Sultam and Sultim Structures, Part 3 [1]. Strong and Weak Hydrogen Bonds in 3-Oxosultams, 3-Oxosultims and 3-Alkoxysultams

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Dedicated to Professor Dr. Klaus Schulze on the occasion of his 70th birthday

In order to study hydrogen bonding networks in cyclic sulfin- and sulfonamides, X-ray structures were determined for 3-oxosultams **3a, c – e**, 3-alkoxysultams **5b, f** and 3-oxosultim **2f**, all of which show predominantly weak intermolecular hydrogen bonds. The 3-oxosultam **3a** forms tetrameric units by combining two symmetry-independent molecules through weak aromatic C-H···O-S-O hydrogen bonds without participation of the carbonyl groups. The 3-oxosultam **3c**, with two chloro substituents in the N-aryl ring show a polymer arrangement of the molecules through intermolecular association of the SO_2 and CO groups also with the aromatic H-atoms of the aryl rings. Sultam **3d** shows the first polymer chain in the 3-oxosultam series by the strong O-H···O=C hydrogen bonds without participation of the SO_2 group. Two new 'head-to-head' dimers with a 10-membered ring are found for 3-alkoxysultams **5b**, **5f** through weak C-H···O-S-O hydrogen bonds. In the 3-oxosultim **2f** weak intermolecular hydrogen bonds are observed to form a two-dimensional network with the two methylene groups, the carbonyl function and the chloro atom but, surprisingly, without the strong S-oxide acceptor group.

Key words: Sultims, Sultams, Intermolecular Hydrogen Bonds

Introduction

Isothiazol-3(2*H*)-ones and their metal salt complexes are effective industrial microbiocides because of their antibacterial and antifungal activities, particularly the 2-octyl- and mixtures of 2-methylisothiazol-3(2*H*)-one with 5-chloro analogue [2a]. Furthermore they are reactive intermediates in the synthesis of various organic substances [2b, c], including pharmaceutical chemicals [2d, e].

The 3-oxosultams are prepared by oxidation of isothiazolones with CPBA or by oxidation of 3-unsubstituted isothiazoles [3 – 5]. A series of monocyclic 2-phenyl-isothiazol-3(2*H*)-one 1,1-dioxides were synthesized by oxidation of isothiazolium perchlorates [6] and the inhibition of the serine proteases cathepsin G, chymotrypsin and human leukocyte elastase (HLE) was verified [7].

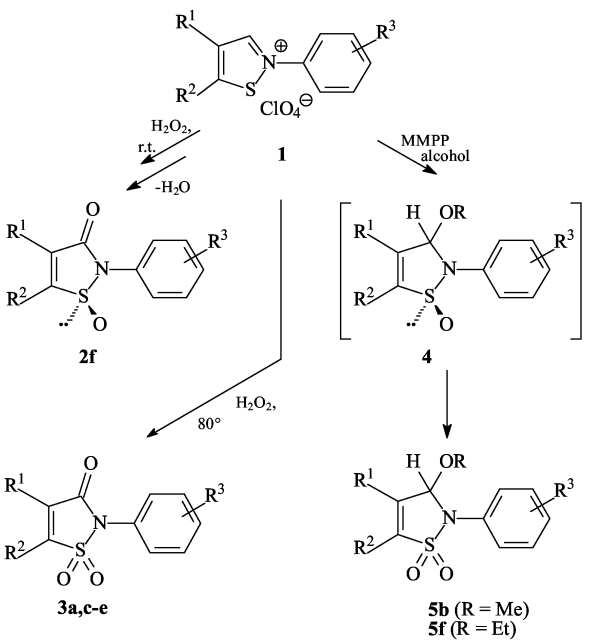
We have recently described the X-ray diffraction analysis of 3-hydroxy- and 3-hydroperoxysultims and -sultams, which are precursors of 3-oxosultams **3** [1]. We have found a variety of intermolecular contacts leading to 'head-to-tail' cyclodimers, tetramers, and polymers with strong intermolecular S-O···H-O hydrogen bonds and weak C-H···O=C interactions.

In this paper, we wish to report on the synthesis and X-ray diffraction analysis of compounds **2, 3** with sulfonyl, sulfoxide and carbonyl group which are efficient hydrogen-bonding acceptors. 3-Alkoxy-sultams **5** were also included in the series. Although described in the literature [8, 9], these compounds have not been thoroughly characterized yet.

We will show here how the three-dimensional structure of highly oxy-functionalized sultim **2** and sultams **3**, **5** results from noncovalent interactions between molecules with predominantly weak hydrogen bonds.

Results and Discussion

The 2-aryl-3-oxosultams **3a** [6d] and **3c – e** are conveniently synthesized by the oxidation of isothi-



	R^1	R^2	R^3
a	Me	Me	2-Cl
b	Me	Me	4-Me
c	Ph	Me	2,5-Cl_2
d	Ph	Me	2-OH
e	Ph	Me	4-CF_3
f	-$(CH_2)_4$-		4-Cl

Scheme 1.

azolium salts **1** with H_2O_2 in glacial acetic acid (80 °C, 8 h). *S*-oxide **2f** is obtained from the *rac-cis*-3-hydroperoxysultim by elimination of water [2c] (Scheme 1).

The oxidation of salts **1** with magnesium monoperoxyphthalate (MMPP·$6H_2O$) in alcohol (ultrasound, 50 °C) gives the 3-alkoxysultams **5b, f** [8,9].

Physical properties and spectroscopic data of the novel 3-oxosultams **3c – e** are described in the experimental part. The solid-state structure of the sulfonamides **3a, c – e** is revealed with the aid of X-ray crystallography. The crystallographic data are presented in Table 1, selected bond distances and angles in Table 2. We compare the solid-state structure of these compounds with each other and with those of **2f** [2c], **5b** [8] and **5f** [9].

The structure of 3-oxosultam **3a** is presented in Fig. 1. The behavior of the two symmetry-independent molecules of **3a** towards the hydrogen bonds varies.

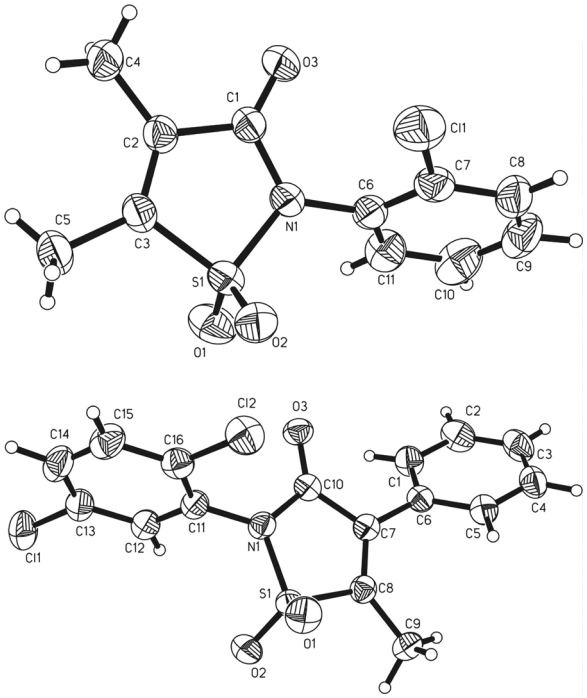


Fig. 1. Molecular structure of **3a** (top) and **3c** (bottom) with labelling and displacement ellipsoids at the 50% probability level.

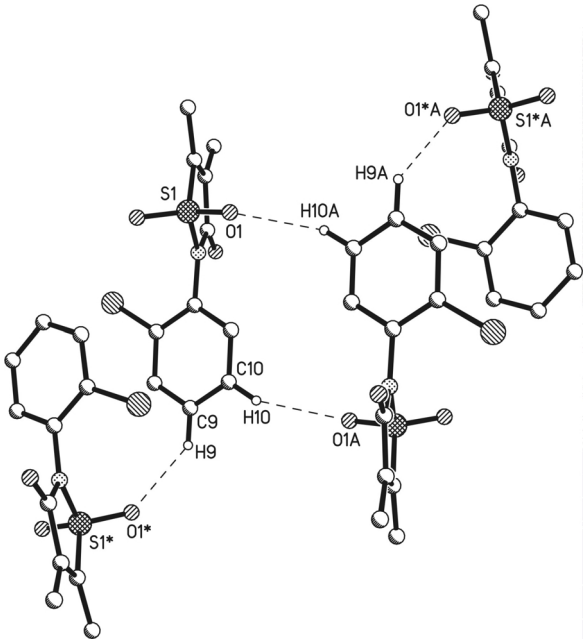


Fig. 2. Tetrameric arrangement of **3a** with hydrogen bonds C(10)-H(10)···O(1A)-S(1A) and C(10A)-H(10A)···O(1)-S(1), which are generated a centre of symmetry and a weak hydrogen bond C(9)-H(9)···O(1*)-S(1*); (Symmetry code A: $-x, -y, -z$).

Table 1. Crystal data and structure refinment for 3-oxosultams **3a, c – e**.

	3a	**3c**	**3d**	**3e**
Empirical formula	$C_{11}H_{10}ClNO_3S$	$C_{16}H_{11}Cl_2NO_3S$	$C_{16}H_{13}NO_4S$	$C_{17}H_{12}F_3NO_3S$
Formula weight	271.71	368.22	315.33	367.34
Temperature [K]	218(2)	213(2)	243(2)	223(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$Pna2(1)$	$P2_1/n$
a [Å]	11.6206(4)	8.075(3)	7.3309(13)	5.2956(4)
b [Å]	25.6859(10)	10.161(4)	15.803(3)	13.719(1)
c [Å]	8.0354(3)	19.715(7)	12.135(2)	22.104(2)
α [°]	90	90	90	90
β [°]	93.963(1)	98.314(6)	90.0	93.460(2)
γ [°]	90	90	90	90
Volume [Å^3]	2392.72(15)	1600.6(10)	1405.8(4)	1602.9(2)
Z	8	4	4	4
Density [Mg/m^3]	1.509	1.528	1.490	1.522
Absorption coeff. [mm^{-1}]	0.488	0.549	0.249	0.251
Crystal size [mm]	$0.25\times0.25\times0.20$	$0.30\times0.20\times0.20$	$0.30\times0.20\times0.20$	$0.80\times0.20\times0.10$
θ Range for data collect. [°]	$1.59-28.74$	$2.09-27.00$	$2.12-25.98$	$1.75-28.27$
Index ranges	$-15\le h\le15$, $-34\le k\le34$, $-7\le l\le10$	$-10\le h\le9$, $-11\le k\le12$, $-25\le l\le24$	$-9\le h\le6$, $-19\le k\le18$, $-14\le l\le14$	$-6\le h\le6$, $-18\le k\le17$, $-29\le l\le15$
Reflections collected	14839	9229	7437	10182
Independent reflections	5697 [$R_{int}=0.0178$]	3489 [$R_{int}=0.0143$]	2652 [$R_{int}=0.0301$]	3864 [$R_{int}=0.0214$]
Absorption correction	SADABS	SADABS	SADABS	SADABS
Max./min. transmission	0.9087/0.8877	0.8982/0.8527	0.9520/0.9292	0.9753/0.8243
Data/parameters	5697/388	3489/252	2652/252	3864/274
Goodness-of-Fit on F^2	0.916	1.048	1.139	1.084
Final R indices [$I>2\sigma(I)$]	$R_1=0.0368$ $wR_2=0.0988$	$R_1=0.0307$ $wR_2=0.0823$	$R_1=0.0385$ $wR_2=0.0768$	$R_1=0.0497$ $wR_2=0.1166$
R Indices (all data)	$R_1=0.0521$ $wR_2=0.1082$	$R_1=0.0379$ $wR_2=0.0865$	$R_1=0.0486$ $wR_2=0.0804$	$R_1=0.0696$ $wR_2=0.1244$
Lgst diff peak/hole [e Å^{-3}]	0.324/−0.330	0.302/−0.256	0.235/−0.270	0.380/−0.278

One of the independent molecules forms a dimer with centrosymmetrically related molecule through intermolecular hydrogen bonds C(10)-H(10)···O(1A)-S(1A) and C(10A)-H(10A)···O(1)-S(1) (Fig. 2). The other molecule is connected to this dimeric unit by the hydrogen bond C(9)-H(9)···O(1*)-S(1*) and these completes a tetrameric unit. The strong hydrogen bond acceptor of the C=O functional group is not involved. The interplanar angle between the N-aryl substituent and the isothiazole ring is 68.2° in **3a** and 65.7° in **3a***.

The 3-oxosultam **3c**, with two chloro substituents at the N-aryl ring, is arranged as a polymer and indicates the intermolecular association between the O-atom of the SO_2 and CO groups and the H-atoms of the aryl rings (Fig. 3). The *o*-chloro substituted N-aryl (79.5°) and also the 4-aryl ring (99.6°) are almost perpendicular to the isothiazole plane. Compound **3c** builds up a complex three-dimensional network structure with weak hydrogen bonds. Each molecule contributes three hydrogen bonds (Fig. 3, molecule with atom S(1B)). The hydrogen bonds over the C(15)-H(15)···O(3B) form a helix along the monoclinic *b*-axis, caused by the

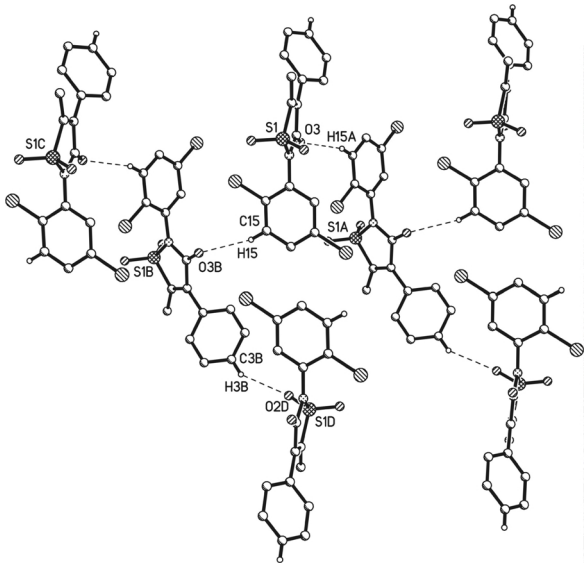


Fig. 3. Polymer arrangement of the molecules **3c** by hydrogen bonds C(15)-H(15)···O(3B) and C(3B)-H(3B)···O(2D)-S(1D).

Table 2. Selected bond lengths [Å] and angles [°] for **3a, c – e** with estimated standard deviations in parentheses.

	Bond lengths [Å]		Angles[°]	
3a	S(1)-O(1)	1.4287(16)	O(1)-S(1)-O(2)	117.41(10)
	S(1)-O(2)	1.4268(15)	O(1)-S(1)-N(1)	110.50(9)
	S(1)-N(1)	1.6697(16)	O(2)-S(1)-N(1)	109.59(9)
	S(1)-C(3)	1.7552(19)	O(1)-S(1)-C(3)	110.33(10)
	O(3)-C(1)	1.204(2)	O(2)-S(1)-C(3)	113.24(9)
	N(1)-C(1)	1.388(2)	O(3)-C(1)-N(1)	124.26(17)
	N(1)-C(6)	1.428(2)	O(3)-C(1)-C(2)	126.18(17)
	C(1)-C(2)	1.495(2)	N(1)-S(1)-C(3)	93.12(8)
	C(2)-C(3)	1.337(3)	C(1)-N(1)-S(1)	113.41(12)
	C(2)-C(4)	1.485(3)	C(1)-C(2)-C(3)	113.18(17)
3c	S(1)-O(1)	1.4298(14)	O(1)-S(1)-O(2)	117.04(8)
	S(1)-O(2)	1.4257(13)	O(1)-S(1)-N(1)	110.08(8)
	S(1)-N(1)	1.6658(15)	O(2)-S(1)-N(1)	110.13(8)
	S(1)-C(8)	1.7595(17)	O(1)-S(1)-C(8)	110.47(8)
	O(3)-C(10)	1.2044(19)	O(2)-S(1)-C(8)	113.24(8)
	N(1)-C(10)	1.396(2)	O(3)-C(10)-N(1)	123.21(15)
	N(1)-C(11)	1.429(2)	O(3)-C(10)-C(7)	127.47(15)
	C(7)-C(10)	1.502(2)	N(1)-S(1)-C(8)	93.36(7)
	C(7)-C(8)	1.339(2)	C(10)-N(1)-S(1)	113.42(11)
	C(8)-C(9)	1.495(2)	C(10)-C(7)-C(8)	113.21(14)
3d	S(1)-O(1)	1.425(2)	O(1)-S(1)-O(2)	118.34(12)
	S(1)-O(2)	1.422(2)	O(1)-S(1)-N(1)	109.62(13)
	S(1)-N(1)	1.684(2)	O(2)-S(1)-N(1)	109.38(12)
	S(1)-C(1)	1.769(3)	O(1)-S(1)-C(1)	112.51(13)
	O(3)-C(3)	1.215(3)	O(2)-S(1)-C(1)	110.97(14)
	N(1)-C(3)	1.374(3)	O(3)-C(3)-N(1)	123.3(3)
	N(1)-C(10)	1.434(3)	O(3)-C(3)-C(2)	125.9(2)
	C(2)-C(3)	1.499(4)	N(1)-S(1)-C(1)	93.07(13)
	C(1)-C(2)	1.341(4)	C(3)-N(1)-S(1)	112.51(18)
	C(1)-C(16)	1.481(4)	C(1)-C(2)-C(3)	112.7(2)
3e	S(1)-O(1)	1.4207(16)	O(1)-S(1)-O(2)	117.95(9)
	S(1)-O(2)	1.4270(15)	O(1)-S(1)-N(1)	110.28(9)
	S(1)-N(1)	1.6684(17)	O(2)-S(1)-N(1)	109.59(10)
	S(1)-C(8)	1.7615(19)	O(1)-S(1)-C(8)	111.94(9)
	O(3)-C(10)	1.204(2)	O(2)-S(1)-C(8)	111.19(9)
	N(1)-C(10)	1.390(2)	O(3)-C(10)-N(1)	123.14(18)
	N(1)-C(11)	1.439(3)	O(3)-C(10)-C(7)	127.21(18)
	C(7)-C(10)	1.502(3)	N(1)-S(1)-C(8)	93.09(9)
	C(7)-C(8)	1.337(3)	C(10)-N(1)-S(1)	113.50(13)
	C(8)-C(9)	1.487(3)	C(8)-C(7)-C(10)	112.88(17)

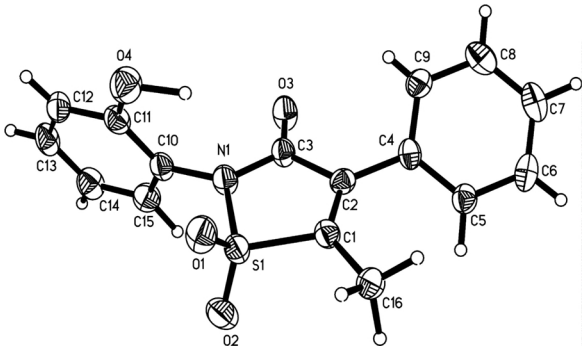


Fig. 4. Molecular structure of **3d** with labelling and displacement ellipsoids at the 50% probability level.

Table 3. Geometric data[a] for the hydrogen bonds, in the solid-state of 3-oxo-sultim **2f**, 3-oxo-sultams **3a, c – e** and 3-alkoxy-sultams **5b** and **5f**.

	D-H···A[b]	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
2f	C(4E)-H(4E)···Cl(1B)	1.08	2.77	3.848	175.5
	C(7F)-H(7F)···O(1E)	0.99	2.43	3.140	128.2
3a	C(9)-H(9)···O(1*)	0.99	2.42	3.233	139.0
	C(10)-H(10)···O(1A)	0.98	2.55	3.476	157.0
3c	C(3B)-H(3B)···O(2D)	0.89	2.49	3.279	147.3
	C(15)-H(15)···O(3B)	0.91	2.59	3.466	161.5
3d	O(4)-H(4)···O(3)	1.15	1.80	2.829	145.5
3e	C(1)-H(1)···O(3)	0.93	2.56	3.001	109.8
	C(13)-H(13)···F(2)	0.89	2.44	2.746	100.3
5b	C(1)-H(1)···O(2)	1.01	2.51	3.400	147.1
5f	C(1)-H(1)···O(2)	0.96	2.52	3.248	132.2
	C(7)-H(7B)···O(3)	0.95	2.60	3.472	153.5

[a] Data calculated by using the program SHELXL [10]; [b] D: donor atom; A: acceptor atom.

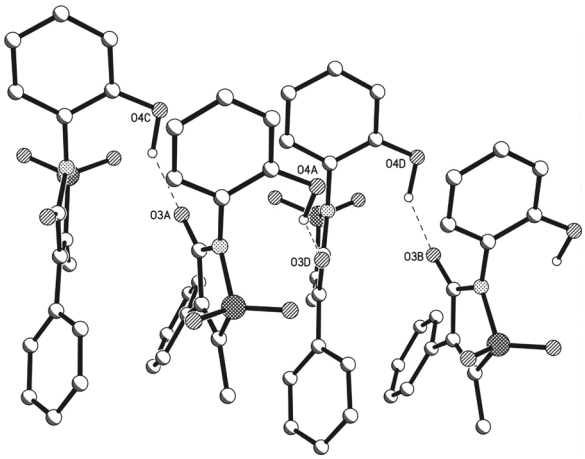


Fig. 5. Polymer structure of **3d** with strong O-H···O=C bonds. The chains are formed by a glide plane in the space group $P2_1/c$.

2_1-screw axis. The symmetry connections between the atoms S(1B) and S(1), respectively S(1C) and S(1B) are $-x$, $0.5+y$, $0.5-z$. The S(1C)-atom and the S(1)-atom are transferred into each other by the translation x, $1+y$, z. The third hydrogen bond is built up between the atoms C(3B)-H(3B)···O(2D)-S(1D). These hydrogen bonds are formed by the *c*-glide plane. The symmetry relation among S(1B) and S(1D) is x, $0.5-y$, $0.5+z$. By combination of the screw axis and the glide plane, the molecules with the atoms S(1) and S(1A) are situated centrosymmetrically to each other.

Interestingly, the 3-oxosultam **3d** (Fig. 4 and 5), with a 2-hydroxy substituent in the N-aryl ring, forms polymer chains through strong intermolecular C=O···H-O bridges (2.829 Å) in which the 2-OH sub-

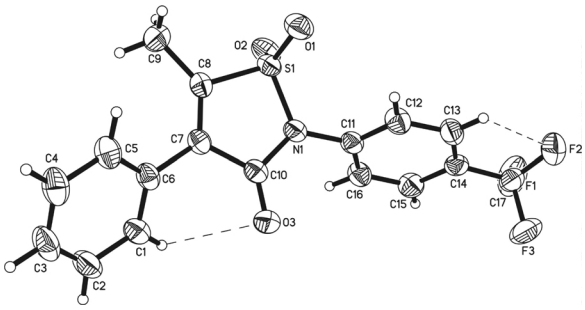


Fig. 6. Molecular structure of **3e** with labelling and displacement ellipsoids at the 50% probability level.

stituted N-aryl ring (96.1°) is perpendicular to the sultam ring (Fig. 5). The chains are formed by a glide plane in the space group $P2_1/c$ and proceed in direction of the *a*-axis. The SO_2 group is not involved.

In the structure **3e** (Fig. 6), only the intramolecular hydrogen bonds C(13)-H(13)···F(2) and C(1)-H(1)···O(3)-C(10) exist in the solid state. The N-aryl and 4-aryl ring maintain angles of 140.2° and 113.9° with the isothiazole plane.

The bicyclic 1-oxide **2f** (Fig. 7) shows intermolecularly stabilized associations with participation of the allylic methylene groups, the carbonyl group, and the chloro atoms (3.139 Å and 3.848 Å) in the three further molecules. Therefore the structure exists in the two-dimensional network with hydrogen bonds. The N-aryl group is 51.0° out of the plane of the isothiazole ring. The connections of the molecules in the direction of the *a*-axis is built up by the atoms C(7F)-H(7F)···O(1E)-C(1E) by translation, and in the *b*-direction with the atoms C(4E)-H(4E)···Cl(1B) also by translation; the S-O bonds are not involved in the hydrogen bond system.

For a comparative study, we also investigated sultams **5b** and **5f** with 3-alkoxy substituents. Compound **5b** forms, surprisingly, new 'head-to-head' dimers in the solid-state with a 10 membered ring stabilized through two interactions C(1)-H(1)···O(2A)-S(1A) and C(1A)-H(1A)···O(2)-S(1) related by the centre of symmetry inversion (Fig. 8).

The sultam **5f** forms also centrosymmetric 'head-to-head' dimers. These dimers are then translated along the *a*-axis by the slipping-mirror-plane *a*. For the sake of clearness, the *p*-chloro phenyl ring is not shown in Fig. 8. The torsion angle between the isothiazole ring and the N-aryl substituent is 9.5° in **5b** and 12.7° in **5f**, respectively.

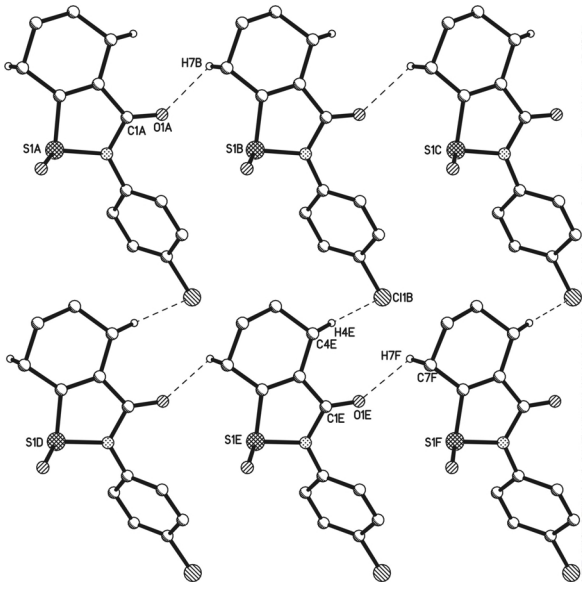


Fig. 7. Two dimensional network of **2f**.

In conclusion, the discussed sultams and the sultim were found to exist as centrosymmetric dimers, polymer structures and a two-dimensional network through predominantly weak intermolecular hydrogen bonds with participation of CO, SO_2, aromatic CH, CH_2 groups, and also a chloro substituent.

The 3-oxosultams **3a** and **3c** form weak hydrogen bonds between the O-acceptor of the SO_2 group and the aromatic CH donor function of a aryl ring. If there is only one chloro substituent in the N-aryl ring, a tetrameric structure **3a** is created by a second C-H···O-S-O hydrogen bond, the strong O-acceptor of the CO group does not participate. In the case of two chloro substituents in the N-aryl ring and another 4-aryl substituent in **3c**, the CO group forms additional hydrogen bonds with the aromatic CH function of the N-aryl ring. In 3-alkoxy sultams **5b, f**, 1,1-dioxides without a CO function, intermolecular O-S-O···H-C hydrogen bonds to centrosymmetric dimers are also found.

Surprisingly, a two dimensional network with one weak C=O···H-CH and another Cl···H-CH hydrogen bond was found in the 1-oxide **2f**. The participation of the SO group, a strong hydrogen bond acceptor, could not be observed.

The 3-oxosultam **3d** shows the typical polymer structure through the strong O-H···O=C hydrogen bonds.

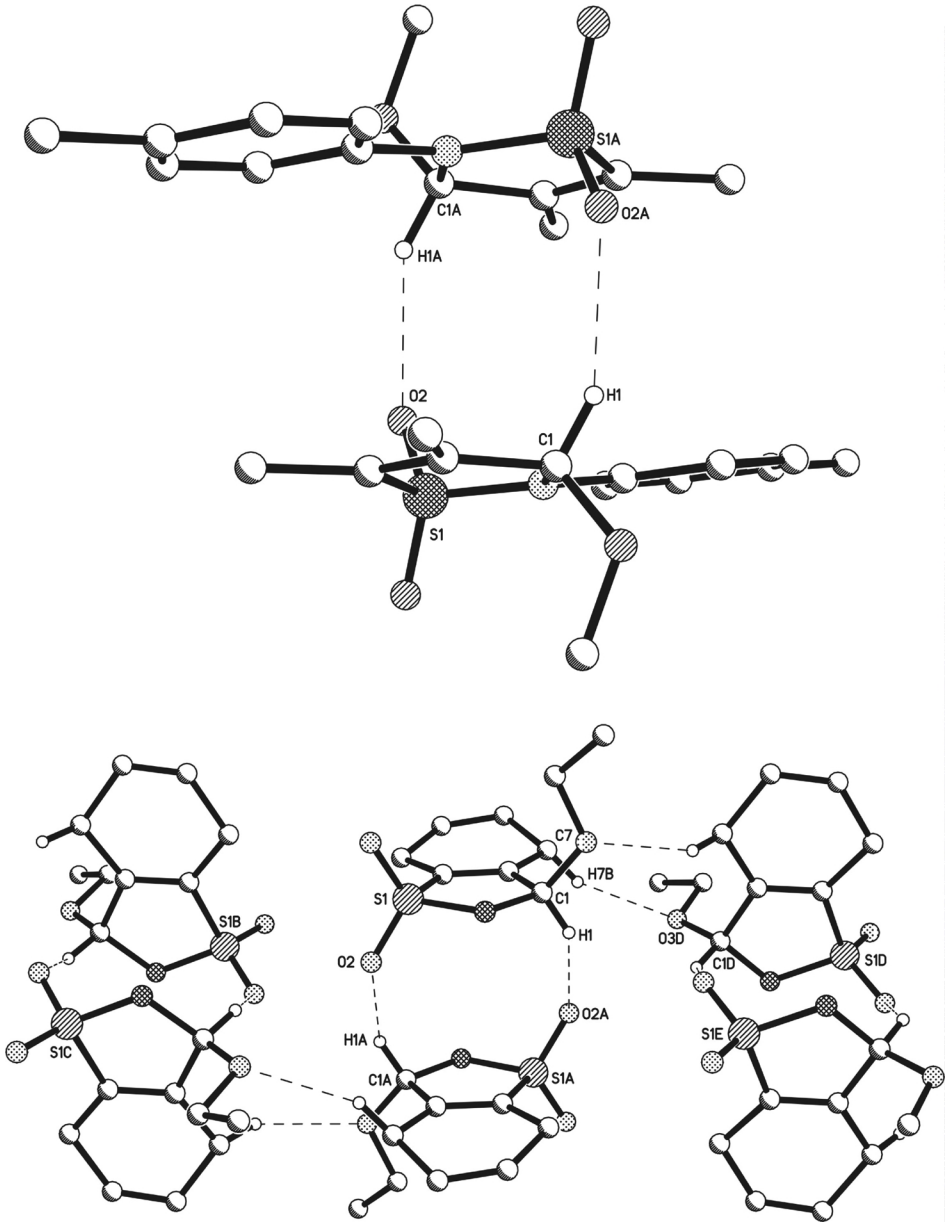


Fig. 8. The centrosymmetric dimers of **5b** (top) and **5f** (bottom) with C(1)-H(1)···O(2)-S(1) hydrogen bonds.

Experimental Section

General. M. p.: Boetius micro-melting-point apparatus; corrected. IR spectra: Genisis FTIR Unicam Analytical System (ATI Mattson); KBr pellets; values in cm^{-1}. ^1H NMR: Varian Gemini-200 and Varian Unity-400; δ in ppm rel. to TMS as internal standard, J in Hz. ^{13}C NMR spectra: 50 or 100 MHz, recorded on the above-mentioned spectrometers. ^{19}F NMR spectrum has also been measured at 188 MHz on the named spectrometer with $CFCl_3$ as standard. MS: Quadrupol-MS VG 12-250; 70 eV. Elemental analysis: Heraeus CHNO Rapid Analyzer.

Syntheses. The salts **1c – e** were prepared according to the literature procedure [6d]. **1c**: yield 91%, m. p. 147 – 148 °C; **1d**: yield 78%, m.p. 115 – 116 °C; **1e**: yield 73%, m. p. 101 – 104 °C. The 1-oxide **2f** is described in [2c], the 3-oxosultam **3a** in [6d], and the 3-alkoxysultams **5b, f** in [8, 9].

*2-Aryl-5-methyl-4-phenyl-2,3-dihydro-isothiazol-3-one 1,1-dioxide (**3**)*

H_2O_2 (0.7 ml, 30%) was added to a stirred suspension of **1** (0.26 mmol) in AcOH (0.7 ml) at 80 °C. After 8 h a colorless precipitate **3** crystallized. The crude product was washed with H_2O, recrystallized from ethanol.

*2-(2,5-Dichlorophenyl)-5-methyl-4-phenyl-2,3-dihydro-isothiazol-3-one 1,1-dioxide (**3c**)*

Yield: 56%. M. p. 143 – 145 °C. – IR (KBr): ν = 1160s (SO_2), 1332s (SO_2), 1737s (CO). – UV (ethanol): λ_{max} (lg ε): 205.5 (3.92) nm. – ^{1}H NMR ([D$_6$]-DMSO): δ = 2.55 (s, 3H, 5-CH_3), 7.60 – 7.84 (m, 8H, arom. H). – ^{13}C NMR ([D$_6$]-DMSO): δ = 9.3 (5-CH_3), 127.8, 129.0, 129.5, 130.9, 131.3, 132.8, 133.0, 133.1, 133.9, 134.6, 134.9 (C-4), 145.4 (C-5), 159.3 (C-3). – MS: *m/z* = 368.0 ($M^{+\bullet}$). – $C_{16}H_{11}Cl_2NO_3S$ (368.24): calcd. C 52.19, H 3.01, N 3.80, S 8.71; found C 52.31, H 2.98, N 3.76, S 8.78.

*2-(2-Hydroxyphenyl)-5-methyl-4-phenyl-2,3-dihydro-isothiazol-3-one 1,1-dioxide (**3d**)*

Yield: 38%. M. p. 187 – 189 °C. – IR (KBr): ν = 1132s (SO_2), 1328s (SO_2), 1734s (CO). – UV (ethanol): λ_{max} (lg ε): 210.5 (4.20) nm. – ^{1}H NMR ([D$_6$]-DMSO): δ = 2.33 (s, 3H, 5-CH_3), 7.00 – 7.14 (m, 4H, arom. H), 7.35 – 7.66 (m, 5H, arom. H). – ^{13}C NMR ([D$_6$]-DMSO): δ = 8.0 (5-CH_3), 117.3, 120.2, 127.6, 128.7, 130.1, 130.2, 131.4, 132.0, 133.1, 133.9 (C-4), 145.6 (C-5), 158.9 (C-3), 161.7. – MS: *m/z* = 315.0 ($M^{+\bullet}$). – $C_{16}H_{13}NO_4S$ (315.35): calcd. C 60.94, H 4.16, N 4.44, S 10.17; found C 61.03, H 4.06, N 4.51, S 10.23.

*2-(4-Trifluoromethylphenyl)-5-methyl-4-phenyl-2,3-dihydroisthiazol-3-one 1,1-dioxide (**3e**)*

Yield: 43%. M. p. 124 – 125 °C. – IR (KBr): ν = 1124s (SO_2), 1332s (SO_2), 1737s (CO). – UV (ethanol): λ_{max} (lg ε): 223.0 (4.19) nm. – ^{1}H NMR ([D$_6$]-DMSO): δ = 2.47 (s, 3H, 5-CH_3), 7.56 – 7.65 (m, 5H, arom. H), 7.83 – 8.00 (m, 4H, arom. H). – ^{19}F NMR ([D$_6$]-DMSO): δ = −63.88 (s, 3F, CF_3). – ^{13}C NMR ([D$_6$]-DMSO): δ = 8.3 (5-CH_3), 124.6, 127.1, 128.3, 128.8, 130.1, 130.3, 130.5, 131.1, 134.1 (C-4), 134.6, 145.3 (C-5), 159.3 (C-3). – MS: *m/z* = 367.0 ($M^{+\bullet}$). – $C_{17}H_{12}F_3NO_3S$ (367.35): calcd. C 55.58, H 3.29, N 3.81, S 8.73; found C 55.49, H 3.18, N 3.98, S 8.75.

Single crystal X-ray diffractometry

The crystals of **3a, 3c – e** were obtained from acetone. The intensities were measured on a Siemens SMART CCD diffractometer. The relevant crystallo-graphic data are listed in Table 1. The structures were solved by direct methods with SHELXS-97 [10]. The refinement was done with SHELXL-97 [10]. The details of the structure analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC-245824 for **3a**, -245825 for **3c**, -245826 for **3d** and -245827 for **3e**. The copies of the data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44-1233-336033; e-Mail: deposite@ccdc.cam.ac.uk; internet: //www.ccdc.cam.ac.uk).

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