Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-(3-Cyano-2-oxo-2,5,6,7,8,9-hexahydro-1*H*-cyclohepta[*b*]pyridin-1-yl)-4-methylbenzenesulfonamide

Galal H. Elgemeie,[a] Mahmoud A. Mahmoud[b] and Peter G. Jones[c]*

[a]Chemistry Department, Faculty of Science, Helwan University, Helwan, Cairo, Egypt, [b]Chemistry Department, Faculty of Science, Cairo University (Bani Sueí Branch), Bani Sueí, Egypt, and [c]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Correspondence e-mail: jones@xray36.anchem.nat.tu-bs.de

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.097
Data-to-parameter ratio = 13.0

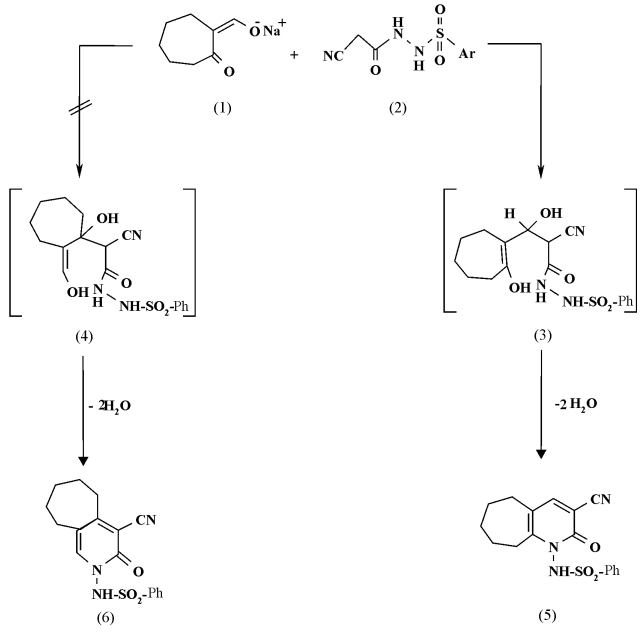
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 16 October 2002
Accepted 17 October 2002
Online 25 October 2002

The title compound, $C_{18}H_{19}N_3O_3S$, was identified as one of two possible isomers. Key bond lengths are N—N 1.402 (2) Å and N—S 1.6894 (18) Å. Classical hydrogen bonds N—H···O connect the molecules to form inversion-symmetric dimers, which are further linked by a weak C—H···O hydrogen bond, forming ribbons.

Comment

We have recently reported various successful approaches for the synthesis of a new class of *N*-arylsulfonylaminated pyridones (Elgemeie *et al.*, 1999, 2000). The synthesized compounds are important as intermediates for the synthesis of the biologically active deazapurine ring system, hence our interest in this class of compounds (Elgemeie *et al.*, 2001).



We report here a novel one-step synthesis of *N*-arylsulfonylamino-2-pyridone derivatives by reaction of the sodium salt (1) of 2-(hydroxymethylene)-1-cycloheptanone with a cyanohydrazide. Thus, (1) reacted with *N*-cyanoaceto-*p*-tolylsulfonylhydrazide, (2), in piperidine acetate to give a product of molecular formula $C_{18}H_{19}N_3O_3S$, for which two isomeric structures, (5) and (6), seemed possible, corresponding to two feasible modes of cyclization. In the first, initial attack by a carbanion takes place at the formyl group of salt (1) and subsequent Michael cyclization, followed by elimination of two moles of water, leads to the product (5), whereas in the second, initial nucleophilic attack by the methylene carbon takes place at the ketonic group, followed by cyclization and elimination of water, leading to isomer (6).

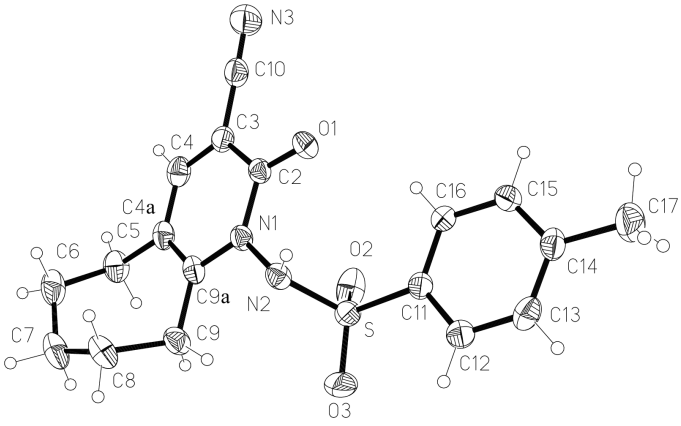


Figure 1
The molecule of compound (5) in the crystal. Displacement ellipsoids are drawn at the 30% probability level. H-atom radii are arbitrary.

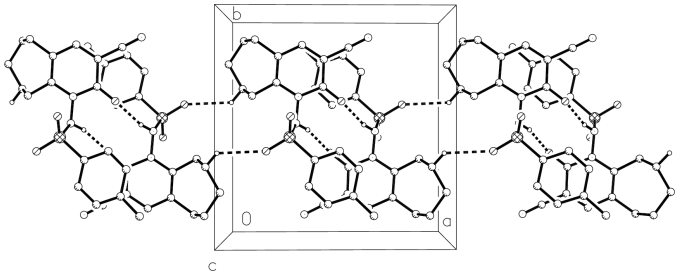


Figure 2
Packing diagram of the title compound, viewed parallel to the *c* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted.

Only one isomer was obtained, but spectroscopy did not allow us to distinguish between structures (5) and (6). ^{1}H NMR spectra of the product revealed the presence of an NH proton at δ = 11.4 p.p.m. in solution. In order to establish unambiguously the structure of the product, the crystal structure was determined, confirming the exclusive presence of the tautomer (5) in the solid state.

The molecule of (5) is shown in Fig. 1. Molecular dimensions, such as the bond lengths N1—N2 = 1.402 (2) Å and N2—S = 1.6894 (18) Å, may be regarded as normal. The heterocycle is planar (r.m.s. deviation 0.011 Å). The ring atoms C16 and C11 form an antiperiplanar sequence with S and O3; the S—O3 bond is thereby shorter than S—O2 [1.4186 (16) *versus* 1.4355 (17) Å]. The seven-membered ring displays approximate mirror symmetry, with alternating positive and negative torsion angles about the bond sequence C4a—C5—C6—C7—C8—C9—C9a.

The molecules are connected in pairs across inversion centres by classical hydrogen bonds N2—H0···O1; a further weak C8—H8*A*···O3 hydrogen bond connects the dimers, to form a ribbon parallel to the *a* axis (Table 2 and Fig. 2).

Experimental

A solution of the sodium salt of 2-(hydroxymethylene)-1-cycloheptanone [(1); 1.60 g, 0.01 mol], *N*-cyanoaceto-*p*-tolylsulfonylhydrazide [(2); 3.4 g, 0.01 mol] and piperidine acetate (1 ml) in water (30 ml) and ethanol (30 ml) was refluxed for 10 min. Acetic acid (1.5 ml) was added to the hot solution. The precipitated solid was collected by filtration and crystallized from ethanol in 80% yield (m.p. 528 K).

Crystal data

$C_{18}H_{19}N_3O_3S$
M_r = 357.42
Monoclinic, $P2_1/n$
a = 11.7423 (16) Å
b = 11.9050 (14) Å
c = 12.2458 (14) Å
β = 91.816 (12)°
V = 1711.0 (4) Å^3
Z = 4
D_x = 1.388 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 72 reflections
θ = 4–12.5°
μ = 0.21 mm^{-1}
T = 173 (2) K
Irregular prism, colourless
0.7 × 0.4 × 0.2 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3649 measured reflections
2995 independent reflections
2241 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 25.0°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 2$
$l = -14 \rightarrow 0$
3 standard reflections
every 247 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.097
S = 1.02
2995 reflections
231 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—O3	1.4189 (16)	S—C11	1.7583 (19)
S—O2	1.4355 (17)	N1—N2	1.402 (2)
S—N2	1.6894 (18)		
N1—N2—S	114.73 (13)		
C9a—C4a—C5—C6	66.3 (3)	C7—C8—C9—C9a	80.8 (2)
C4a—C5—C6—C7	−77.2 (2)	C5—C4a—C9a—C9	−3.1 (3)
C5—C6—C7—C8	60.6 (3)	C8—C9—C9a—C4a	−61.9 (3)
C6—C7—C8—C9	−64.2 (3)	O3—S—C11—C16	172.53 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H0···O1^{i}	0.79 (2)	2.02 (2)	2.793 (2)	166 (2)
C8—H8*A*···O3^{ii}	0.99	2.54	3.279 (3)	131

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

The H atom on N2 was refined freely. Methyl H atoms were located in difference syntheses, idealized (C—H = 0.98 Å and H—C—H = 109.5°) and refined on the basis of rigid groups allowed to rotate but not tip. Other H atoms were included using a riding model with fixed C—H bond lengths (aromatic = 0.95 Å and methylene = 0.99 Å); U_{iso}(H) values were fixed at 1.2U_{eq} of the parent atom.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

Financial support from the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Mr A. Weinkauf for technical assistance.

References

Elgemeie, G. H., Elghandour, A. H., Ali, H. A. & Abdel-Azzez, H. M. (1999). *J. Chem. Res.* (*S*), pp. 6–7.
Elgemeie, G. H., Elghandour, A. H., Ali, H. A. & Abdel-Azzez, H. M. (2001). *Phosphorus Sulfur Silicon*, **170**, 171–179.
Elgemeie, G. H., Elghandour, A. H., Elzanate A. M. & Masoud, W. A. (2000). *Phosphorus Sulfur Silicon*, **163**, 91–97.
Fait, J. (1991). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.