

The Crystal and Molecular Structures of Two Reaction Products of Geminal Dicyano Oxirane with Thiohydantoine (Compound I) and Thioxobenzoxazole (Compound II)

Ivan Leban^a, Alenka Majcen Le Marechal,^b and Albert Robert^c

^a Department of Chemistry and Chemical Technology,
University of Ljubljana, POB 537, 61001 Ljubljana, Slovenia

^b Faculty of Technical Sciences, University of Maribor,
62000 Maribor, Slovenia,

^cGroupe de Recherches de Chimie Structurale,
Université de Rennes, 35042 Rennes, France

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The crystal and molecular structures of two reaction products of geminal dicyano oxiranes with thiohydantoine and thioxobenzoxazole have been determined from Mo-K α X-ray diffraction data. The two reaction products were: 2H-2-(*p*-tolyl)-imidazo[1,2-*b*]thiazole-3,6-dione (compound **I**) and Z-3-benzoxazole-3-phenyl-2-oxo-2-propanenitrile (compound **II**) with the following crystal data at 293(1) K: Compound **I**, C₁₂H₁₀N₂O₂S, monoclinic *P*2₁/*c*, *a* = 15.057(3), *b* = 5.200(3), *c* = 14.724(4) Å, β = 104.24(3)°, *Z* = 4; final *R* and *R*_w values were 0.034 and 0.049 for 1647 observed reflexions. Compound **II**, C₁₆H₁₀N₂O₂, monoclinic, *P*2₁/*n*, *a* = 14.396(3), *b* = 4.326(1), *c* = 21.335(4) Å, β = 107.79(1)°, *Z* = 4; final *R* and *R*_w values 0.040 and 0.053 for 1516 observed reflections.

INTRODUCTION

Geminal dicyano oxiranes (*gem*-dicyanoepoxides) normally react with *N*-monosubstituted thioamides to yield mezoionic thiazoles, or with *N,N'*-disubstituted thioamides to yield thiazoles.^{1,2,3,4} In some cases, transposition products are obtained.⁵ In order to elucidate some of the mechanisms of these organic reactions, the crystal structures of the two reaction products of *gem*-dicyanoepoxide with thiohydantoine as well as with 2-thioxobenzoxazole were determined (Sketch). In the case of compound **II**, there was also a keto - enol ambiguity.

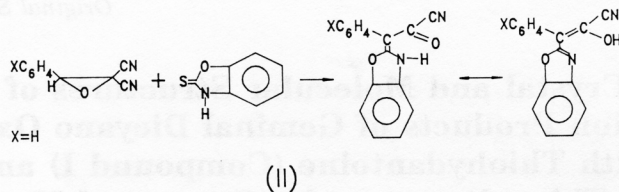
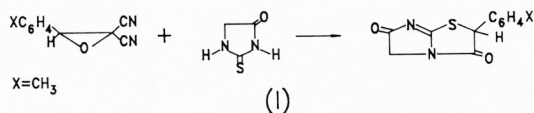


TABLE I

Crystal and Data Collection Summary for Compounds I and II at 293(1) K

	Compound I	Compound II
Molecular Formula	C ₁₂ H ₁₀ N ₂ O ₂ S	C ₁₆ H ₁₀ N ₂ O ₂
Molecular Weight (g mol ⁻¹)	246.3	262.3
Crystal System	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	15.057(3)	14.396(3)
<i>b</i> (Å)	5.200(3)	4.326(1)
<i>c</i> (Å)	14.724(4)	21.335(4)
β (°)	104.23(3)	107.79(1)
Volume (Å ³)	1117.4(8)	1265.1(5)
<i>D</i> _m (flotation (g cm ⁻³))	1.48(5)	1.39(5)
<i>Z</i>	4	4
<i>D</i> _x	1.464	1.377
X-rays (Å)	Mo-K α , λ =0.71069	
Diffractometer	CAD-4, Enraf-Nonius	
Scan method	$\omega/2\theta$	
2θ scan width(°)	0.7 + 0.3tan θ	0.8 + 0.3tan θ
Maximum scan time (s)	60	60
Scan rate (°min ⁻¹) min max	1.10 16.48	1.27 16.48
Aperture (mm)	2.4 + 0.9tan θ	2.4 + 0.9tan θ
Reference reflexions	3	3
Background	1/4 of the scan time at each of the scan limits	
$2\theta_{\max}$ (°)	56	56
Colour of the crystal	pale-yellow	yellow
Shape of the crystal	prismatic	plates
Size of the crystal (mm)	0.35x0.41x0.22	0.42x0.11x0.03
Intensity decrease (%)	-1.06	-0.85
Measured reflexions	6091	7045
Mean discrepancy on <i>I</i> (%)	1.3	1.1
Averaged reflexions	2589	3036
Observed reflexions [<i>I</i> \geq 3 σ (<i>I</i>)]	1647	1516
Unobserved reflexions	942	1520
σ (<i>I</i>) based on	counting statistics	
μ (cm ⁻¹)	2.66	0.86

EXPERIMENTAL

Preparation

Compound **I**: 0.01 mole of epoxide and 0.01 mole of thiohydantoine reacted in the solution of dimethylformamide (40 cm³) for 18 hours at room temperature to produce 2H-2-(*p*-tolyl-imidazo[1,2-*b*]thiazole-3,6-dione). The solution was left to evaporate at room temperature. The crystals were recrystallized from ethanol. Compound **II**: 0.01 mole of epoxide and 0.01 mole of thioxobenzoxazole were heated for 20 hours at the boiling point of benzene (40 cm³) to produce Z-3-benzoxazole-3-phenyl-2-oxo-2-propanenitrile. The crystals were recrystallized from benzene.

X-ray Diffraction Work

Cell dimensions were obtained from the least-squares fit on angular settings of 25 moderately high-order reflexions measured on a CAD-4 Enraf Nonius automated diffractometer with radiation. The space groups were uniquely determined from systematic absences. Full details of the crystal data, data collection and reduction summary are presented in Table I.

Common data corrections for variations in reference reflexions and Lorentz-polarization effects were applied. Absorption correction was negligible. Both structures were solved in a routine way by SHELXS86.⁶ The initial positions of non-hydrogen atoms were refined by full-matrix least squares using SHELX76,⁷ minimizing $\sum w(|F_o| - k|F_c|)^2$, where the weighting function was chosen to keep $\sum w(\Delta F)^2$ uniform over the ranges of $(\sin\theta/\lambda)$ and $|F_o|$. Difference electron-density maps revealed all the hydrogen atoms at expected positions. The calculated positions of hydrogens with a common isotropic thermal displacement parameter were included in the final stages of the refinement. The hydrogen atom involved in the intramolecular hydrogen bond in compound **II** was fully refined. The final conventional *R* and *R_w* factors were: 0.034 and 0.049 for 1647 observed reflexions [$I \geq 3\sigma(I)$] with $w = [\sigma^2(F_o) + 0.0019|F_o|]^{-1}$ for compound **I**, and 0.040 and 0.053 for 1516 observed reflexions [$I \geq 3\sigma(I)$] with $w = 2.45/(\sigma^2(F_o) + 0.0019|F_o|)$, respectively. The final difference Fourier maps showed residual density within +0.15 and -0.10 e.Å⁻³ for compound **I** and within +0.16 and -0.21 e.Å⁻³ for compound **II**. Maximum values of Δ/σ at convergence were 0.07 (for U₃₃ of S(1) in compound **I** and 0.14 (for scale factor) in compound **II**. Scattering factors for S, O, N and C were taken from reference 8, for H from reference 9.

All calculations were performed on the VAX 8550 cluster at the University Computer Centre, Ljubljana. Additionally, the GX package¹⁰ was used for data processing and final interpretation of molecular geometry. Supplementary materials (lists of structure factors, anisotropic thermal displacement parameters, H-atoms coordinates, computer listings) are available on request from the authors.

The final atomic coordinates with equivalent thermal displacement parameters *U_{eq}* for both structures are given in Table II.

RESULTS AND DISCUSSION

Figure 1 shows separate molecules of compound **I** and compound **II** with the corresponding atomic numbering scheme. The appropriate bond distances and angles are given in Table III. Figure 2 shows molecular packings in crystal unit cells.

The main feature of both structure determinations is a rather short, monoclinic *b* crystallographic axis, 5.200(3) Å in compound **I** and an even shorter one, 4.326(1) Å in compound **II**, suggesting a roughly planar shape of the molecules. In both structures, there are pairs of constituent molecules. Whilst in compound **I** molecules are linked across the centre of inversion by polar interactions, in compound **II** two molecules are linked by intermolecular hydrogen bonds.

TABLE II

Fractional Atomic Coordinates for Non-hydrogen Atoms and Equivalent Thermal Displacement Parameters^a (\AA^2) with e.s.d.s in parentheses

Compound I	x	y	z	U_{eq}
S1	0.4117(1)	0.1759(1)	-0.0961(1)	0.034
C2	0.3216(2)	-0.0706(5)	-0.1055(2)	0.034
C3	0.3020(2)	-0.0968(5)	-0.0090(2)	0.036
O3	0.2509(1)	-0.2546(4)	0.0116(1)	0.054
N4	0.3485(1)	0.0882(4)	0.0499(1)	0.034
C5	0.3512(2)	0.1636(5)	0.1457(1)	0.039
C6	0.4124(2)	0.4022(5)	0.1544(1)	0.035
O6	0.4293(1)	0.5475(4)	0.2203(1)	0.046
N7	0.4447(1)	0.4305(4)	0.0729(1)	0.038
C7A	0.4055(1)	0.2503(4)	0.0166(1)	0.030
C8	0.2362(2)	0.0082(4)	-0.1795(1)	0.033
C9	0.2110(2)	-0.1214(5)	-0.2638(2)	0.046
C10	0.1364(2)	-0.0433(7)	-0.3332(2)	0.056
C11	0.0850(2)	0.1670(7)	-0.3202(2)	0.055
C12	0.1098(2)	0.2966(6)	-0.2357(2)	0.062
C13	0.1850(2)	0.2190(6)	-0.1659(2)	0.051
C14	0.0032(2)	0.2620(9)	-0.3965(2)	0.087
Compound II				
N1	0.0522(2)	0.9424(6)	-0.1916(1)	0.072
C1	0.0794(2)	0.7982(6)	-0.1448(1)	0.050
C2	0.1014(2)	0.6180(6)	-0.0826(1)	0.044
O2	0.0314(1)	0.5960(5)	-0.0597(1)	0.058
C3	0.1955(2)	0.4969(5)	-0.0565(1)	0.039
C4	0.2107(1)	0.3220(5)	0.0011(1)	0.038
O5	0.2988(1)	0.1913(4)	0.0323(1)	0.044
C6	0.2869(2)	0.0229(5)	0.0852(1)	0.041
C7	0.3561(2)	-0.1490(6)	0.1302(1)	0.050
C8	0.3240(2)	-0.2947(5)	0.1777(1)	0.055
C9	0.2279(2)	-0.2678(6)	0.1786(1)	0.054
C10	0.1595(2)	-0.0905(6)	0.1328(1)	0.049
C11	0.1923(2)	0.0546(5)	0.0861(1)	0.039
N2	0.1473(1)	0.2479(5)	0.0330(1)	0.041
C12	0.2742(2)	0.5344(5)	-0.0880(1)	0.040
C13	0.3644(2)	0.6557(6)	-0.0537(1)	0.049
C14	0.4360(2)	0.6990(7)	-0.0838(1)	0.059
C15	0.4180(2)	0.6192(6)	-0.1493(1)	0.057
C16	0.3296(2)	0.4910(6)	-0.1837(1)	0.055
C17	0.2583(2)	0.4473(6)	-0.1534(1)	0.048

^a U_{eq} is defined as one third of the trace of the U_{ij} tensor.

Compound I

The results of the crystal structure determination show that the reaction product exists as 2H-2-(*p*-tolyl)-imidazo[1,2-*b*]thiazole-3,6-dione. The fused imidazo and thiazolo rings are nearly coplanar with the dihedral angle of 5.0(5)°. The tolyl ring is twisted with respect to the fused rings about the C2–C8 bond by 89.6(6)°. The largest deviations from planarity in the separate rings are: -0.028(3) Å for C5 in imidazole ring; 0.051(3) Å in thiazole ring and 0.013(4) Å in tolyl entity. The endocyclic torsion angles in the imidazo-thiazole moiety are: S1–C2–C3–N4 7.0(2), C2–C3–N4–C7A -3.0(2),

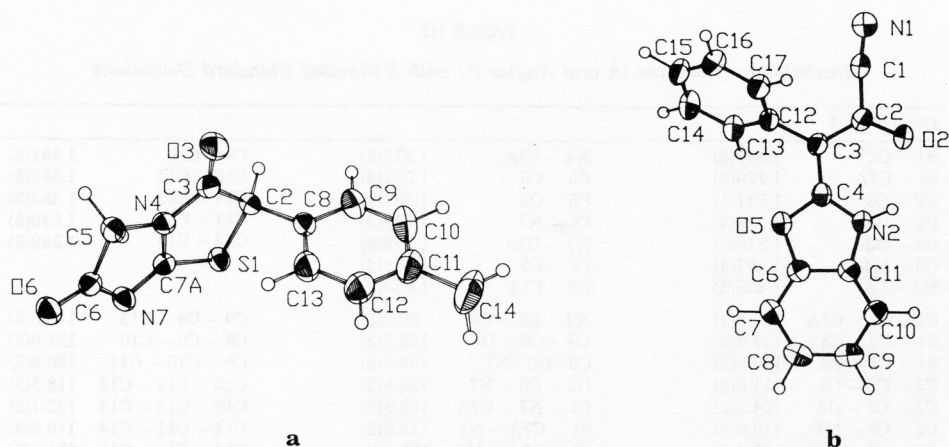


Figure 1. ORTEP¹¹ view of the molecules. The atoms are represented by thermal ellipsoids at 50% probability level. a) Compound I. b) Compound II.

C3–N4–C7A–S1 $-3.0(2)$, N4–C7A–S1–C2 $6.1(2)$, C7A–S1–C2–C3 $-7.3(2)$, N4–C5–C6–N7 $-5.0(2)$, C5–C6–N7–C7A $4.0(2)$, C5–N7–C7A–N4 $-1.2(2)$, N7–C7A–N4–C5 $-2.2(2)$ and C7A–N4–C5–C6 $4.2(2)^\circ$ From the inspection of Table III and after a comparison with the average bond lengths obtained *via* Cambridge Database for organic compounds,¹² it can be observed that bonds C2–C8 $1.523(4)$, C5–C6 $1.532(4)$ and N4–C5 $1.455(3)$ Å are single, whereas the distance $1.293(3)$ Å of N7–C7A bond is typical of a double bond. Distances C3–O3 $1.213(4)$ and C6–O6 $1.207(3)$ Å are common for the carbonyl groups. The length of bond S1–C7A is $1.729(3)$ Å and S1–C2 is $1.847(3)$ Å, the angle C2–S1–C7A being 90.9° The S1–C2 bond is in accordance with the slightly elongated C–S single bonds in the planar system, whereas S1–C7A could be an intermediate between single and double S–C bonds. There are two, rather short, intermolecular contacts between S1 and N7 (at $1-x, -y, -z$) of $2.936(3)$ Å and between S1 and O6 (at $x, 1/2-y, -1/2+z$) of $3.01(3)$ Å. These contacts could be explained by possible canonical forms of the molecule with a positive charge on sulphur atoms.

Compound II

The crystal structure determination revealed that the compound exists as *Z*-3-benzoxazole-3-phenyl-2-oxo-2-propanenitrile; the proposed keto form of the compound. The benzoxazole, 2-oxo-2-propanenitrile and phenyl parts of the molecule are planar. The largest deviations from the above planes are: $-0.015(2)$ Å for C4 of benzoxazole; $-0.005(3)$ Å for C1 of 2-oxo-2-propanenitrile and $-0.013(2)$ Å for C12 of phenyl entity. The corresponding dihedral angle between benzoxazole and 2-oxo-2-propanenitrile is $5.1(6)^\circ$; thus, the molecule as whole is planar to within 0.1 Å. The reason for the planarity is hydrogen bond N2–H \cdots O2 and N2–H \cdots O2($-x, 1-y, -z$) (see Table III for full details). The phenyl group is twisted by $57.1(6)^\circ$ around bond C3–C12 with respect to the plane of benzoxazole moiety. The majority of bond lengths (apart from the bond length C1–N1 $1.140(4)$ Å which is clearly a triple bond) are intermediate between

TABLE III
Interatomic Distances (Å and Angles (°) with Estimated Standard Deviations

Compound I					
S1 - C2	1.847(3)	N4 - C7A	1.376(3)	C9 - C10	1.381(5)
S1 - C7A	1.729(3)	C5 - C6	1.532(4)	C10 - C11	1.380(5)
C2 - C3	1.527(5)	C6 - O6	1.207(3)	C11 - C12	1.383(5)
C2 - C8	1.523(4)	C6 - N7	1.409(3)	C11 - C14	1.530(5)
C3 - O3	1.213(4)	N7 - C7A	1.293(3)	C12 - C13	1.389(5)
C3 - N4	1.367(4)	C8 - C9	1.381(4)		
N4 - C5	1.455(3)	C8 - C13	1.383(4)		
C2 - S1 - C7A	90.9(2)	N4 - C5 - C6	99.9(2)	C9 - C8 - C13	118.5(3)
S1 - C2 - C3	107.4(2)	C5 - C6 - O6	125.3(2)	C8 - C9 - C10	121.0(3)
S1 - C2 - C8	110.0(2)	C5 - C6 - N7	109.9(2)	C9 - C10 - C11	120.8(3)
C3 - C2 - C8	111.6(3)	O6 - C6 - N7	124.8(2)	C10 - C11 - C12	118.3(3)
C2 - C3 - O3	124.9(2)	C6 - N7 - C7A	105.8(2)	C10 - C11 - C14	122.1(3)
C2 - C3 - N4	110.0(3)	S1 - C7A - N4	113.0(2)	C12 - C11 - C14	119.6(3)
O3 - C3 - N4	125.1(3)	S1 - C7A - N7	130.8(2)	C11 - C12 - C13	121.0(3)
C3 - N4 - C5	133.8(2)	N4 - C7A - N7	116.2(2)	C8 - C13 - C12	120.4(3)
C3 - N4 - C7A	118.2(2)	C2 - C8 - C9	120.6(2)		
C5 - N4 - C7A	108.2(2)	C2 - C8 - C13	120.8(2)		
Compound II					
N1 - C1	1.140(4)	O5 - C6	1.397(3)	C12 - C13	1.384(4)
C1 - C2	1.487(4)	C6 - C7	1.372(4)	C12 - C17	1.395(3)
C2 - O2	1.251(4)	C6 - C11	1.375(4)	C13 - C14	1.384(4)
C2 - C3	1.400(4)	C7 - C8	1.387(4)	C14 - C15	1.385(3)
C3 - C4	1.402(3)	C8 - C9	1.394(4)	C15 - C16	1.377(4)
C3 - C12	1.492(4)	C9 - C10	1.387(4)	C16 - C17	1.383(4)
C4 - O5	1.362(3)	C10 - C11	1.377(4)		
C4 - N2	1.334(3)	C11 - N2	1.398(3)		
N1 - C1 - C2	172.1(1)	C4 - O5 - C6	106.6(2)	C10 - C11 - N2	133.0(2)
C1 - C2 - O2	114.3(3)	O5 - C6 - C7	127.3(2)	C4 - N2 - C11	109.7(2)
C1 - C2 - C3	117.9(3)	O5 - C6 - C11	109.0(2)	C3 - C12 - C13	121.4(2)
O2 - C2 - C3	127.8(2)	C7 - C6 - C11	123.7(2)	C3 - C12 - C17	120.4(2)
C2 - C3 - C4	115.1(2)	C6 - C7 - C8	115.1(3)	C13 - C12 - C17	118.2(3)
C2 - C3 - C12	123.8(2)	C7 - C8 - C9	121.7(2)	C12 - C13 - C14	121.2(2)
C4 - C3 - C12	121.1(2)	C8 - C9 - C10	122.0(2)	C13 - C14 - C15	119.9(3)
C3 - C4 - O5	121.7(2)	C9 - C10 - C11	115.8(3)	C14 - C15 - C16	119.7(3)
C3 - C4 - N2	129.0(2)	C6 - C11 - C10	121.6(2)	C15 - C16 - C17	120.2(2)
O5 - C4 - N2	109.3(2)	C6 - C11 - N2	105.3(2)	C12 - C17 - C16	120.8(3)
Intramolecular Hydrogen Bond and Short Contacts					
N2 ... O2	2.636(3)	N2 - H ... O2	121(2)		
C13 ... O5	3.058(3)	C13 - H13 ... O5	96(1)		
C17 ... C1	3.043(4)	C17 - H17 ... C1	94(1)		
Intermolecular Hydrogen Bond and Short Contacts					
N2 ... O2 ⁱ	2.880(2)	N2 - H ... O2 ⁱ	142(1)		
O2 ... O2 ⁱ	3.067(3)	O2 ... H ... O2 ⁱ	96(1)		
C13 ... O5 ⁱⁱ	3.269(3)	C13 - H13 ... O5 ⁱⁱ	122(1)		

Symmetry code: i) $-x, 1-y, -z$ ii) $x, 1+y, z$

double and single bonds, therefore indicating the presence of considerable conjugation in separate parts as well as in the molecules as a whole.¹²

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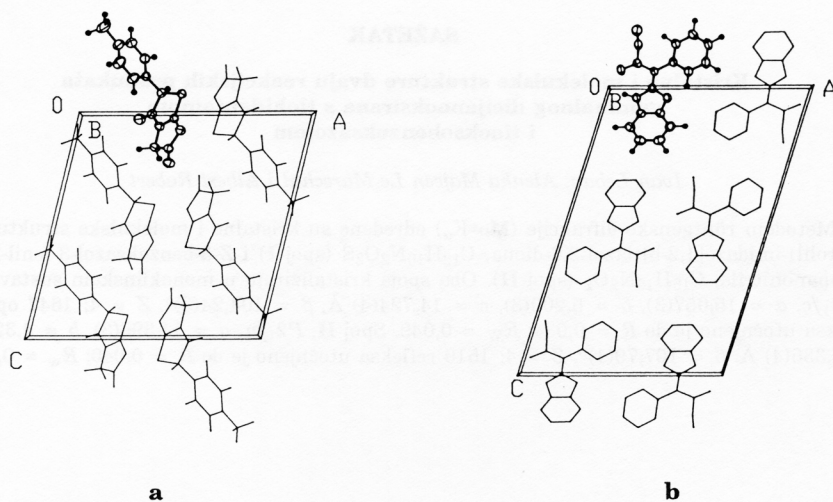


Figure 2. View of the molecular packing along b -axes. a) Compound I. b) Compound II.

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SAŽETAK

Kristalne i molekulske strukture dvaju reakcijskih produkata geminalnog dicijanooksirana s tiohidantoinom i tiooksobenzoksazolom

Ivan Leban, Alenka Majcen Le Marechal i Albert Robert

Metodom röntgenske difrakcije (Mo-K α) određene su kristalne i molekulske strukture 2H-2-(*p*-tolil)-imidazo[1,2-*b*]tiazol-3,6-diona, C₁₂H₁₀N₂O₂S (spoj I) i Z-3-benzoksazol-3-fenil-2-okso-2-propanonitrila, C₁₆H₁₀N₂O₂ (spoj II). Oba spoja kristaliziraju u monoklinskom sustavu. Spoj I; *P*2₁/*c*, *a* = 15,057(3), *b* = 5,200(3), *c* = 14,724(4) Å, β = 104,24(3)°, *Z* = 4; 1647 opaženih refleksa utočnjeno je do *R* = 0,034; *R*_w = 0,049. Spoj II; *P*2₁/*n*, *a* = 14,396(3), *b* = 4,326(1), *c* = 21,335(4) Å, β = 107,79(1)°, *Z* = 4; 1516 refleksa utočnjeno je do *R* = 0,040; *R*_w = 0,053.