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5-[(1,3-Dimethyl-5-oxo-2-sulfanylideneimidazolidin-4-ylidene)amino]-2-methylisoindoline-1,3-dione

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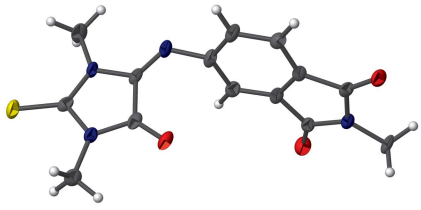
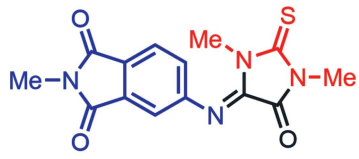
Structural data: full structural data are available from iucrdata.iucr.org

The title *N*,*N*-dimethylthiohydantoin containing an *N*-methylated pthalimide group, $C_{14}H_{12}N_4O_3S$, arose from an unexpected reaction in a deep eutectic dimethylthiourea–tartaric acid solvent system. The mean planes of the ring systems are twisted at an angle of 73.84 (17)°. In the crystal, weak C—H···O hydrogen bonds connect the molecules.

3D view



Chemical scheme



Structure description

Thiohydantoins are effective in treating various biological disorders (Spicer *et al.*, 2013; Wang *et al.*, 2021; Huang *et al.*, 2018; Manzanaro *et al.*, 2006). In an attempt to synthesize 5-amino-substituted hydantoins and thiohydantoins (Kotha *et al.*, 2019), we unexpectedly obtained the title imino-substituted thiohydantoin **1**.

The ^{1}H NMR spectrum confirmed the absence of two H atoms (CH—NH grouping) and the ^{13}C spectrum showed the downfield shift for the carbon atom of the C—N bond. To establish its structure unambiguously, the crystal structure was determined, which confirmed the presence of the C10═N3 double bond [1.252 (4) Å] (Fig. 1). The remaining geometrical parameters are comparable with those of a 5-aniline-substituted thiohydantoin reported by our group (Kotha *et al.*, 2019; Cambridge Structural Database refcode FOWGOQ).

The molecular structure of **1** has an angular shape and the mean planes defined by the C10–C12/N1/N2 imidazole ring and C1–C9/N4 pthalimide ring system subtend a dihedral angle of 73.84 (17)°. The bond angle of the C8—N3—C10 linker , which connects the thiohydantoin ring with the *N*-phenyl substituent is 120.6 (3)°, some 4° less than the corresponding angle in FOWGOQ (Fig. 2).

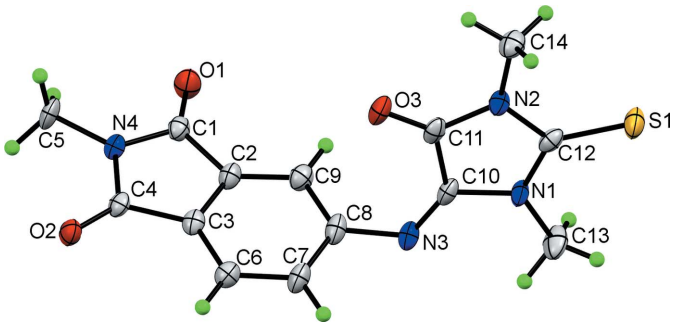


Figure 1
The molecular structure of **1**, showing 50% displacement ellipsoids.

The N1 and N2 nitrogen atoms in the imidazole ring are protected by methyl groups, which rules out the possibility of classical hydrogen bonding in the packing (Fig. 2), but several weak C—H···O links occur (Table 1).

Synthesis and crystallization

Initially, a deep eutectic mixture was obtained by mixing dimethylthiourea and L-tartaric acid (DMTU:L-(+)TA) in 70:30 ratio at 80°C. After obtaining the melt, aniline 2 (100 mg, 0.57 mmol) and ethylglyoxalate 3 (0.12 ml, 1.14 mmol) were added and the mixture was stirred at the same temperature for 6 h. After completion of the reaction (TLC monitoring), the product was concentrated and purified by silica-gel column chromatography using petroleum ether and ethyl acetate as the eluent to afford the title compound **1** (Fig. 3). Yellow plates were recrystallized from chloroform solution (Kotha *et al.*, 2019).

Yield 108 mg, 60%, m.p. 268–270°C, R_f = 0.76 (60% EtOAc–petroleum ether), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (*d*, *J* = 7.5 Hz, 1H), 7.38 (*d*, *J* = 2.0 Hz, 1H), 7.20 (*dd*, *J* = 8.0, 1.5 Hz, 1H), 3.42 (*s*, 3H), 3.15 (*s*, 3H), 3.03 (*s*, 3H) p.p.m., ^{13}C NMR (125 MHz, CDCl3) δ 180.7, 168.3, 168.3, 154.3, 151.9, 141.4, 133.7, 128.3, 125.3, 124.1, 115.3, 29.6, 28.1, 24.2 p.p.m., HRMS (ESI) calculated for $C_{14}H_{12}N_4NaO_3S$ [*M* + Na] 339.0522, found 339.0526, IR (neat) 3376, 3028, 1767, 1749, 1738, 1712, 1615, 1405, 1383 cm^{-1}.

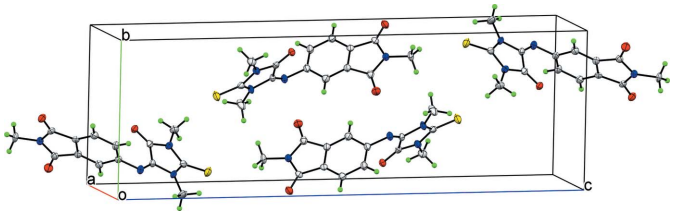


Figure 2
The crystal packing of **1**, viewed along the *a*-axis direction.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*C*···O2^{i}	0.98	2.60	3.519 (5)	157
C7—H7···O3^{ii}	0.95	2.37	3.302 (4)	166
C9—H9···O1^{iii}	0.95	2.47	3.319 (4)	149
C14—H14*B*···O2^{iv}	0.98	2.32	3.272 (5)	164

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{12}N_4O_3S$
M_r	316.34
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, *b*, *c* (Å)	5.4887 (9), 9.2470 (12), 27.457 (2)
β (°)	94.75 (1)
V (Å^3)	1388.7 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.25
Crystal size (mm)	0.31 × 0.27 × 0.22
Data collection	
Diffractometer	Rigaku Oxford Diffraction Saturn724+
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.340, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8048, 2343, 1624
R_{int}	0.105
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.061, 0.153, 1.04
No. of reflections	2343
No. of parameters	202
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, −0.35

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

We thank Darshan S Mhatre for his help in collecting the X-ray data and the structure refinement.

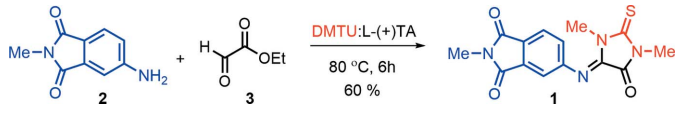


Figure 3
Synthesis scheme for **1**

Funding information

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full crystallographic data

IUCrData (2021). **6**, x210322 [https://doi.org/10.1107/S2414314621003229]

5-[(1,3-Dimethyl-5-oxo-2-sulfanylideneimidazolidin-4-ylidene)amino]-2-methylisoindoline-1,3-dione

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5-[(1,3-Dimethyl-5-oxo-2-sulfanylideneimidazolidin-4-ylidene)amino]-2-methylisoindoline-1,3-dione

Crystal data

$C_{14}H_{12}N_4O_3S$
M_r = 316.34
Monoclinic, $P2_1/n$
a = 5.4887 (9) Å
b = 9.2470 (12) Å
c = 27.457 (2) Å
β = 94.75 (1)°
V = 1388.7 (3) Å^3
Z = 4
$F(000)$ = 656
D_x = 1.513 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2419 reflections
θ = 2.3–31.0°
μ = 0.25 mm^{-1}
T = 150 K
Plate, yellow
0.31 × 0.27 × 0.22 mm

Data collection

Rigaku Oxford Diffraction Saturn724+ diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 28.5714 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysalisPro; Rigaku OD, 2015)
T_{min} = 0.340, T_{max} = 1.000
8048 measured reflections
2343 independent reflections
1624 reflections with $I > 2\sigma(I)$
R_{int} = 0.105
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −6→6
k = −9→10
l = −32→32

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.153
S = 1.04
2343 reflections
202 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.3068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.6276 (2)	0.57457 (11)	0.24925 (3)	0.0309 (3)
O3	0.5648 (5)	0.8470 (2)	0.40427 (8)	0.0257 (7)
O2	0.9716 (5)	0.9678 (3)	0.63093 (8)	0.0257 (7)
O1	0.4516 (5)	0.6022 (3)	0.57964 (8)	0.0316 (7)
N4	0.6704 (5)	0.7946 (3)	0.61393 (9)	0.0209 (7)
N2	0.5470 (6)	0.7361 (3)	0.32835 (9)	0.0221 (7)
N1	0.8657 (6)	0.5885 (3)	0.33889 (9)	0.0220 (7)
N3	1.0073 (6)	0.6355 (3)	0.41971 (9)	0.0248 (8)
C4	0.8759 (7)	0.8769 (4)	0.60409 (11)	0.0207 (9)
C3	0.9437 (7)	0.8266 (4)	0.55580 (11)	0.0203 (9)
C2	0.7823 (7)	0.7184 (4)	0.53916 (11)	0.0227 (9)
C10	0.8555 (7)	0.6584 (4)	0.38396 (11)	0.0213 (9)
C1	0.6097 (7)	0.6926 (4)	0.57754 (11)	0.0216 (9)
C12	0.6818 (7)	0.6322 (4)	0.30574 (11)	0.0214 (9)
C11	0.6395 (7)	0.7596 (4)	0.37603 (11)	0.0221 (9)
C8	0.9789 (7)	0.7009 (4)	0.46559 (11)	0.0250 (9)
C5	0.5476 (7)	0.8074 (4)	0.65885 (11)	0.0289 (10)
H5A	0.664931	0.840036	0.685427	0.043*
H5B	0.481137	0.713115	0.667237	0.043*
H5C	0.414137	0.877738	0.654078	0.043*
C7	1.1494 (7)	0.8039 (4)	0.48344 (11)	0.0268 (10)
H7	1.279648	0.829387	0.464394	0.032*
C9	0.7927 (7)	0.6529 (4)	0.49413 (11)	0.0247 (9)
H9	0.680360	0.579570	0.483004	0.030*
C6	1.1326 (7)	0.8698 (4)	0.52850 (11)	0.0238 (9)
H6	1.246289	0.941822	0.540186	0.029*
C14	0.3422 (7)	0.8152 (4)	0.30389 (12)	0.0284 (10)
H14A	0.403902	0.886751	0.281610	0.043*
H14B	0.251819	0.864661	0.328326	0.043*
H14C	0.233247	0.747504	0.285278	0.043*
C13	1.0409 (8)	0.4761 (4)	0.33055 (13)	0.0360 (11)
H13A	1.175975	0.479863	0.356201	0.054*
H13B	1.104667	0.490714	0.298611	0.054*
H13C	0.960755	0.381459	0.331176	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0393 (8)	0.0339 (7)	0.0201 (5)	0.0062 (5)	0.0060 (4)	−0.0072 (4)
O3	0.0335 (18)	0.0206 (15)	0.0247 (12)	0.0004 (12)	0.0136 (12)	−0.0036 (11)
O2	0.0278 (17)	0.0253 (15)	0.0248 (12)	−0.0008 (12)	0.0064 (11)	−0.0070 (11)
O1	0.0362 (19)	0.0289 (16)	0.0305 (13)	−0.0074 (14)	0.0077 (13)	−0.0029 (12)
N4	0.024 (2)	0.0215 (17)	0.0180 (13)	0.0009 (14)	0.0059 (13)	−0.0003 (12)
N2	0.025 (2)	0.0213 (17)	0.0200 (14)	0.0033 (14)	0.0048 (13)	−0.0030 (13)
N1	0.028 (2)	0.0238 (18)	0.0148 (13)	0.0072 (14)	0.0045 (14)	−0.0038 (12)

N3	0.032 (2)	0.0265 (19)	0.0169 (14)	0.0020 (15)	0.0070 (15)	−0.0017 (13)
C4	0.024 (2)	0.017 (2)	0.0221 (17)	0.0047 (16)	0.0056 (17)	−0.0017 (16)
C3	0.026 (2)	0.016 (2)	0.0191 (16)	0.0056 (16)	0.0027 (16)	0.0020 (14)
C2	0.028 (3)	0.022 (2)	0.0189 (16)	0.0036 (17)	0.0056 (16)	0.0011 (15)
C10	0.027 (2)	0.019 (2)	0.0197 (17)	0.0010 (17)	0.0116 (17)	−0.0003 (15)
C1	0.024 (2)	0.023 (2)	0.0182 (16)	0.0041 (18)	0.0024 (16)	0.0017 (15)
C12	0.023 (2)	0.017 (2)	0.0257 (17)	0.0012 (16)	0.0101 (17)	0.0025 (15)
C11	0.026 (2)	0.019 (2)	0.0225 (16)	−0.0058 (16)	0.0115 (16)	−0.0010 (15)
C8	0.037 (3)	0.021 (2)	0.0177 (16)	0.0078 (18)	0.0074 (17)	0.0006 (15)
C5	0.037 (3)	0.032 (2)	0.0193 (16)	0.0032 (19)	0.0157 (17)	−0.0030 (16)
C7	0.035 (3)	0.026 (2)	0.0208 (17)	0.0046 (19)	0.0112 (17)	0.0000 (16)
C9	0.027 (3)	0.024 (2)	0.0228 (17)	0.0017 (17)	0.0048 (17)	0.0029 (15)
C6	0.026 (3)	0.021 (2)	0.0243 (17)	0.0019 (17)	0.0055 (17)	0.0022 (15)
C14	0.031 (3)	0.026 (2)	0.0290 (18)	0.0074 (18)	0.0048 (17)	0.0010 (17)
C13	0.047 (3)	0.032 (2)	0.0284 (18)	0.020 (2)	0.0041 (19)	−0.0047 (18)

Geometric parameters (Å, º)

S1—C12	1.644 (3)	C2—C1	1.493 (4)
O3—C11	1.215 (4)	C2—C9	1.382 (4)
O2—C4	1.209 (4)	C10—C11	1.512 (5)
O1—C1	1.210 (4)	C8—C7	1.395 (5)
N4—C4	1.405 (5)	C8—C9	1.410 (5)
N4—C1	1.394 (4)	C5—H5A	0.9800
N4—C5	1.459 (4)	C5—H5B	0.9800
N2—C12	1.390 (4)	C5—H5C	0.9800
N2—C11	1.382 (4)	C7—H7	0.9500
N2—C14	1.458 (5)	C7—C6	1.389 (4)
N1—C10	1.401 (4)	C9—H9	0.9500
N1—C12	1.363 (5)	C6—H6	0.9500
N1—C13	1.448 (4)	C14—H14A	0.9800
N3—C10	1.252 (4)	C14—H14B	0.9800
N3—C8	1.417 (4)	C14—H14C	0.9800
C4—C3	1.481 (4)	C13—H13A	0.9800
C3—C2	1.389 (5)	C13—H13B	0.9800
C3—C6	1.387 (5)	C13—H13C	0.9800
C4—N4—C5	123.6 (3)	C7—C8—N3	118.9 (3)
C1—N4—C4	112.1 (3)	C7—C8—C9	121.0 (3)
C1—N4—C5	124.1 (3)	C9—C8—N3	119.9 (3)
C12—N2—C14	124.0 (3)	N4—C5—H5A	109.5
C11—N2—C12	111.4 (3)	N4—C5—H5B	109.5
C11—N2—C14	124.5 (3)	N4—C5—H5C	109.5
C10—N1—C13	123.1 (3)	H5A—C5—H5B	109.5
C12—N1—C10	111.8 (3)	H5A—C5—H5C	109.5
C12—N1—C13	124.9 (3)	H5B—C5—H5C	109.5
C10—N3—C8	120.6 (3)	C8—C7—H7	119.3
O2—C4—N4	125.1 (3)	C6—C7—C8	121.4 (3)

O2—C4—C3	129.4 (3)	C6—C7—H7	119.3
N4—C4—C3	105.5 (3)	C2—C9—C8	116.4 (3)
C2—C3—C4	108.7 (3)	C2—C9—H9	121.8
C6—C3—C4	130.4 (3)	C8—C9—H9	121.8
C6—C3—C2	121.0 (3)	C3—C6—C7	117.5 (3)
C3—C2—C1	107.9 (3)	C3—C6—H6	121.2
C9—C2—C3	122.5 (3)	C7—C6—H6	121.2
C9—C2—C1	129.6 (3)	N2—C14—H14A	109.5
N1—C10—C11	104.3 (3)	N2—C14—H14B	109.5
N3—C10—N1	122.8 (3)	N2—C14—H14C	109.5
N3—C10—C11	132.9 (3)	H14A—C14—H14B	109.5
O1—C1—N4	124.3 (3)	H14A—C14—H14C	109.5
O1—C1—C2	130.1 (3)	H14B—C14—H14C	109.5
N4—C1—C2	105.7 (3)	N1—C13—H13A	109.5
N2—C12—S1	125.7 (3)	N1—C13—H13B	109.5
N1—C12—S1	126.9 (3)	N1—C13—H13C	109.5
N1—C12—N2	107.4 (3)	H13A—C13—H13B	109.5
O3—C11—N2	126.3 (3)	H13A—C13—H13C	109.5
O3—C11—C10	128.5 (3)	H13B—C13—H13C	109.5
N2—C11—C10	105.1 (3)		

O2—C4—C3—C2	179.0 (4)	C12—N2—C11—C10	−0.3 (4)
O2—C4—C3—C6	−0.2 (7)	C12—N1—C10—N3	−179.6 (3)
N4—C4—C3—C2	−0.5 (4)	C12—N1—C10—C11	−1.4 (4)
N4—C4—C3—C6	−179.6 (4)	C11—N2—C12—S1	179.7 (3)
N1—C10—C11—O3	−176.8 (3)	C11—N2—C12—N1	−0.6 (4)
N1—C10—C11—N2	1.0 (3)	C8—N3—C10—N1	−175.4 (3)
N3—C10—C11—O3	1.1 (6)	C8—N3—C10—C11	7.1 (6)
N3—C10—C11—N2	178.9 (4)	C8—C7—C6—C3	1.8 (6)
N3—C8—C7—C6	−179.0 (3)	C5—N4—C4—O2	−1.0 (6)
N3—C8—C9—C2	177.7 (3)	C5—N4—C4—C3	178.5 (3)
C4—N4—C1—O1	174.2 (4)	C5—N4—C1—O1	−1.3 (6)
C4—N4—C1—C2	−4.0 (4)	C5—N4—C1—C2	−179.5 (3)
C4—C3—C2—C1	−1.9 (4)	C7—C8—C9—C2	3.1 (5)
C4—C3—C2—C9	177.7 (3)	C9—C2—C1—O1	5.9 (7)
C4—C3—C6—C7	−179.1 (3)	C9—C2—C1—N4	−175.9 (4)
C3—C2—C1—O1	−174.6 (4)	C9—C8—C7—C6	−4.3 (6)
C3—C2—C1—N4	3.6 (4)	C6—C3—C2—C1	177.4 (3)
C3—C2—C9—C8	0.6 (5)	C6—C3—C2—C9	−3.1 (6)
C2—C3—C6—C7	1.9 (5)	C14—N2—C12—S1	−3.3 (5)
C10—N1—C12—S1	−179.0 (3)	C14—N2—C12—N1	176.4 (3)
C10—N1—C12—N2	1.3 (4)	C14—N2—C11—O3	0.6 (5)
C10—N3—C8—C7	−113.3 (4)	C14—N2—C11—C10	−177.2 (3)
C10—N3—C8—C9	72.0 (5)	C13—N1—C10—N3	4.7 (5)
C1—N4—C4—O2	−176.6 (3)	C13—N1—C10—C11	−177.1 (3)
C1—N4—C4—C3	2.9 (4)	C13—N1—C12—S1	−3.4 (5)
C1—C2—C9—C8	−180.0 (4)	C13—N1—C12—N2	176.9 (3)
C12—N2—C11—O3	177.6 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*C*···O2^{i}	0.98	2.60	3.519 (5)	157
C7—H7···O3^{ii}	0.95	2.37	3.302 (4)	166
C9—H9···O1^{iii}	0.95	2.47	3.319 (4)	149
C14—H14*B*···O2^{iv}	0.98	2.32	3.272 (5)	164

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.