Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

4-(4-Methoxyphenyl)-3-phenyl-2,4,8,10-tetraazaspiro[5.4]dec-1-ene-6,8,10-trione acetone solvate monohydrate

Giuseppe Bruno,[a]* Archimede Rotondo,[a] Francesco Nicoló,[a] Francesco Foti,[b] Giovanni Grassi[b] and Francesco Risitano[b]

[a]Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Universitá degli Studi di Messina, Via Salita Sperone 31, 98166 Vill. S. Agata – Messina, Italy, and [b]Dipartimento di Chimica Organica e Biologica, Universitá degli Studi di Messina, Via Salita Sperone 31, I-98166 Vill. S. Agata – Messina, Italy

Correspondence e-mail: gbruno@unime.it

Received 17 November 2004
Accepted 10 December 2004
Online 18 December 2004

Key indicators

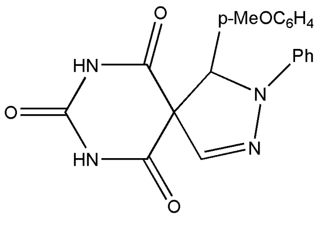
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.055
wR factor = 0.170
Data-to-parameter ratio = 12.8

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

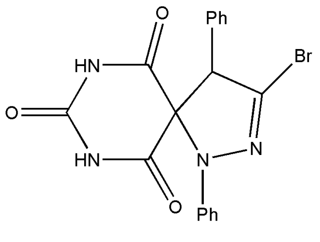
Conformational analyses and structural comparison of the title spiropyrazolebarbiturate, $C_{19}H_{16}N_4O_4\cdot C_3H_6O\cdot H_2O$, and the related structure 3-bromo-1,4-diphenyl-1,2,7,9-tetraazaspiro[5.4]dec-2-ene-6,8,10-trione acetone solvate [Bruno, Rotondo, Nicoló, Foti, Grassi & Risitano (2005). *Acta Cryst.* E**61**, o142–o144], are presented. Both compounds were synthesized by cycloaddition of C—H and C—Br nitrilimines, generated *in situ*, starting from the same substrate [Foti, Grassi & Risitano (2005). *Synlett*. Submitted]. However, different experimental conditions led to products with reverse regioselectivity.

Comment

It is known that barbituric acid derivatives, because of the presence of two N—H hydrogen-bond donors and three C═O acceptors, bind tightly to small dipolar species (solvents), as well as to other similar complementary molecules (Chang *et al.*, 1991). This accounts for the wide use of barbituric acid derivatives in the field of molecular recognition (Berl *et al.*, 1999). Often, the crystallization process, which is a form of self-recognition, readily takes place when these substrates are oriented relative to one another in a suitable fashion. Sometimes, unsaturated connection sites may link other dipolar species (solvents), which will be found inside the solid crystal samples. The title spiro compound, (I), and the related spiro compound, (II) (Bruno *et al.*, 2005), both obtained as crystalline solvates, are composed of a barbituric acid moiety connected to a substituted pyrazoline ring through the non-chiral spiro centre C6 (Fig. 1). These compounds contain the unique chiral atom C10 and, since both crystallize in centrosymmetric space groups, the crystal samples are (10R)–(10S) racemic mixtures.



(I)



(II)

The asymmetric unit of (I) consists of one spiro-fused bicyclic molecule, one acetone and one water molecule (Fig. 1). The two core rings do not present evident puckering [maximum deviation from the barbituric acid mean plane for atom C6 is 0.156 (2) Å, and from the pyrazoline mean plane

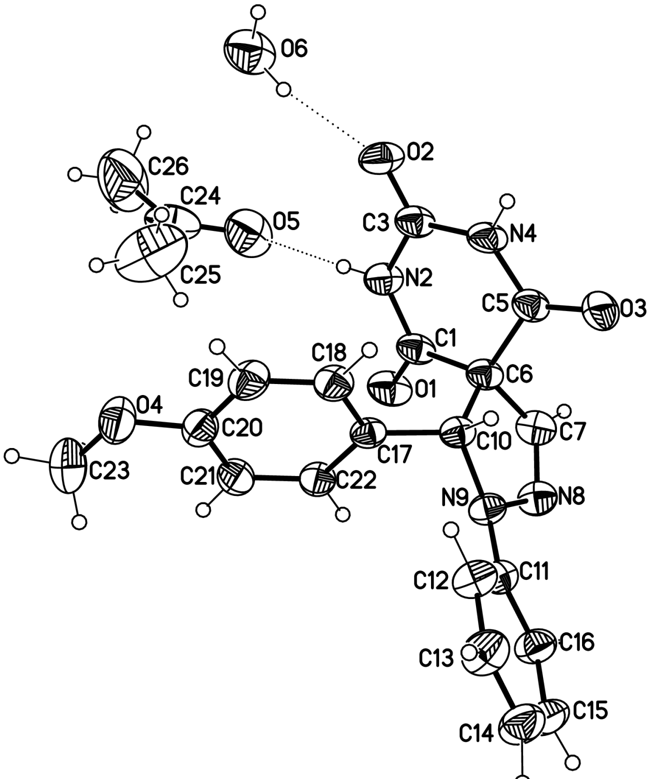


Figure 1
The (10*R*) isomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii. Dotted lines indicate hydrogen bonds.

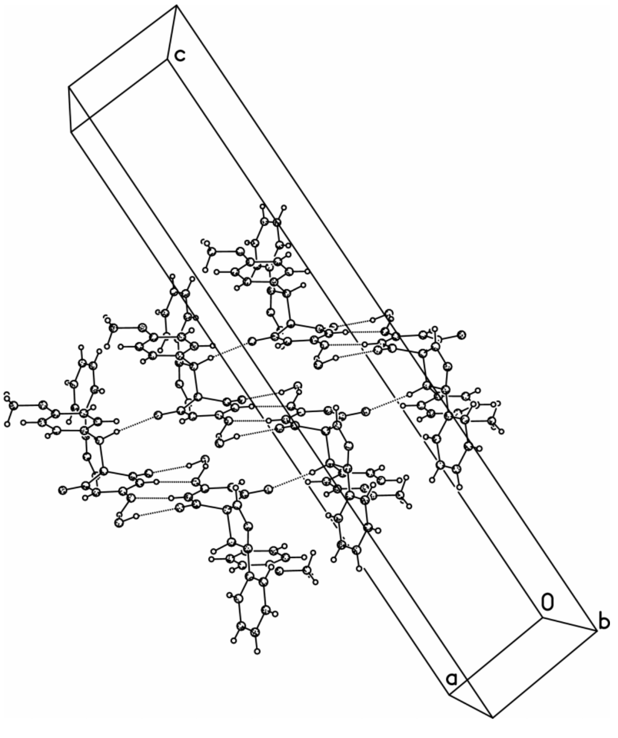


Figure 2
Part of the crystal packing of (I), showing ribbons formed by pairs of molecules along the [100] direction. Dotted lines indicate hydrogen bonds.

for atom C10 is 0.075 (2) Å]. They are almost perpendicular to one another, with a dihedral angle between their mean planes of 89.2 (1)°. Despite the presence of two sp^3-hybridized C atoms within the pyrazoline ring, the conjugation with the phenyl system attached to N9 is evidenced by the torsion angles around N9—C11 (Table 1) and the angle between the mean planes of the rings of 20.5 (1)°.

Pairs of molecules are linked by an N4—H4···O2^{i} hydrogen bond (symmetry code as in Table 2), dimerized by the crystallographic inversion centre in an $R_2^2(6)$ first-order centrosymmetric graph set. These dimers are, in turn, able to interact with co-crystallized solvent molecules (Figs. 1 and 2).

A weaker C10—H10···O1^{ii} hydrogen-bond interaction (Table 2) connects to the molecule at (x + 1, y, z), generating one-dimensional C(5) chains along the crystallographic a axis, such that dimers are stacked one above another in a stair-like molecular ribbon reminiscent of the duplex DNA structure (Table 2 and Fig. 2).

We note that the water molecule interacting with a dimeric pair is exactly above the barbituric acid plane of the dimer obtained by translation along the diagonal of the *ab* plane, [110], such that the water O atom is close to the two internal carbonyl groups [O6···C1^{i} 3.057 (4) and O6···C5^{i} 3.186 (4) Å; symmetry code: (i) $1 - x$, $1 - y$, $-z$]. Other weak dipolar interactions keep the above-mentioned ribbons together in the three-dimensonal packing.

Experimental

Cycloadduct (I) was obtained from an arylidenebarbiturate and a nitrilimine prepared *in situ*, as described by Foti *et al.* (2004). After purification of the product, crystals suitable for X-ray analysis were obtained by slow evaporation of an acetone solution.

Crystal data

$C_{19}H_{16}N_4O_4 \cdot C_3H_6O \cdot H_2O$
M_r = 440.45
Monoclinic, $P2_1/c$
a = 6.1539 (10) Å
b = 10.7908 (17) Å
c = 34.057 (6) Å
β = 94.504 (14)°
V = 2254.6 (6) Å^3
Z = 4

D_x = 1.298 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 61 reflections
θ = 5.7–20.5°
μ = 0.10 mm^{-1}
T = 298 (2) K
Prism, colourless
0.58 × 0.48 × 0.34 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan
(North *et al.*, 1968)
$T_{\min}$ = 0.873, $T_{\max}$ = 0.964
10 362 measured reflections
3815 independent reflections
2715 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.022
$\theta_{\max}$ = 25°
$h = -1 \rightarrow 6$
$k = -12 \rightarrow 12$
$l = -40 \rightarrow 40$
3 standard reflections
every 197 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.17
S = 1.05
3815 reflections
297 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 1.0558P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.004
$\Delta\rho_{\max}$ = 0.63 e Å^{-3}
$\Delta\rho_{\min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL97*
(Sheldrick, 1997)
Extinction coefficient: 0.0082 (16)

o140 Bruno *et al.* • $C_{19}H_{16}N_4O_4 \cdot C_3H_6O \cdot H_2O$ *Acta Cryst.* (2005). E**61**, o139–o141

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.208 (3)	N8—N9	1.381 (3)
O2—C3	1.225 (3)	N9—C11	1.405 (3)
O3—C5	1.202 (3)	N9—C10	1.475 (3)
N8—N9—C11—C12	154.0 (2)	N8—N9—C11—C16	−28.2 (4)
C10—N9—C11—C12	8.3 (4)	C10—N9—C11—C16	−173.9 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4$\cdots$O2$^{\rm i}$	0.86	2.05	2.909 (3)	175
O6—H6$A\cdots$O3$^{\rm i}$	0.96	2.14	2.997 (3)	148
C10—H10$\cdots$O1$^{\rm ii}$	0.98	2.33	3.280 (3)	164
O6—H6$B\cdots$O2	0.96	2.08	3.014 (4)	165
N2—H2$\cdots$O5	0.86	2.01	2.865 (4)	172

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

All H atoms were treated as riding, with alkyl C—H distances of 0.98, methyl C—H distances of 0.96 and aromatic C—H distances of 0.93 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The disordered water molecule was refined as a rigid group through the AFIX176 instruction in *SHELXL97* (Sheldrick, 1997) (O—H distances were set at 0.942 Å and H—O—H angles to 104.557°).

Data collection: *XSCANS* (Siemens, 1989); cell refinement: *XSCANS*; data reduction: *XPREP* (Bruker, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1997); software used to prepare material for publication: *PARST*97 (Nardelli, 1995) and *WinGX-PC* (Version 1.6.4.05; Farrugia, 1999).

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Berl, V., Huc, I., Lehn, J.-M., DeCian, A. & Fischer, J. (1999). *Eur. J. Org. Chem.* pp. 3089–3094.

Bruker (1997). *XPREP* and *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruno, G., Rotondo, A., Nicoló, F., Foti, F., Grassi, G. & Risitano, F. (2005). *Acta Cryst.* E**61**, o142–o143.

Chang, S.-K., Van Engen, D., Fan, E. & Hamilton, A. D. (1991). *J. Am. Chem. Soc.* **113**, 7640–7645.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Foti, F., Grassi, G. & Risitano, F. (2005). *Synlett.* Submitted.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Siemens (1989). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (2005). E**61**, o139–o141 Bruno *et al.* • $C_{19}H_{16}N_4O_4{\cdot}C_3H_6O{\cdot}H_2O$ **o141**