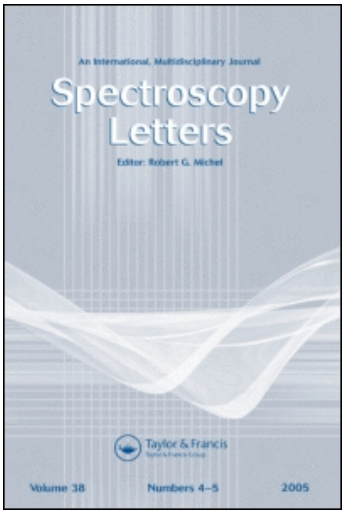

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An X-Ray Analysis on Restricted Rotational Isomers of 2-Thioxo-4-oxazolidinone

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AN X-RAY ANALYSIS ON RESTRICTED ROTATIONAL ISOMERS OF 2-THIOXO-4-OXAZOLIDINONE

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ABSTRACT

The thermodynamically more stable diastereomeric rotational isomer I, of 3-(o-tolyl)-5-methyl-2-thioxo-4-oxazolidinone, which is first crystallized out in solution, shows that the ortho methyl substituent is cisoid to the methyl group of the hetero ring, and the thermodynamically less stable isomer II, crystallized later, has both methyl groups in transoid conformation, as is found in X-ray studies. The carbonyl and thiocarbonyl bonds are found to be longer in isomer II than in isomer I, which is attributed to the favored conjugation interaction of carbonyl, thiocarbonyl groups with the lone pair electrons of nitrogen,

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that may cause the lessened stability of isomer II.

INTRODUCTION

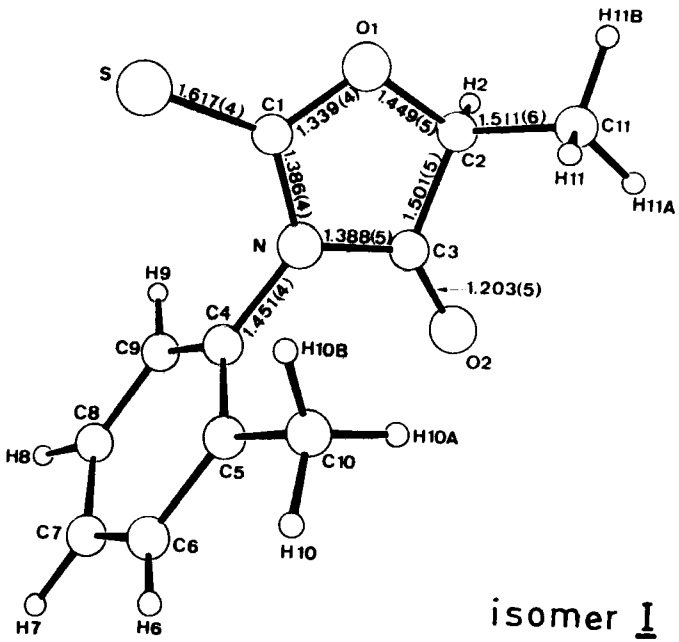
We have reported earlier the detection of isomeric nuclei arising from conformations of aryl substituted oxazolidinediones[1], thioxooxazolidinones[2], rhodanines[2] and thiazolidinediones[3] at ^{1}H and ^{13}C NMR spectroscopy studies. Steric interactions between the aryl and heterocyclic moieties in these five membered heterocycles are known to produce sufficient restriction to rotation about the aryl C-N bond that the presence of torsional isomers may be detected at magnetic non-equivalence of diastereotopically related nuclei[1-3]. The free energies of rotation of these compounds have been reported at NMR studies of enantiomeric and diastereomeric rotational isomers. The conformational preferences of the rotational diastereomers in such aryl substituted heterocyclic compounds were evident in the ^{1}H NMR spectra, on observation of isomeric signals at unequal intensities[1-3]. In order to relate the conformational preferences to the structures, we have selected the 3-(o-tolyl)-5-methyl-2-thioxo-4-oxazolidinone for X-ray studies. The barrier to internal rotation in this compound was reported to be higher than those of the aryloxazolidinediones and arylthiazolidinediones[2,3]. The free energy of activation ($\Delta G^{\neq}$) was found to be 24.2 kcalmol^{-1}. This value corresponds nearly to the upper limit of dynamic NMR

studies. Thus the chemical isolation of the isomers were possible.

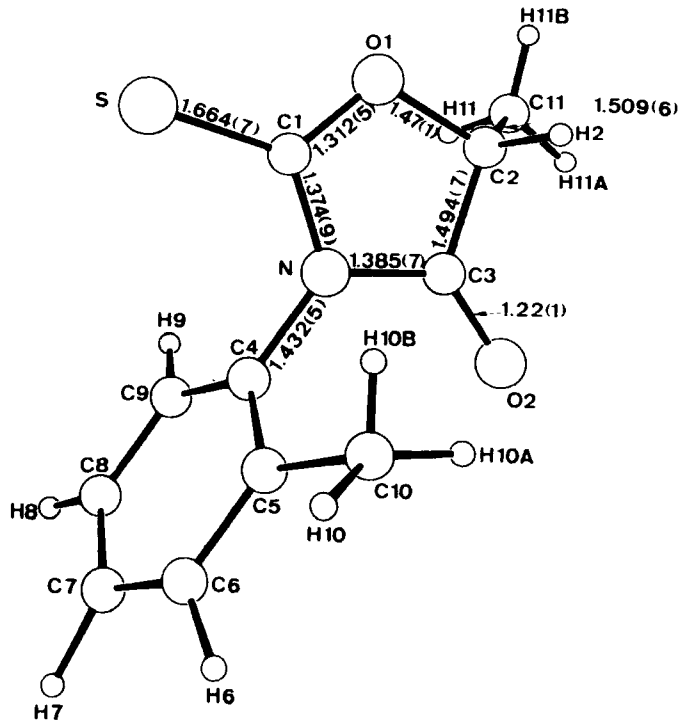
RESULTS AND DISCUSSION

Slow crystallization from p.ether/ether/ligroin, 4/3/2 respectively, solvent mixtures first yielded the thermodynamically more stable isomer I, in 99 % isomeric purity (NMR), than the thermodynamically less stable isomer II, in 99 % purity (NMR). Both isomers were equilibrated to isomeric mixtures in pyridine solutions in about an hour as followed from the diastereotopic signals of the methine proton. The specific rotations of the pure diastereomers were $+0.80^{o}$ and -0.02^{o} for the thermodynamically more and less stable isomer, respectively. The thioxooxazolidinone was synthesized from L(-)-ethyllactate, thus the differing conformations of isomers can only be attributed to a rotation about aryl C-N bond.

The molecular structures of both of the diastereomers have been established by X-ray crystallography. Isomer I is found to crystallize in the monoclinic system (a=10.146(1) Å, b=9.524(2) Å, c=11.992(1) Å, β=98.938(6) Å, Space Group=$p2_1/a$, Z=4, V=1148.35 Å, D_c=1.2838 gcm^{-3}, reflections measured 2239, observed reflections 1897, refined parameters 180, R=0.0748, R_w=0.0889). Isomer II forms orthorhombic crystals (a=



isomer I



isomer II

Bond distances of Isomer I in Å.

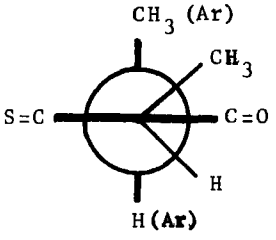
S - C1	1.617(4)	C4 - C5	1.386(4)
C1 - N	1.386(4)	C5 - C6	1.396(5)
C1 - O1	1.339(4)	C6 - C7	1.358(6)
O1 - C2	1.449(5)	C7 - C8	1.382(6)
C2 - C11	1.511(6)	C8 - C9	1.374(6)
C2 - C3	1.501(5)	C9 - C4	1.391(5)
C3 - O2	1.203(5)	C5 - C10	1.486(5)
C3 - N	1.388(5)		
N - C4	1.451(4)		

Bond angles of Isomer I in °.

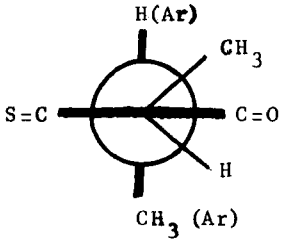
S - C1 - O1	124.1(2)	C3 - N - C1	111.4(3)
S - C1 - N	127.3(3)	N - C4 - C5	118.7(3)
N - C1 - O1	108.6(3)	C4 - C5 - C10	121.6(3)
C1 - O1 - C2	110.8(3)	C4 - C5 - C6	116.3(3)
O1 - C2 - C3	103.8(3)	C10 - C5 - C6	122.1(3)
C11 - C2 - C3	113.2(3)	C5 - C6 - C7	121.6(3)
C2 - C3 - O2	128.5(4)	C6 - C7 - C8	120.9(4)
C2 - C3 - N	105.3(3)	C7 - C8 - C9	119.8(4)
O2 - C3 - N	126.2(3)	C8 - C9 - C4	118.4(3)
C3 - N - C4	123.4(3)	C9 - C4 - C5	122.9(3)
C1 - N - C4	125.2(3)	C9 - C4 - N	118.3(3)

10.491(2) Å, b=12.201(1) Å, c=8.1288(9) Å, Space Group =$Pca2_1$, Z=4, V=1125.767, D_c=1.305 gcm^{-3}, reflections measured 2245, observed reflections 1466, refined parameters 136, R=0.0515, R_w=0.0514. The absolute configuration of II has been established on a 99 %

confidence level.). Figure shows both molecules in similar orientation. From this it is obvious that the molecular geometries of both compounds interconvert by rotation about N-C4 bond. In I as well as in II, atoms O1, C1, N and C3 are exactly planar. The tetrahedral atom C2 is bent by 0.03 Å out of plane of the remaining heterocyclic fragment. Significant differences in the C-S bond (1.664 Å versus 1.617 Å) may be attributed to intermolecular interactions with neighbouring atoms. Intramolecular interactions cause slight differences in the attachment of the planar (±0.02 Å) phenyl rings to the heterocycles. Whereas in I the interplanar angle between both rings is found t o be 87.2°, it is reduced to 78.2° in II. A contact between one of the hydrogen atoms at C10 and the carbonyl oxygen O2 (2.75 Å), which is also reflected in an elongated C-O bond (1.22 Å in II, as compared 1.203 Å in I) may cause this effect.



Isomer I



Isomer II

The ortho methyl group is cisoid to the C2 methyl group in the thermodynamically more stable isomer I and transoid in the less stable isomer II, as seen on the figure and on above projections. An X-ray study, for only one diastereomer of an aryl hydantoin derivative has shown the similar result[4]. The diastereomer of the hydantoin studied was the thermodynamically less stable one and was reported to crystallize first. The better solubility of thioxooxazolidinone isomer II than isomer I,

Crystallographic data for isomer I.

$C_{11}H_{11}NO_2S$
Crystal system - monoclinic
Space Group $P2_1/a$
a = 10.146(1) Å
b = 9.524(2)
c = 11.992(1)
β = 98.938(6) °
V = 1144.835 Å^3
Reflections measured : 2339
Observed Reflections : 1897
Refined Parameters 180
D_c = 1.2838 gcm^{-3}
Z = 4
μ = 23.100
R = 0.0748
R_w = 0.0889

Crystallographic data for Isomer II.

$C_{11}H_{11}NO_2S$
Crystal System - orthorhombic
Space Group $Pca2_1$
a = 10.491(2)
b = 13.201(1)
c = 8.1288(9)
V = 1125.767 $Å^3$
D_c = 1.305 gcm^{-3}
Z = 4
μ = 23.489
Reflections measured : 2245
Observed Reflections : 1466
Refined Parameters : 136
R = 0.0515
R_w = 0.0514

brings ambiguity to the argument that the cisoid conformation is preferred in the thermodynamically more stable isomer because of favored solvation as compared to transoid isomer. The enhanced polar interactions with the solvent are expected in aryl hydantoin diastereomer, where the ortho aryl substituent is bromo, which may cause the change of solubilities of isomers respect to thioxooxazolidinone.

On the other hand, X-ray data of both of the thioxooxazolidinone isomers indicate the evidence to some vary-

Bond distances of Isomer II in Å

S - C1	1.664(7)	N - C4	1.432(5)
C1 - O1	1.312(5)	C4 - C5	1.391(8)
O1 - C2	1.47(1)	C5 - C10	1.514(7)
C2 - C11	1.509(6)	C5 - C6	1.388(7)
C2 - C3	1.494(7)	C6 - C7	1.363(8)
C3 - O2	1.22(1)	C7 - C8	1.392(8)
C3 - N	1.385(7)	C8 - C9	1.363(6)
N - C1	1.374(9)	C9 - C4	1.374(7)

Bond angles of Isomer II in °.

S - C1 - O1	122.6(6)	C1 - N - C4	125.6(5)
S - C1 - N	126.5(3)	N - C4 - C5	119.5(4)
N - C1 - O1	110.9(6)	C4 - C5 - C10	122.4(4)
C1 - O1 - C2	110.2(5)	C4 - C5 - C6	116.9(5)
O1 - C2 - C11	110.6(8)	C10 - C5 - C6	120.7(5)
O1 - C2 - C3	102.5(4)	C5 - C6 - C7	121.7(5)
C11 - C2 - C3	114.0(4)	C6 - C7 - C8	120.0(5)
C2 - C3 - O2	128.3(5)	C7 - C8 - C9	119.7(5)
C2 - C3 - N	106.8(7)	C8 - C9 - C4	119.8(5)
O2 - C3 - N	124.9(4)	C9 - C4 - C5	121.9(4)
C3 - N - C1	109.6(4)	C9 - C4 - N	118.5(4)
C3 - N - C4	124.8(6)		

ing interactions between isomers, that could be related to the relative stabilities of isomers. The lone-pair electrons of nitrogen appear to be conjugated more with the carbonyl and thiocarbonyl groups in transoid isomer II, because the C3-O2 and C1-S bonds are lengthened significantly, from 1.203 Å to 1.22 Å and from 1.617 Å to 1.664 Å, respectively, in this isomer. Probably the favored interaction of the nitrogen lone pair electrons towards aromatic moiety and the lessened conjugation with the neighbouring carbonyl and thiocarbonyl groups may have caused the better stability of cisoid isomer I.

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