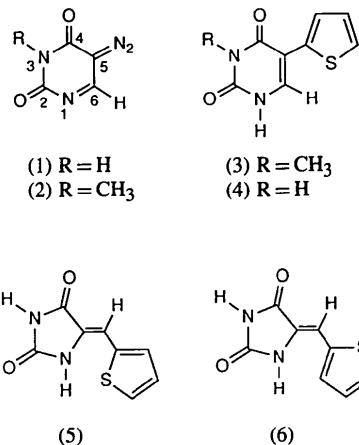


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Comment

Recently, Mathur & Shechter (1990) reported some spectacular differences in the thermal behaviour of 5-diazouracil, (1), and 5-diazo-3-methyluracil, (2). Thermolysis of (2) in thiophene at 423–433 K yields 3-methyl-5-(2-thienyl)uracil, (3). Thermolysis of (1) under the same conditions, however, has now been found to give (Z)-5-(2-thienylmethylene)-2,4-imidazolidinedione, (5), as the major product and 5-(2-thienyl)uracil, (4), as the minor product. Details of the X-ray analysis of (5) are now reported.



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(Z)-5-(2-Thienylmethylene)-2,4-imidazolidinedione

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Abstract

The major product formed in the thermolysis of 5-diazouracil in thiophene at 423–433 K has been identified as the unexpected compound (Z)-5-(2-thienylmethylene)-2,4-imidazolidinedione, C₈H₆N₂O₂S, by X-ray analysis. The molecule is a hydantoin derivative with a thienylmethylene group substituted at the 5-position. The structure is disordered in that the thiophene ring exists in two orientations which are related by an approximate 180° rotation about the C(6)—C(7) bond. All of the N and O atoms are involved in an intermolecular hydrogen-bonding network via N—H...O interactions. This network consists of an infinite chain along the *a*-axis direction and a cyclic trimer arrangement which branches from this chain. The molecules are arranged in the unit cell in pleated sheets which are approximately perpendicular to the *c* axis.

The title molecule consists of a 2,4-imidazolidinedione ring (also known as hydantoin) with a thienylmethylene group substituted at the 5-position. The structure is disordered with respect to rotation of the thiophene group by approximately 180° about the C(6)—C(7) bond. The orientation shown in structure (5) is adopted by 80% of the molecules and the orientation seen in structure (6) is adopted by 20%. While introduction of a disorder model improved this structure considerably, the bond lengths within the thiophene ring remain unsatisfactory. The C(7)—C(8) bond length is slightly too long for a double bond and the C(8)—C(9) bond length is too short for a single bond. The metric parameters for the hydantoin ring agree well with those reported for (*E*)-5-(methoxymethylene)-2,4-imidazolidinedione (Gallucci, Mathur & Shechter, 1992); the largest discrepancy is in the N(1)—C(2) bond length which is 1.362 (3) Å for (5) and 1.346 (2) Å for the methoxymethylene derivative. The two external angles at C(5) are significantly different from one another; N(1)—C(5)—C(6) is 131.1 (2)° and C(4)—C(5)—C(6) is 123.3 (2)°. This distortion is in the direction expected for a *Z* isomer. The molecule is not planar and the dihedral angle between the least-squares plane through atoms S, C(7), C(8), C(9) and C(10) and the least-squares plane through atoms C(5), N(1), C(2), N(3), C(4), O(2) and O(4) is 171°.

A displacement ellipsoid diagram of (5) is shown in Fig. 1. The packing diagram (Fig. 2) shows that

the molecules are arranged in pleated sheets approximately perpendicular to the *c* axis. Within each sheet, an infinite chain of N—H···O hydrogen bonds runs along the *a*-axis direction with N(1)···O(4) distances of 2.924 (2) Å. In addition, the molecules are hydrogen bonded in a cyclic trimer arrangement, which consists of two N(3)···O(2) bonds of 2.826 (2) Å, together with the N(1)···O(4) bond mentioned above. The metric parameters for the intermolecular hydrogen-bonded network are listed in Table 3.

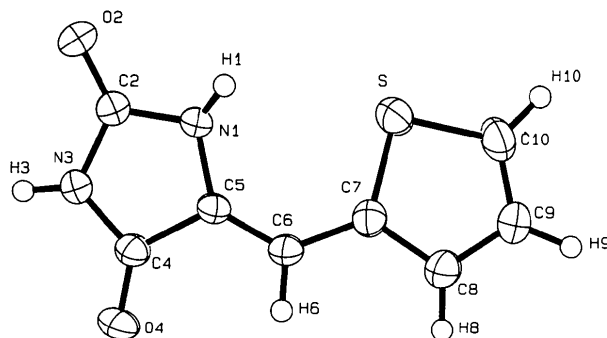


Fig. 1. ORTEP (Johnson, 1976) drawing with the labeling scheme for (5). The non-H atoms are represented by 50% probability displacement ellipsoids, while the H atoms are drawn with arbitrary radii. Only the major isomer is shown.

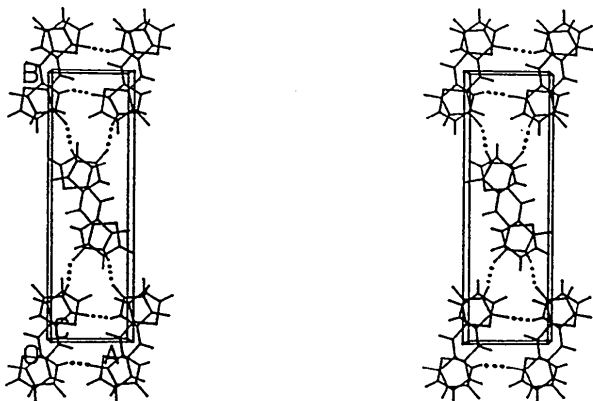


Fig. 2. A stereodrawing of the unit cell with the *a* axis horizontal, the *b* axis vertical and the *c* axis pointing out of the drawing. Hydrogen-bonding interactions are represented by dotted lines.

The molecules are stacked in columns along the *c*-axis direction. Adjacent molecules within a column are related by an inversion center so that the hydantoin ring of one molecule is stacked on top of the thiophene ring of an adjacent molecule. The average stacking distance is 3.48 Å.

Experimental

5-Diazouracil and anhydrous thiophene were heated at 433 K for 6–8 h in a pressure reactor followed by removal of

thiophene *in vacuo*. The residue thus obtained was chromatographed over silica gel using ethyl acetate as eluent. Compound (5) was crystallized from ethanol as pale-yellow plates.

Crystal data

C₈H₆N₂O₂S

M_r = 194.21

Monoclinic

*P*2₁/*a*

a = 6.137 (1) Å

b = 19.405 (2) Å

c = 7.187 (1) Å

β = 104.72 (1)°

V = 827.7 (2) Å³

Z = 4

D_x = 1.56 Mg m^{−3}

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 14–15°

μ = 0.338 mm^{−1}

T = 296 K

Rectangular plate

0.46 × 0.31 × 0.12 mm

Pale yellow

Data collection

Rigaku AFC-5S diffractometer

θ–2θ scans

Absorption correction:

analytical (de Meulenaer & Tompa, 1965)

T_{min} = 0.90, *T_{max}* = 0.97

2136 measured reflections

1967 independent reflections

1477 observed reflections

[*I* > σ(*I*)]

R_{int} = 0.017

θ_{max} = 27.5°

h = 0 → 7

k = 0 → 25

l = −9 → 9

6 standard reflections

monitored every 150

reflections

intensity variation: −0.3

to 0.9%

Refinement

Refinement on *F*

R = 0.041

wR = 0.046

S = 1.65

1477 reflections

143 parameters

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.31 e Å^{−3}

Δρ_{min} = −0.26 e Å^{−3}

Atomic scattering factors

from Cromer & Waber

(1974) for S, O, N and C

atoms, and from Stewart,

Davidson & Simpson

(1965) for H atoms

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

B_{iso} for starred atoms; *B_{eq}* = (8π²/3)Σ_{*i,j*} *U_{ij}* *a_i^{*}* *a_j^{*}* *a_i* *a_j* for others.

	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> / <i>B_{iso}</i>
S	0.8	0.3040 (1)	0.06360 (4)	0.8215 (1)	3.18 (3)
O(2)	1.0	0.1840 (2)	−0.20369 (8)	0.8742 (2)	4.12 (7)
O(4)	1.0	−0.4898 (2)	−0.09145 (8)	0.6769 (2)	3.59 (6)
N(1)	1.0	0.0958 (3)	−0.08953 (8)	0.8068 (3)	2.62 (6)
N(3)	1.0	−0.1838 (3)	−0.16324 (9)	0.7861 (3)	2.89 (7)
C(7)	1.0	0.0239 (3)	0.0708 (1)	0.7178 (3)	2.66 (7)
C(8)	0.8	−0.0329 (5)	0.1416 (1)	0.6703 (4)	3.8 (1)
C(9)	0.8	0.1540 (5)	0.1834 (1)	0.7001 (4)	3.6 (1)
C(10)	0.8	0.3480 (5)	0.1494 (1)	0.7884 (4)	3.7 (1)
C(6)	1.0	−0.1368 (3)	0.0154 (1)	0.6980 (3)	2.56 (7)
C(5)	1.0	−0.1028 (3)	−0.0519 (1)	0.7387 (3)	2.32 (7)
C(2)	1.0	0.0485 (3)	−0.1573 (1)	0.8275 (3)	2.77 (7)
C(4)	1.0	−0.2880 (3)	−0.1019 (1)	0.7263 (3)	2.54 (7)*
S'	0.2	−0.0424 (7)	0.1463 (2)	0.6508 (6)	5.48 (8)*
C(8')	0.2	0.3020 (15)	0.0633 (5)	0.7711 (15)	2.3 (2)*
C(9')	0.2	0.3849 (20)	0.1291 (6)	0.8023 (17)	3.7 (2)*
C(10')	0.2	0.2304 (17)	0.1770 (5)	0.7404 (14)	2.7 (2)*

Table 2. *Selected geometric parameters* (Å, °)

S—C(7)	1.697 (2)	N(3)—C(4)	1.368 (3)
S—C(10)	1.713 (3)	C(7)—C(8)	1.438 (3)
O(2)—C(2)	1.214 (2)	C(7)—C(6)	1.441 (3)
O(4)—C(4)	1.215 (2)	C(8)—C(9)	1.376 (4)
N(1)—C(5)	1.398 (2)	C(9)—C(10)	1.368 (4)
N(1)—C(2)	1.362 (3)	C(6)—C(5)	1.344 (3)
N(3)—C(2)	1.385 (2)	C(5)—C(4)	1.479 (3)
C(7)—S—C(10)	92.1 (1)	N(1)—C(5)—C(6)	131.1 (2)
C(5)—N(1)—C(2)	110.5 (2)	N(1)—C(5)—C(4)	105.5 (2)
C(2)—N(3)—C(4)	111.6 (2)	C(6)—C(5)—C(4)	123.3 (2)
S—C(7)—C(8)	109.9 (2)	O(2)—C(2)—N(1)	126.6 (2)
S—C(7)—C(6)	125.0 (1)	O(2)—C(2)—N(3)	126.3 (2)
C(8)—C(7)—C(6)	124.8 (2)	N(1)—C(2)—N(3)	107.1 (2)
C(7)—C(8)—C(9)	112.6 (2)	O(4)—C(4)—N(3)	126.7 (2)
C(8)—C(9)—C(10)	112.4 (2)	O(4)—C(4)—C(5)	128.2 (2)
S—C(10)—C(9)	112.5 (2)	N(3)—C(4)—C(5)	105.1 (2)
C(7)—C(6)—C(5)	129.7 (2)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

<i>D</i> —H... <i>A</i>	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N(1)—H(1)...O(4 ⁱ)	2.17 (2)	2.924 (2)	159 (2)
N(3)—H(3)...O(2 ⁱⁱ)	1.96 (3)	2.826 (2)	165 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, z$.

Part of the molecule is disordered. The thiophene ring exists in two different orientations which are related to each other by an approximate 180° rotation about the C(6)—C(7) bond. The major isomer is shown in Fig. 1. The disorder became obvious from observations made during the course of refinement of a model consisting of only the major isomer. At the anisotropic stage the difference electron density map contained two large peaks near atom C(8) of 0.88 and 1.0 e Å⁻³. The C(7)—C(8) bond was too long at 1.493 (6) Å for a double bond. In comparison the C(9)—C(10) bond length was 1.334 (9) Å. The S—C bond lengths were slightly short at 1.694 (5) and 1.684 (6) Å. An ORTEPII (Johnson, 1976) drawing showed a smaller than expected displacement ellipsoid for C(8) and a larger than expected one for S; the ellipsoids for C(9) and C(10) were elongated. The *R* factor for the final model converged at the rather high value of 0.072.

Many of these observations had been made earlier for the thiophene derivatives of 3,3'-dithienyl and β-thiophenic acid (Visser, Heeres, Wolters & Vos, 1968). In both of these cases, inclusion in the model of a second orientation of the thiophene ring improved the results considerably.

The disorder in this structure was modeled as follows; initially, the S and C(8) atoms were treated as composite atoms, *i.e.* the S site was occupied by both atoms S and C(8') with their occupancy factors totaling 1.0. Likewise, the C(8) site was occupied by atoms C(8) and S' with their occupancy factors totaling 1.0. The occupancy factor for C(8) was constrained to be equal to that of S, so that only the occupancy factor for S was allowed to refine and it converged at 0.804 (3). This model decreased the *R* factor, cleaned up the difference electron density map and improved the *B* values for the thiophene ring. However, the bond lengths for the thiophene ring still appeared as described above. So, a second orientation of the thiophene ring was included in the model; its coordinates were obtained by rotating the original ring by 180° about the C(6)—C(7) bond. This second orientation is referred to as the 'rotated' ring and its occupancy factor was fixed at 0.20, while the 'original' ring had its occupancy factor fixed at 0.80. The 'original' ring and the 'rotated' ring were refined in alternate cycles. Atoms S', C(8'), C(9') and C(10')

of the 'rotated' ring were kept isotropic. H atoms were added to both orientations of the thiophene ring and to atom C(6) at calculated positions [*C*—H = 0.98 Å and *B*(H) = 1.2*B*_{eq}(C)], and were fixed. The two H atoms bonded to atoms N(1) and N(3) were refined isotropically.

The inclusion of the 'rotated' ring in the model improved the geometry of the 'original' thiophene ring. However, the metrical parameters for the rotated ring are not very good.

Data reduction was carried out using TEXSAN (Molecular Structure Corporation, 1987). The structure was solved by the direct-methods program MITHRIL (Gilmore, 1984). Full-matrix least-squares refinements also used TEXSAN.

We thank the National Institutes of Health for financial support of this research.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, least-squares-planes data and geometry for the disordered thiophene ring have been deposited with the IUCr (Reference: BK1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Lumiflavinium (7,8,10-Trimethyl-isoalloxazinium) Nitrate

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Abstract

The crystal and molecular structure of lumiflavine in its protonated form (lumiflavinium nitrate, 2C₁₃H₁₂N₄O₂·