

Crystal Structure of 5-Phenyl-2-thioxo-4-imidazolidinone

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The crystal structure of 5-phenyl-2-thioxo-4-imidazolidinone has been determined by X-ray diffraction. The crystal, $C_9H_8N_2OS$, belongs to space group $P\bar{1}$ with cell dimensions of $a=8.971(3)\text{\AA}$, $b=9.651(3)\text{\AA}$, $c=10.497(3)\text{\AA}$, $\alpha=82.39(2)^\circ$, $\beta=80.15(2)^\circ$, $\gamma=79.16(2)^\circ$. The final R value is 0.045 for 2683 reflections ($I > 2.00\sigma(I)$). There are two independent molecules, A and B, in the asymmetric unit. The molecules differ mainly in the orientation of the phenyl ring with respect to the five-membered ring. In crystals, the thioamide groups of molecules A and B form centrosymmetric dimers A-A and B-B via the N-H...S hydrogen bonds. The amide groups of two neighboring molecules, A and B, form pseudo-centrosymmetric dimers A-B through N-H...O hydrogen bonds.

(Received June 25, 2007; Accepted September 3, 2007; Published on web October 25, 2007)

2-Thiohydantoins (2-thioxo-imidazolizin-4-one), 2-thioxo analogs of hydantoins (imidazolidine-2,4-diones), form a wide range of biologically active compounds.^{1,2} These compounds are considered as useful intermediates in peptide synthesis and the structure determination of polypeptides.³ Since the biological activities and physicochemical properties of the compounds are closely related to the electronic structure, conformation and intermolecular interactions, experimental data pertaining to these features are therefore very important. However, there have been few reports on the molecular and crystal structures of 2-thiohydantoins, compared to hydantoins.⁴ In this paper, we report on the crystal structure of 5-phenyl-2-thiohydantoin (5-phenyl-2-thioxo-4-imidazolidinone) (I, see Figs. 1 and 2), in order to clarify the crystal and molecular characteristics of 5-substituted 2-thiohydantoin.

Compound I was prepared from L-phenylglycine and ammonium thiocyanate using the conventional thiocyanate method.⁵ The crude product was washed with cold water several times and purified by repeated crystallization from ethanol: Yield: 53%; m.p. 230–235°C; Found: C, 56.15; H, 4.14; N, 14.65% Calcd for $C_9H_8N_2OS$: C, 56.23; H, 4.19; N, 14.57%; ¹H NMR (400 MHz, DMSO- d_6): δ 5.38 (s, 1H, -CH-), 7.26–7.45 (m, 5H, -C₆H₅), 10.47 (s, 1H, -NH-), 11.83 (s, 1H, -NH-).

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution at room temperature. Table 1 gives the crystal and experimental data. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods, and all hydrogen atoms were refined

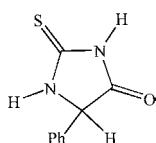


Fig. 1 Structural formula of the title compound.

isotropically. The final fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 2. Selected bond distances, bond angles and torsion angles are listed in Table 3.

Compound I is crystallized in the triclinic form with four molecules in a unit cell. As shown in Fig. 2, there are two independent molecules (A and B) in a unit cell. The structures of molecules A and B are very similar to each other, except for the orientation of the phenyl ring with respect to the five-membered ring. The torsion angles, C(2)–C(3)–C(4)–C(5), are 105.3(2) and 151.4(2)°, respectively, for molecules A and B. The C(1)–S(1) bond distances, 1.667(2) and 1.668(2) Å for molecules A and B, are intermediate between those of a C–S single bond (1.82 Å) and a C=S double bond (1.56 Å), and the C(2)–O(1) bond distances, 1.215(3) and 1.215(2) Å, are between those of a C–O single bond (1.426 Å) and a C=O double bond (1.215 Å). Likewise, the thioamide C(1)–N(2) bond distances, 1.337(3) and 1.330(3) Å, and the amide C(2)–N(1) bond distances, 1.373(3) and 1.366(3) Å, are between those of a C–N single bond (1.47 Å) and a C=N double bond (1.27 Å).⁶ These thioamide and amide bond distances suggest extensive electron delocalization in the whole molecule.

As shown in Fig. 3, the thioamide groups of molecules A and B form centrosymmetric dimers, A–A and B–B, through N–H...S hydrogen bonds. The amide groups of two neighboring

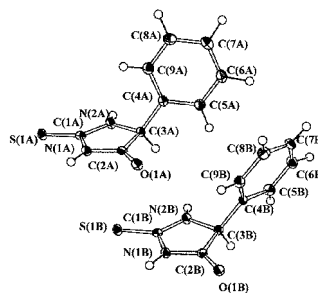


Fig. 2 Molecular structure of the title compound along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level. H atoms are indicated by small circles.

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Table 1 Crystal and experimental data

Formula: C ₉ H ₈ N ₂ OS	
Formula weight: 192.24	
Crystal system: triclinic	
$a = 8.971(3)\text{Å}$	$\alpha = 82.39(2)^\circ$
$b = 9.651(3)\text{Å}$	$\beta = 80.15(2)^\circ$
$c = 10.497(3)\text{Å}$	$\gamma = 79.16(2)^\circ$
$V = 874.7(5)\text{Å}^3$	
Space group: $P\bar{1}$	$Z = 4$
$D_{\text{calc}} = 1.460\text{ g/cm}^3$	
$F(0\ 0\ 0) = 400.00$	
$\mu(\text{Mo } K\alpha) = 3.26\text{ cm}^{-1}$	
$T = 123\text{ K}$	
$2\theta_{\text{max}} = 55.0^\circ$ with Mo $K\alpha$ (0.7107 Å)	
No. observations = 2683 ($I > 2.00\sigma(I)$)	
No. variables = 299	
$R = 0.045$	
Goodness-of-fit = 1.30	
$(\Delta/\sigma)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 0.30\text{ e/Å}^3$	
$(\Delta\rho)_{\text{min}} = -0.22\text{ e/Å}^3$	
Diffractometer: Rigaku/MSC Mercury CCD	
Program system: teXsan	
Structure determination: direct method (SIR88)	
Refinement: full-matrix least-squares	
CCDC: 662296	

Table 2 Fractional atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms

	x	y	z	$B_{\text{eq}}/\text{Å}^2$
molecule A				
S(1A)	0.81579(6)	1.02826(5)	-0.12565(5)	1.26(1)
O(1A)	0.5642(2)	0.6546(2)	0.1560(1)	1.33(3)
N(1A)	0.6524(2)	0.8393(2)	0.0180(2)	1.10(3)
N(2A)	0.8648(2)	0.8500(2)	0.0908(2)	1.11(4)
C(1A)	0.7802(2)	0.9049(2)	-0.0027(2)	1.04(4)
C(2A)	0.6569(2)	0.7338(2)	0.1195(2)	1.00(4)
C(3A)	0.8041(2)	0.7339(2)	0.1752(2)	0.99(4)
C(4A)	0.7785(2)	0.7496(2)	0.3184(2)	1.01(4)
C(5A)	0.8186(2)	0.6307(2)	0.4054(2)	1.37(4)
C(6A)	0.7923(3)	0.6431(2)	0.5379(2)	1.63(4)
C(7A)	0.7292(3)	0.7722(2)	0.5843(2)	1.50(5)
C(8A)	0.6902(3)	0.8913(2)	0.4976(2)	1.54(4)
C(9A)	0.7138(2)	0.8792(2)	0.3654(2)	1.37(4)
molecule B				
S(1B)	0.81514(6)	0.53451(5)	-0.12489(5)	1.26(1)
O(1B)	0.5664(2)	0.1551(1)	0.1491(1)	1.23(3)
N(1B)	0.6548(2)	0.3407(2)	0.0132(2)	1.09(3)
N(2B)	0.8598(2)	0.3577(2)	0.0925(2)	1.12(4)
C(1B)	0.7787(2)	0.4100(2)	-0.0031(2)	1.01(4)
C(2B)	0.6576(2)	0.2361(2)	0.1146(2)	1.00(4)
C(3B)	0.8006(2)	0.2385(2)	0.1741(2)	0.99(4)
C(4B)	0.7746(2)	0.2509(2)	0.3193(2)	0.98(4)
C(5B)	0.8927(2)	0.1923(2)	0.3905(2)	1.36(4)
C(6B)	0.8726(3)	0.2025(2)	0.5231(2)	1.62(4)
C(7B)	0.7338(3)	0.2686(2)	0.5848(2)	1.56(5)
C(8B)	0.6152(3)	0.3271(2)	0.5145(2)	1.57(4)
C(9B)	0.6362(2)	0.3190(2)	0.3813(2)	1.32(4)

$$B_{\text{eq}} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha).$$

molecules A and B form a pseudo-centrosymmetric dimer, A-B, through the N-H...O hydrogen bonds [N(2A)...S(1A)⁽ⁱ⁾ 3.386(2) Å, N(2A)-H...S(1A)⁽ⁱ⁾ 171(2)°, N(1A)...O(1B)⁽ⁱⁱ⁾ 2.836(2) Å, N(1A)-H...O(1B)⁽ⁱⁱ⁾ 170(3)°, N(1B)...O(1A)⁽ⁱⁱⁱ⁾ 2.856(2) Å, N(1B)-H...O(1A)⁽ⁱⁱⁱ⁾ 166(3)°, N(2B)...S(1B)⁽ⁱⁱⁱ⁾ 3.358(2) Å, N(2B)-H...S(1B)⁽ⁱⁱⁱ⁾ 174(2)° [symmetry code: (i) $-x + 2, -y + 2, -z$, (ii) $-x + 1, -y + 1, -z$, (iii) $-x + 2, -y + 1, -z$].

Acknowledgements

The authors thank Mrs. M. Arai of Kanazawa University for

Table 3 Selected bond lengths (Å), bond angles (°) and torsion angles (°)

Atom	Atom	Atom	Atom	molecule A	molecule B
S(1)	C(1)			1.667(2)	1.668(2)
O(1)	C(2)			1.215(3)	1.215(2)
N(1)	C(1)			1.384(3)	1.377(3)
N(1)	C(2)			1.373(3)	1.366(3)
N(2)	C(1)			1.337(3)	1.330(3)
N(2)	C(3)			1.462(3)	1.467(3)
C(2)	C(3)			1.533(3)	1.525(3)
C(3)	C(4)			1.505(3)	1.519(3)
C(4)	C(5)			1.400(3)	1.392(3)
C(4)	C(9)			1.391(3)	1.388(3)
C(5)	C(6)			1.388(3)	1.387(3)
C(6)	C(7)			1.382(3)	1.382(3)
C(7)	C(8)			1.397(3)	1.389(3)
C(8)	C(9)			1.385(3)	1.389(3)
C(1)	N(1)	C(2)		112.2(2)	112.4(2)
C(1)	N(2)	C(3)		112.9(2)	112.7(2)
S(1)	C(1)	N(1)		123.9(1)	124.0(1)
S(1)	C(1)	N(2)		128.5(2)	128.3(2)
N(1)	C(1)	N(2)		107.6(2)	107.6(2)
O(1)	C(2)	N(1)		126.7(2)	127.0(2)
O(1)	C(2)	C(3)		127.0(2)	126.6(2)
N(1)	C(2)	C(3)		106.3(2)	106.3(2)
N(2)	C(3)	C(2)		100.8(2)	100.6(2)
N(2)	C(3)	C(4)		115.3(2)	114.9(2)
C(2)	C(3)	C(4)		114.1(2)	115.7(2)
S(1)	C(1)	N(1)	C(2)	175.0(2)	175.3(2)
S(1)	C(1)	N(2)	C(3)	-174.5(2)	-173.9(2)
O(1)	C(2)	N(1)	C(1)	-176.6(2)	-177.6(2)
O(1)	C(2)	C(3)	N(2)	179.4(2)	-179.6(2)
O(1)	C(2)	C(3)	C(4)	-56.5(3)	-55.0(3)
N(1)	C(1)	N(2)	C(3)	4.8(2)	5.1(2)
N(1)	C(2)	C(3)	N(2)	0.7(2)	1.8(2)
N(1)	C(2)	C(3)	C(4)	124.8(2)	126.4(2)
N(2)	C(1)	N(1)	C(2)	-4.3(2)	-3.8(2)
N(2)	C(3)	C(4)	C(5)	-138.7(2)	-91.8(2)
N(2)	C(3)	C(4)	C(9)	42.3(3)	88.2(2)
C(1)	N(1)	C(2)	C(3)	2.1(2)	1.0(2)
C(1)	N(2)	C(3)	C(2)	-3.4(2)	-4.3(2)
C(1)	N(2)	C(3)	C(4)	-126.7(2)	-129.4(2)
C(2)	C(3)	C(4)	C(5)	105.3(2)	151.4(2)
C(2)	C(3)	C(4)	C(9)	-73.7(3)	-28.6(3)

Estimated standard deviations in the least significant figure are given in parentheses.

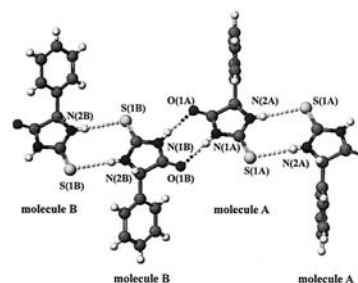


Fig. 3 Perspective views of intermolecular hydrogen bonds.

technical assistances.

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