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5-Nitro-*N*-phenyl-2-thiofuramide

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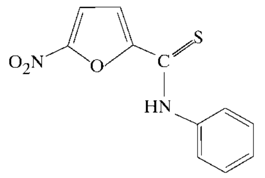
The title compound, $C_{11}H_8N_2O_3S$, crystallizes with two crystallographically independent molecules, which are conformationally almost identical, per asymmetric unit. The dihedral angles between the phenyl and 2-thiofuramide planes are 46.3 (1) and 47.0 (1)° for the first and second molecule, respectively. Strong intramolecular N—H···O hydrogen bonds [N···O 2.664 (2) and 2.661 (2) Å] dictate an *anti* conformation of the C=S groups in relation to the furan-O atoms.

Comment

5-Nitrofurans substituted in the 2-position became very important after their biological activity was discovered about 30 years ago by Dodd *et al.* (1970). Numerous papers have been published on the chemistry of biological and pharmacological studies of 5-nitrofuran derivatives, mostly concerning antibacterial activities (Dean & Sargent, 1984). Moreover, it is established that some thioamides exhibit pharmacological activity (Landquist, 1984). In the course of our studies of the syntheses and reactions of furan (Fišer-Jakić & Jakopčić, 1981) and 5-nitrofuran thioamides (Hahn *et al.*, 1970; Mance & Jakopčić, 1994), we have now prepared and structurally characterized the title compound, (I); its antitumor activity is currently under preliminary investigation.



(I)

The title compound crystallizes with two crystallographically independent molecules per asymmetric unit (Fig. 1). The difference in orientation of the phenyl rings is less than 1° indicating that the molecules are essentially identical, but not mutually connected by any global symmetry element. The dihedral angles between two planes defined by the thiofuramide moiety and phenyl-ring atoms amount to 46.3 (1) and 47.0 (1)° for the first and second molecule, respectively. The molecules are not planar, exhibiting twisting around the single Nsp^2—Csp^2 bond (N11—C61 and N12—C62, respectively). The measure of twisting is described by torsion angles of 137.8 (2) and −138.1 (2)° for C71—C61—N11—C11 and C72—C62—N12—C12, respectively.

A survey of the Cambridge Structural Database (Version 5.17; Allen & Kennard, 1993) revealed 60 structures containing the 5-nitro-2-furyl moiety and only four with the 5-nitro-2,5-dihydrofuryl fragment. Moreover, the structure of only one thiofuramide *i.e.* *N*-(2-hydroxyethyl)-2-thiofuramide has been known up to now (Galešić *et al.*, 1987).

The bond distances in both molecules are the same within the 3σ criterion. The Csp^2=Csp^2 bond distance values within the furan ring are the same and in agreement with the literature data (Allen *et al.*, 1987), while the Csp^2—Csp^2 single bond [C31—C41 1.398 (4) and C32—C42 1.403 (3) Å] is slightly shorter (average value 1.423 Å; Allen *et al.*, 1987). The

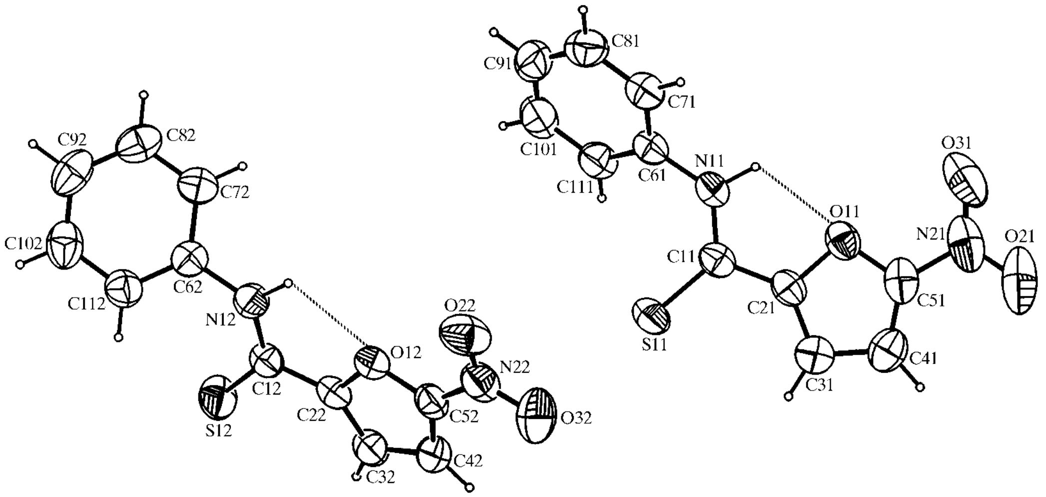


Figure 1
A perspective view of the two independent molecules of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The H atoms are drawn as small circles of arbitrary radius. The intramolecular hydrogen bonds are indicated by dashed lines.

Csp^2—O bond values [O11—C21 1.374 (3), O11—C51 1.351 (3), O12—C22 1.377 (2) and O12—C52 1.347 (3) Å] correspond with the average O—Csp^2 value of 1.368 Å (Allen *et al.*, 1987). However, the O11—C51 and O12—C52 distances are shortened by the effect of the NO_2 groups directly attached to C51 and C52. The pattern of one shorter and one longer O—Csp^2 bond distance of 1.350 and 1.375 Å, respectively, is observed in all database structures containing the 5-nitro-2-furyl fragment.

The C═S bonds [C11—S11 1.655 (2) and C12—S12 1.655 (2) Å] are slightly shorter than those found in the structural fragment X_2—C═S (X = C, N, O, S), 1.671 Å (Allen *et al.*, 1987) and in *N*-(2-hydroxyethyl)-2-thiofuramide (Galešić *et al.*, 1987), 1.673 (3) Å. Such shortening, associated with the significant π character of N11—C11 and N12—C12 [1.344 (3) and 1.348 (3) Å, respectively], is in agreement with delocalization of π electrons within the 5-nitro-2-thiofuramide moieties. In the structure of *N*-(2-hydroxyethyl)-2-thiofuramide (Galešić *et al.*, 1987), the analogous bond length is even shorter at 1.317 (4) Å.

The angle sum around thiofuramide N atoms N11 and N12 is 359.9 (2) and 359.6 (2)°, confirming sp^2 hybridization. The N11—C61 and N12—C62 bond lengths of 1.419 (3) and 1.422 (3) Å are shorter even than the partially delocalized single N—Csp^3 bond distance value of 1.460 (3) Å found in *N*-(2-hydroxyethyl)-2-thiofuramide (Galešić *et al.*, 1987).

The *anti* conformation (spatial orientation of C═S group with respect to the furan O atom) of the molecules is adopted as a result of intramolecular hydrogen bonding of the type N—H···O (Table 2; Taylor *et al.*, 1984). The packing also involves two weak intermolecular C—H···O hydrogen bonds involving NO_2 O atoms and phenyl C—H proton donors (Table 2).

Experimental

We employed an alternative preparation of 5-nitro-*N*-phenyl-2-thiofuramide by thionation of furancarboxamide with Lawesson's reagent (Cava & Levinson, 1985) instead of phosphorous pentasulfide (Mance & Jakopčić, 1994; Fărcasăn & Paiu, 1966). To a solution of 5-nitro-*N*-phenyl-2-furamide (2.3 g, 10 mmol) in dry ethylene glycol dimethyl ether (15 ml) Lawesson's reagent (2.2 g, 5.4 mmol) was added. The reaction mixture was heated at 333 K for 30 min and the solvent evaporated. The product was chromatographed on a silica-gel column with petroleum ether/chloroform (1:1). The purified product (2.4 g, 96%) obtained on evaporation of the solvents was recrystallized from ethanol, yielding red crystals (m.p. = 414–415 K) suitable for X-ray single-crystal diffractometry.

Crystal data

$C_{11}H_8N_2O_3S$
M_r = 248.25
Triclinic, $P\bar{1}$
a = 7.4990 (10) Å
b = 9.114 (2) Å
c = 16.717 (2) Å
α = 86.06 (2)°
β = 88.610 (10)°
γ = 76.73 (2)°
V = 1109.4 (3) Å^3

Z = 4
D_x = 1.486 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
θ = 10.05–14.90°
μ = 0.289 mm^{-1}
T = 293 (2) K
Prism, red
0.76 × 0.53 × 0.24 mm

Data collection

Philips PW1100 updated by Stoe diffractometer
ω scans
4817 measured reflections
4817 independent reflections
2867 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 27.06°

$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 240 min
intensity decay: 1.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.130
S = 0.958
4817 reflections
324 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.2951P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.23 e Å^{-3}
$\Delta\rho_{\min}$ = −0.40 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.024 (2)

Table 1
Selected geometric parameters (Å, °).

S11—C11	1.655 (2)	S12—C12	1.655 (2)
O11—C51	1.351 (3)	O12—C52	1.347 (3)
O11—C21	1.374 (3)	O12—C22	1.377 (2)
N11—C11	1.344 (3)	N12—C12	1.348 (3)
N11—C61	1.419 (3)	N12—C62	1.422 (3)
C11—N11—C61	127.37 (19)	C12—N12—C62	127.53 (19)
N11—C11—C21	114.81 (19)	N12—C12—C22	114.54 (19)
N11—C11—S11	126.59 (18)	N12—C12—S12	126.66 (18)
C21—C11—S11	118.56 (17)	C22—C12—S12	118.78 (16)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···O11	0.94	2.18	2.664 (2)	111
N12—H12···O12	0.94	2.20	2.661 (2)	110
C111—H111···O22^{i}	0.93	2.54	3.271 (3)	136
C112—H112···O31^{ii}	0.93	2.58	3.267 (4)	131

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

H atoms of furan and the phenyl rings were generated at idealized geometrical positions with the C—H distance 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm iso}$ of the carrier C atom, and refined using a riding model. The H atoms H11 and H12 were identified in difference Fourier maps, but in the final stage of refinement they were generated and refined by applying a riding model (N—H 0.93 Å).

Data collection: *Stadi*4 (Stoe & Cie, 1995); cell refinement: *Stadi*4; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*98 (Spek, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1378). Services for accessing these data are described at the back of the journal.

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