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X-ray Structure Analysis Online

Crystal Structure of 4,4′-Diphenyl-2,2′-dithioxo-[4,4′-biimidazolidine]-5,5′-dione Bis(dimethylsulfoxide) Solvate

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The crystal structure of the 1:2 dimethylsulfoxide solvate of 4,4′-diphenyl-2,2′-dithioxo-[4,4′-biimidazolidine]-5,5′-dione (I) has been determined by X-ray diffraction. The crystal belongs to space group *C*2/*c* with cell dimensions of *a*=23.81(1)Å, *b*=9.884(5)Å, *c*=12.536(8)Å, *β*=117.38(1)°. The compound, $C_{18}H_{14}N_4O_2S_2{\cdot}2C_2H_6OS$, crystallizes with half a molecule in the asymmetric unit, the molecule being centrosymmetric. The centre of inversion lies on the middle of the C(3)–C(3)′ bond. In crystals, the molecules form two N–H···O cyclic hydrogen bonds in a cyclic $R_2^2(12)$ arrangement, each of which forms on either side. DMSO molecules are hydrogen-bonded to the amide N–H groups. This hydrogen bond network forms an infinite tape structure along the *c*-axis.

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5-Substituted hydantoins and 2-thiohydantoins are known to display significant biological activities, some of which are employed as established drugs, fungicides or herbicides.[1,2] In addition to their biological properties, this class of compounds is also useful for the determination of a C-terminal amino acid in peptide analysis.[3,4] 5-Phenyl derivatives of hydantoin and 2-thiohydantoin were reported to form a dimer, named "diphenylhydantil", by bromine oxidation or air exposure of an alkaline solution.[5] There was, however, some controversies over characterization of the compound.[6] In the course of preparing 5-phenyl-2-thiohydantoin (PTH), we found that it was oxidized to form a dimer in aqueous solution, and the yield of the dimer was dependent on the O_2 concentration. In this work, we undertook X-ray analysis in order to clarify the crystal and molecular characteristics of the PTH dimer (I, see Figs. 1 and 2).

PTH was prepared from L-phenylglycine according to a reported procedure.[7] A solution of PTH (77 mg, 0.4 mmol) in 2

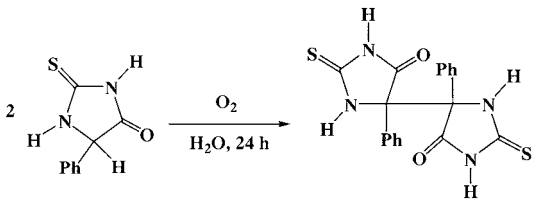

Fig. 1 Preparation scheme of the title compound.

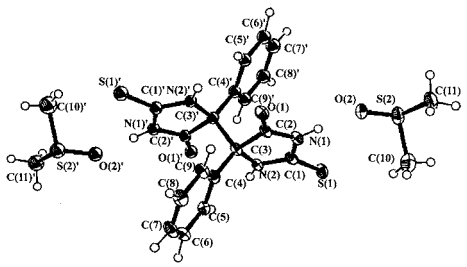

Fig. 2 Molecular structure of the title compound along with the labeling atoms. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level. H atoms are indicated by small circles.

Table 1 Crystal and experimental data

Formula: $C_{18}H_{14}N_4O_2S_2{\cdot}2C_2H_6OS$	
Formula weight: 538.75	
Crystal system: monoclinic	
a = 23.81(1)Å	
b = 9.884(5)Å	β = 117.38(1)°
c = 12.536(8)Å	
V = 2619(2)Å^3	
Space group: C 2/c	Z = 4
D_{calc} = 1.366 g/cm^3	
F(0 0 0) = 1128.0	
μ(Mo K_α) = 3.98 cm^{-1}	
T = 123 K	
$2\theta_{max}$ = 55.0° with Mo K_α (0.7107 Å)	
No. observations = 1816 ($I > 2.00\sigma(I)$)	
No. variables = 206	
R = 0.068	
Goodness-of-fit = 1.07	
$(\Delta/\sigma)_{max}$ = 0.000	
$(\Delta\rho)_{max}$ = 0.73 e/Å^3	
$(\Delta\rho)_{min}$ = –0.52 e/Å^3	
Diffractometer: Rigaku/MSC Mercury CCD	
Program system: teXsan	
Structure determination: direct method (SIR88)	
Refinement: full-matrix least-squares	
CCDC: 662297	

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

	x	y	z	B_{eq}/Å^2
S(1)	0.14545(5)	0.24959(9)	0.27463(8)	2.22(2)
S(2)	0.21664(5)	0.0510(1)	0.0593(1)	2.66(2)
O(1)	0.0600(1)	0.4549(3)	-0.1313(2)	1.90(5)
O(2)	0.1726(1)	0.1636(3)	-0.0121(3)	2.34(6)
N(1)	0.1060(2)	0.3423(3)	0.0489(3)	1.70(6)
N(2)	0.0654(1)	0.4490(3)	0.1508(3)	1.51(6)
C(1)	0.1046(2)	0.3484(4)	0.1587(3)	1.75(7)
C(2)	0.0682(2)	0.4375(3)	-0.0301(3)	1.59(6)
C(3)	0.0371(2)	0.5163(3)	0.0350(3)	1.63(7)
C(4)	0.0508(2)	0.6685(4)	0.0446(3)	1.76(7)
C(5)	0.0619(2)	0.7386(4)	0.1497(3)	1.90(7)
C(6)	0.0743(2)	0.8755(4)	0.1585(4)	2.29(8)
C(7)	0.0745(2)	0.9452(4)	0.0631(4)	2.58(9)
C(8)	0.0635(2)	0.8776(4)	-0.0412(4)	2.39(8)
C(9)	0.0512(2)	0.7394(4)	-0.0517(3)	1.97(7)
C(10)	0.2802(3)	0.1286(6)	0.1845(5)	3.6(1)
C(11)	0.2586(2)	0.0085(5)	-0.0232(5)	3.03(10)

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

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

Atom	Atom	Atom	Atom	Atom
S(1)	C(1)			1.648(4)
S(2)	O(2)			1.508(3)
S(2)	C(10)			1.777(6)
S(2)	C(11)			1.788(5)
O(1)	C(2)			1.204(4)
N(1)	C(1)			1.393(4)
N(1)	C(2)			1.363(5)
N(2)	C(1)			1.335(5)
N(2)	C(3)			1.450(5)
C(2)	C(3)			1.542(4)
C(3)	C(3)'			1.601(7)
C(3)	C(4)			1.522(5)
C(1)	N(1)	C(2)		112.3(3)
C(1)	N(2)	C(3)		113.8(3)
S(1)	C(1)	N(1)		125.0(3)
S(1)	C(1)	N(2)		128.0(3)
N(1)	C(1)	N(2)		107.0(3)
O(1)	C(2)	N(1)		126.6(3)
O(1)	C(2)	C(3)		127.0(3)
N(1)	C(2)	C(3)		106.3(2)
N(2)	C(3)	C(2)		100.5(3)
N(2)	C(3)	C(3)'		110.2(3)
N(2)	C(3)	C(4)		112.7(3)
C(2)	C(3)	C(3)'		106.5(3)
C(2)	C(3)	C(4)		113.5(3)
C(3)'	C(3)	C(4)		112.5(4)
S(1)	C(1)	N(1)	C(2)	-179.1(3)
S(1)	C(1)	N(2)	C(3)	179.8(3)
O(1)	C(2)	N(1)	C(1)	-179.6(3)
O(1)	C(2)	C(3)	N(2)	180.0(3)
O(1)	C(2)	C(3)	C(4)	-59.4(5)
N(1)	C(1)	N(2)	C(3)	0.9(4)
N(1)	C(2)	C(3)	N(2)	1.0(3)
N(1)	C(2)	C(3)	C(4)	121.7(3)
N(2)	C(1)	N(1)	C(2)	-0.1(4)
N(2)	C(3)	C(4)	C(5)	-27.7(5)
C(1)	N(1)	C(2)	C(3)	-0.6(4)
C(1)	N(2)	C(3)	C(2)	-1.2(4)
C(1)	N(2)	C(3)	C(4)	-122.4(3)
C(2)	C(3)	C(4)	C(5)	-141.2(3)

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

ml acetone was added to 1000 ml of water. The solution was bubbled with 100% O_2 gas for 30 min. The container was sealed and left standing overnight at room temperature. Compound I was precipitated out as needles: Yield: 82%; ^{1}H NMR (400 MHz, DMSO-d_6):δ7.27 – 7.54 (m, 5H, –C_6H_5), 11.05 (s, 1H, –NH–), 12.02 (s, 1H, –NH–); Found: C, 56.06; H, 3.76; N, 14.39%. Calcd for $C_{18}H_{14}N_4O_2S_2$: C, 56.53; H, 3.69; N, 14.65%.

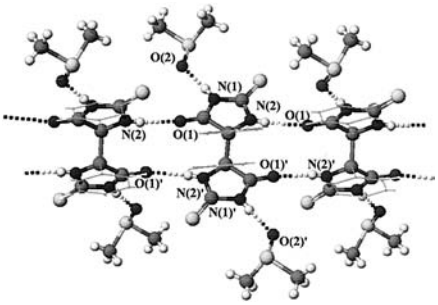

Fig. 3 Perspective views of intermolecular hydrogen bonds in the crystals of compound I. For clarity, two phenyl groups of the molecule are depicted by a wire model.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an aqueous DMSO 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 isotropically. The final fractional atomic coordinates and the 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 monoclinic form with four molecules in a unit cell. The crystal contains two solvent (DMSO) molecules per dimer molecule. There is half a molecule in the asymmetric unit and the molecule is centrosymmetric, as shown in Fig. 2. The center of inversion lies at the middle of the C(3)-C(3)′ bond. The overall molecular geometries and conformation of the 2-thiohydantoin ring are comparable to those of 2-thiohydantoin.[8] In crystals, the molecules form two N–H···O cyclic hydrogen bonds in a cyclic $R_2^2(12)$ arrangement, each of which forms on either side (N(2)–H(2)···O(1)[x,1 – y,1/2 + z]; N···O 2.950(4)Å, N–H···O 174(5)°). DMSO molecules are hydrogen-bonded to the amide N–H groups (N(1)–H(1)···O(2); N···O 2.708(5)Å, N–H···O 169(4)°). This hydrogen-bond network forms an infinite tape structure along the c-axis.

Acknowledgements

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