ( $f' = 0.3$  and  $f'' = 0.6$ ) was applied for S. The heavy atoms were refined anisotropically and H atoms were included as determined from difference Fourier maps. Isotropic thermal parameters were refined for the H atoms. The function minimized was  $\sum w(F_o - F_c)^2$  with weights  $w = 1/\sigma^2(F)$ . An isotropic extinction parameter  $g$  (Larson, 1967) was introduced in the final stages of the refinement. Its refined values are given together with the final  $R$  in Table 2. The atomic positional parameters are listed in Table 3.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33222 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Interatomic distances (Å) and angles (°) for the central part of the molecule, with standard deviations in parentheses*

	(2a)	(2b)
N(1)—C(1)	1.416 (3)	1.410 (4)
N(2)—C(13)	1.457 (4)	1.464 (3)
N(1)—C(14)	1.375 (3)	1.364 (4)
N(2)—C(14)	1.381 (3)	1.385 (3)
C(14)—O(2)	1.217 (3)	1.209 (3)
C(15)—N(1)	1.442 (3)	1.455 (4)
S—C(15)	1.810 (3)	1.808 (3)
S—N(2)	1.676 (2)	1.688 (2)
S—O(1)	1.473 (2)	1.468 (2)
C(2)—C(1)—N(1)	120.4 (2)	120.0 (3)
C(6)—C(1)—N(1)	120.7 (2)	121.6 (3)
C(1)—N(1)—C(14)	124.7 (2)	125.3 (2)
C(1)—N(1)—C(15)	122.2 (2)	121.7 (2)
N(1)—C(14)—N(2)	109.4 (2)	109.6 (2)
N(1)—C(14)—O(2)	126.9 (2)	127.0 (2)
C(14)—N(2)—S	115.4 (2)	117.0 (2)
C(13)—N(2)—S	120.1 (2)	121.7 (2)
C(13)—N(2)—C(14)	120.4 (2)	120.6 (2)
N(2)—C(14)—O(2)	123.7 (2)	123.5 (2)
C(15)—S—N(2)	86.9 (1)	86.3 (1)
C(15)—S—O(1)	107.4 (1)	108.1 (1)
N(2)—S—O(1)	109.9 (1)	109.9 (1)
N(1)—C(15)—S	105.3 (2)	107.4 (2)
C(14)—N(1)—C(15)	112.7 (2)	112.6 (2)

Table 5. *Interatomic distances (Å) and angles (°) in the benzene rings*

	(2a)	(2b)	(2b)	
C(1)—C(2)	1.377 (4)	1.375 (5)	C(7)—C(8)	1.366 (4)
C(1)—C(6)	1.386 (4)	1.385 (4)	C(7)—C(12)	1.373 (4)
C(2)—C(3)	1.382 (4)	1.376 (5)	C(8)—C(9)	1.387 (5)
C(3)—C(4)	1.361 (5)	1.370 (6)	C(9)—C(10)	1.368 (5)
C(4)—C(5)	1.362 (5)	1.362 (5)	C(10)—C(11)	1.363 (5)
C(5)—C(6)	1.375 (4)	1.375 (5)	C(11)—C(12)	1.386 (5)
C(6)—C(1)—C(2)	118.9 (2)	118.4 (4)	C(8)—C(7)—C(12)	118.5 (3)
C(1)—C(2)—C(3)	120.1 (3)	120.8 (3)	C(7)—C(8)—C(9)	121.1 (3)
C(2)—C(3)—C(4)	120.7 (3)	120.3 (3)	C(8)—C(9)—C(10)	119.6 (3)
C(3)—C(4)—C(5)	119.5 (3)	119.5 (3)	C(9)—C(10)—C(11)	120.1 (3)
C(4)—C(5)—C(6)	120.9 (3)	120.7 (3)	C(10)—C(11)—C(12)	119.8 (3)
C(1)—C(6)—C(5)	119.9 (3)	120.4 (3)	C(7)—C(12)—C(11)	120.9 (3)

## Results and discussion

Both molecules are shown in Fig. 1(a) and (b); bond lengths and angles are listed in Tables 4 and 5. The three benzene rings are planar (Table 6) and the mean C—C distance is 1.374 Å in each of the three rings. The average C—H distance is 0.93 Å and the C—C—H angle 119.8°. The two 1,2,4-thiadiazolidine rings are remarkably similar as far as bond lengths, angles and deviations from the mean least-squares plane are concerned. The S atom is 0.6 and 0.5 Å out of the plane of the other four atoms. The torsion angles (Table

Table 6. *Atomic deviations from the planes (Å) and angles between planes (°)*

Atoms excluded from the calculation of the plane are indicated by an asterisk.

	(2a)	(2b)
Plane P1		
C(14)	-0.044	-0.036
C(15)	-0.025	-0.020
N(1)	0.043	0.035
N(2)	0.025	0.021
S*	0.600	0.500
O(2)*	-0.186	-0.148
C(1)*	0.047	-0.002
C(4)*	0.050	-0.040
Plane P2		
C(1)	-0.002	0.001
C(2)	-0.004	-0.005
C(3)	0.009	0.004
C(4)	-0.008	0.000
C(5)	-0.002	-0.004
C(6)	0.003	0.003
Plane P3		
C(7)		0.002
C(8)		0.002
C(9)		0.005
C(10)		0.003
C(11)		0.001
C(12)		0.004
C(13)		-0.045
$\angle P1/P2$	28.0	27.5
$\angle P1/P3$		82.5
$\angle P2/P3$		79.3

7) again reflect the similarity of the two compounds and the deviation from planarity. A similar deviation from a planar ring has been observed for 2,4-dimethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine by Christopher-*sen et al.* (1975) and for phenanthro[9,10-*c*]-1,2,5-thiadiazol-1-one hydrate (Arora, 1974). The central ring in 5-benzoylimino-3-phenyl-2-(4-bromophenyl)-2,5-dihydro-1,2,4-thiadiazole is planar (Kutoglu & Jepsen, 1972).

Table 7. Conformation angles ( $^{\circ}$ )

	(2a)	(2b)
N(1)–C(15)–S–N(2)	29	24
C(14)–N(2)–S–C(15)	–27	–22
N(1)–C(14)–N(2)–S	16	14
N(2)–C(14)–N(1)–C(15)	9	7
S–C(15)–N(1)–C(1)	20	15
N(2)–C(14)–N(1)–C(1)	2	0
N(1)–C(14)–N(2)–C(13)	4	4
C(13)–N(2)–S–C(15)	4	13

The C–N distances near the keto group of (2) are somewhat shortened from the single-bond distance of about 1.45 Å observed for the bonds between N and aryl groups. This bond shortening corresponds to 25% double-bond character (Wheatley, 1955). A similar shortened bond was observed in the planar ring of 3-phenyl-2-phenylimino-1,3-thiazetidine (Schuckmann, Fuess, Möisinger & Ried, 1978). We attributed this partial conjugation to either the imino or the phenyl group. In the two compounds described here only the phenyl group is present. It seems, therefore, that some orbital overlap between the  $p_{\pi}$  orbitals of N and the phenyl group is still present despite the angle between the two rings. The C–O bond lengths of 1.217 and 1.208 Å agree well with known ketonic distances, in particular with thiazolidine-2,4-dione (Form, Raper & Downie, 1975). These authors indicate that a bond order of less than two should be connected with this distance. The S–N and S–C distances are close to observed single bonds. The S–O distances of 1.474 Å

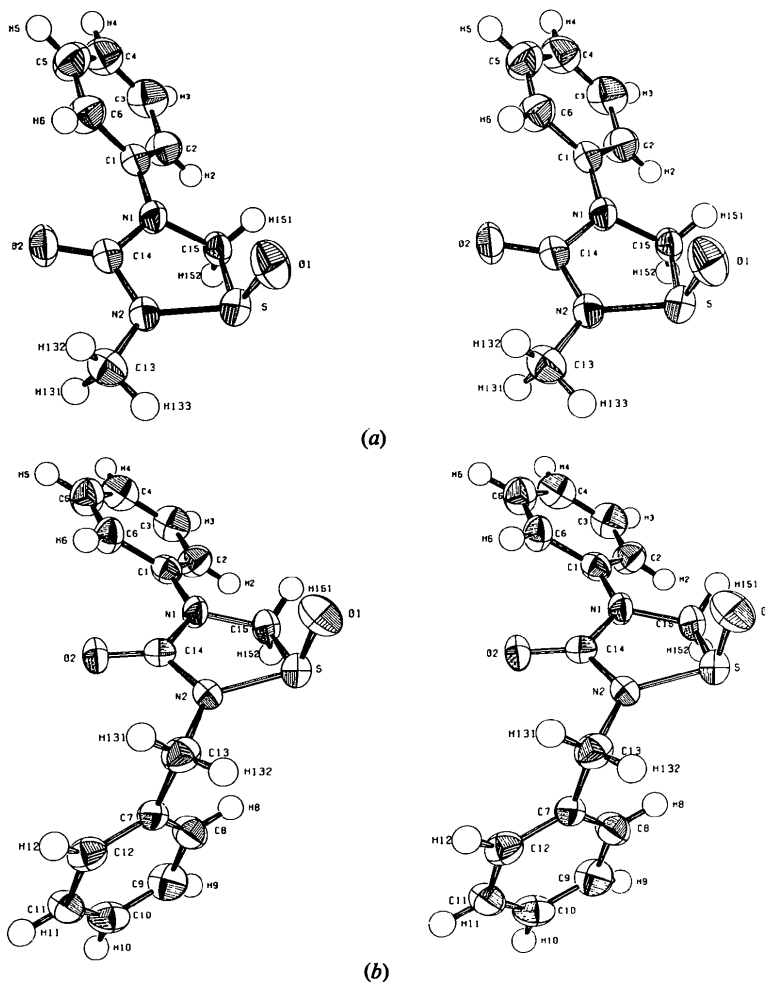


Fig. 1. Stereoscopic views of single molecules (50% probability for thermal ellipsoids) of (a) 2-methyl-4-phenyl-1-oxo-1- $\lambda^4$ -1,2,4-thiadiazolidin-3-one and (b) 2-benzyl-4-phenyl-1-oxo-1- $\lambda^4$ -1,2,4-thiadiazolidin-3-one. H spheres are of arbitrary size.

(2a) and 1.468 Å (2b) are normal for a sulphoxide and agree closely with the value of 1.478 Å found for phenanthro-1,2,5-thiadiazole. The N—S—C angles of 86.4 and 86.9° are slightly smaller than the C—S—C angle of 87.0° in 1,3,4-thiadiazole (La Cour, 1974) and the C—S—C angle of 89.6° in mercaptothiadiazole (Bats, 1976). The S—C distances of 1.810 and 1.809 Å reflect single-bond character, like the values observed by Argay, Kálmán, Lazar, Ribár & Toth (1977) and Petrović, Ribár, Argay, Kálmán & Nowacki (1977) for various amino(imino)thiadiazoles (1.778 to 1.841 Å).

A comparison between the structures of 3-phenyl-2-phenylimino-1,3-thiazetidone and the 1,2,4-thiadiazolidines shows that the higher oxidation state of S puts that atom out of the plane. The degrees of conjugation, indicated by the C—N distances in the heterocycles, seem, however, to be similar. Further oxidation of 1-oxo-1- $\lambda^4$ -1,2,4-thiadiazolidin-3-one is possible and the products obtained have been characterized as S double oxides by spectroscopic methods (Mösinger, 1977). No structure determination of these compounds has so far been carried out.

The computer calculations have been carried out at the Hochschulrechenzentrum der Universität Frankfurt. The support of the computer staff is gratefully acknowledged.

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## Molecular and Crystal Structure of the Free Acid of Cytidine 2',3'-Cyclophosphate

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The crystal structure of cytidine 2',3'-cyclophosphate (free acid) has been determined by X-ray diffraction techniques. The unit cell is orthorhombic, space group  $P2_12_12_1$ , with cell dimensions  $a = 6.680$  (5),  $b = 18.342$  (10),  $c = 10.128$  (7) Å and  $Z = 4$ . The data (1175 reflexions) were collected on a Stoe four-circle diffractometer using Cu  $K\alpha$  radiation. The structure was solved by the tangent formula applying the *MULTAN* program and refined by a full-matrix least-squares procedure to a final  $R$  value of 0.064. All the H atoms were located. The ribose has C(2')-endo, C(3')-exo puckering and the conformation about the glycosidic bond is *anti* ( $\chi_{CN} = 61.6^\circ$ ). This conformation for the cyclic phosphate is different from the earlier observations for similar molecules.

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