Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Bromo-1,4-diphenyl-1,2,7,9-tetraaza-spiro[5.4]dec-2-ene-6,8,10-trione acetone solvate

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

Key indicators

Single-crystal X-ray study
T = 571 K
Mean σ(C–C) = 0.008 Å
R factor = 0.056
wR factor = 0.141
Data-to-parameter ratio = 14.6

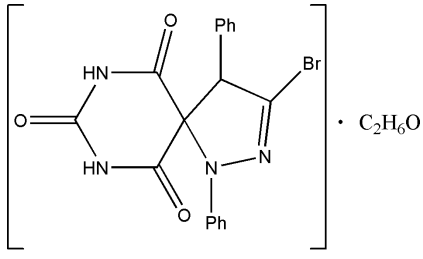
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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

Conformational analyses and structural comparison of the title compound, $C_{18}H_{13}BrN_4O_3\cdot C_2H_6O$, and the related compound 4-(4-methoxyphenyl)-3-phenyl-2,4,8,10-tetraaza-spiro[5.4]dec-1-ene-6,8,10-trione acetone solvate monohydrate [Bruno, Rotondo, Nicoló, Foti, Grassi & Risitano (2005). *Acta Cryst.* E**61**, o139–o141], co-crystallized with solvent molecules, are presented. Both compounds were synthesized by the 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

The background to the study of the title comound, (I), has been discussed in with respect to a related compound, (II), (Bruno et al., 2005). Spiro compound (I), as well (II) , 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 (10*R*)–(10*S*) racemic mixtures.



(I)

The structure of (I) is very similar to that of (II), except for the positions of the N atoms in the pyrazoline ring (scheme and Fig. 1). In the crystallographic asymmetric unit, there are two chemically identical spiro molecules and two ethanol molecules. Atoms are labelled with the suffix *A* or *B* in order to distinguish the two analogous groups, the geometric parameters of which are reported separately. As observed for (II), the core rings are planar [maximum deviations from the barbituric acid mean planes are 0.188 (4) for C6*A* and 0.101 (5) Å for C5*B*, and from the pyrazoline mean planes is 0.024 (5) for C6*A* and 0.100 (4) Å for C6*B*] and perpendicular to one another, the angles between their mean planes being 85.8 (2) and 87.6 (2)°, for molecules *A* and *B*, respectively. In this case, the extended π conjugation, over the pyrazoline moiety from the attached phenyl ring (see Table 1 for

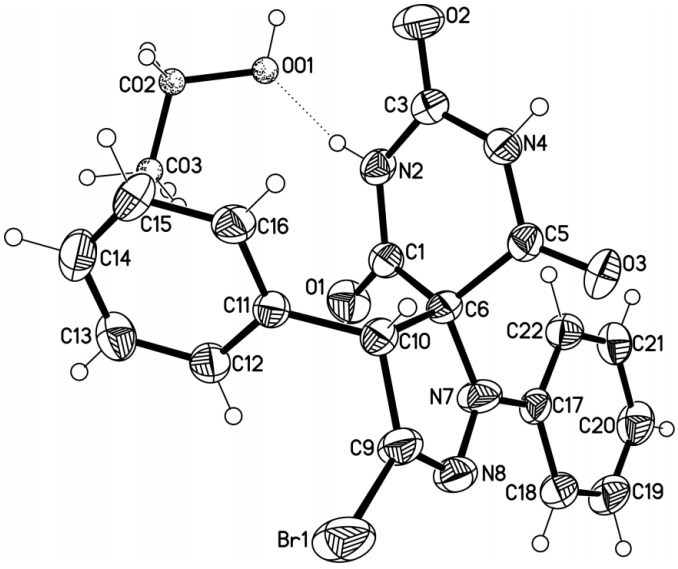


Figure 1
The *A*-labelled (10*R*) isomer of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii. The dotted line represents a hydrogen bond.

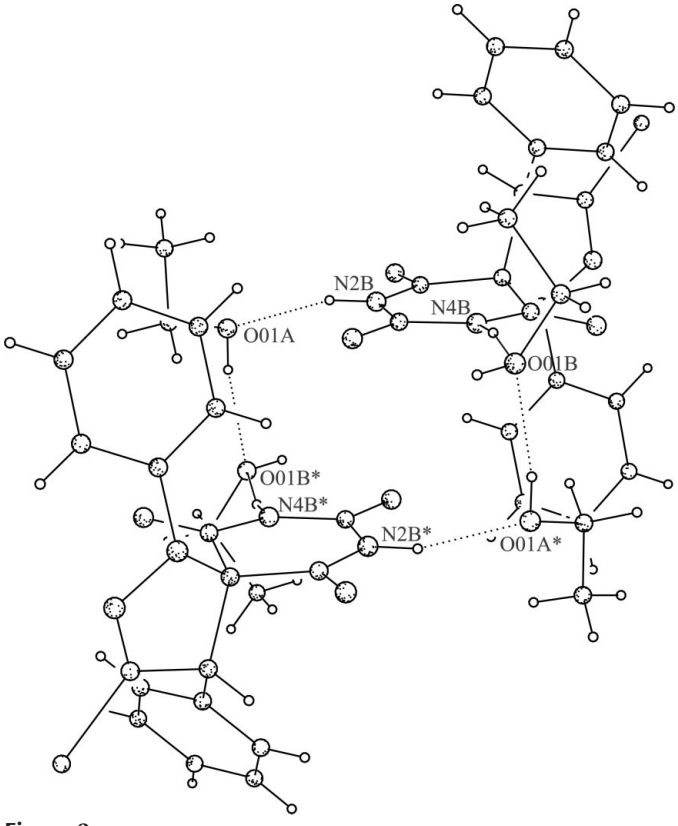


Figure 2
The structure of (I), showing the unusual third-order graph-set $R_6^6(18)$ created by dimers (*B* group) held close together also through four solvent molecules. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, -y, 2-z)$. Dashed lines indicate hydrogen bonds.

geometric parameters involving atoms N7 and C17), is more evident for molecule *A* than for molecule *B* [angles between the ring mean planes are 5.4 (1) and 20.6 (1)°, respectively].

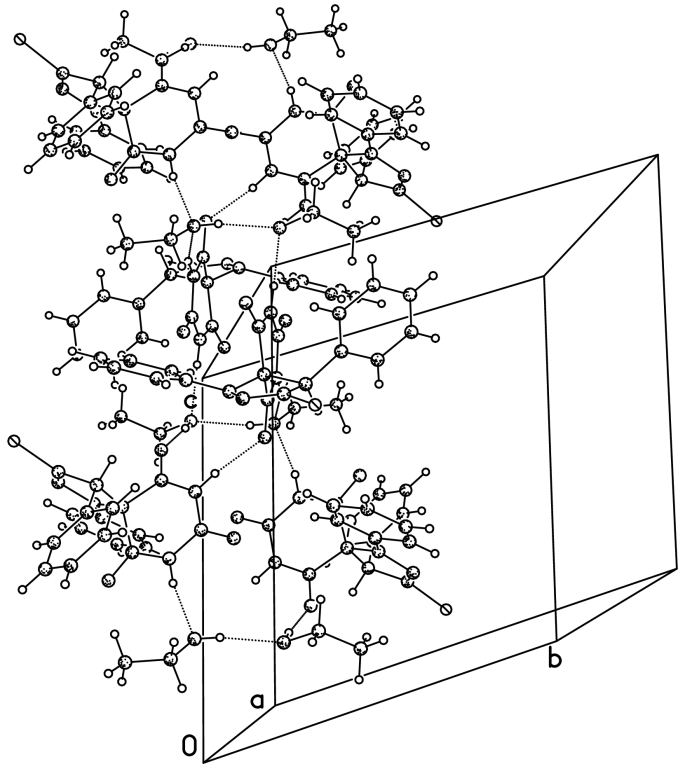


Figure 3
The cystal packing of (I), showing the pairs of molecules (of alternate *A* and B type) forming a chain along the [001] direction. Dotted lines indicate hydrogen bonds.

This is likely to be due to small differences in intermolecular steric hindrance experienced by the crystallographically independent molecules.

The crystal packing of (I) is mainly supported by strong dipolar intermolecular hydrogen bonds. Both *A* and *B* molecules tend to couple with another crystallographically identical molecule. The resulting centrosymmetric loose pairs are kept together by a π–π stacking interaction between their respective barbituric acid moieties [distances between mean planes are 3.29 and 3.17 Å for *A* and *B* pairs, respectively]. Moreover, *A* and *B* pairs are oriented in different directions and are also stabilized by four ethanol molecules entrapped between them through conventional hydrogen bonds (Fig. 2 and Table 2). Alternate *A* and *B* dimeric units are bound through an N4*A*—H4*A*$\cdots$O1*B*^{ii} interaction, developing one-dimensional chains along the [100] direction (Fig. 3; symmetry code as in Table 2). Other weak dipolar interactions, involving mainly Br and O atoms, contribute to the three-dimensional packing.

Experimental

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

Crystal data

$C_{18}H_{13}BrN_4O_3\cdot C_2H_6O$
M_r = 459.3
Triclinic, $P\overline{1}$
a = 12.027 (4) Å
b = 13.380 (5) Å
c = 13.416 (3) Å
α = 71.32 (3)°
β = 86.159 (13)°
γ = 87.84 (3)°
V = 2040.3 (12) Å^3
Z = 4
D_x = 1.495 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
θ = 3.4–18.0°
μ = 2.05 mm^{-1}
T = 571 (2) K
Prism, colourless
0.4 × 0.38 × 0.26 mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.484, T_{max} = 0.584
8832 measured reflections
7668 independent reflections
4687 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 25.7°
$h = -14 \rightarrow 1$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 16$
3 standard reflections
every 197 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.141
S = 1.02
7668 reflections
526 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 3.1246P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.10 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0028 (5)

Table 1
Selected geometric parameters (Å, °).

Br1*A*—C9*A*	1.864 (5)	Br1*B*—C9*B*	1.862 (5)
O1*A*—C1*A*	1.201 (5)	O1*B*—C1*B*	1.214 (5)
O2*A*—C3*A*	1.206 (5)	O2*B*—C3*B*	1.211 (5)
O3*A*—C5*A*	1.211 (5)	O3*B*—C5*B*	1.201 (5)
N7*A*—N8*A*	1.374 (5)	N7*B*—N8*B*	1.385 (5)
N7*A*—C17*A*	1.392 (6)	N7*B*—C17*B*	1.417 (6)
N8*A*—C9*A*	1.273 (6)	N8*B*—C9*B*	1.269 (6)
N8*A*—N7*A*—C17*A*	120.6 (4)	N8*B*—N7*B*—C17*B*	116.4 (4)
N8*A*—N7*A*—C6*A*	113.3 (4)	N8*B*—N7*B*—C6*B*	111.9 (3)
C17*A*—N7*A*—C6*A*	125.9 (4)	C17*B*—N7*B*—C6*B*	122.7 (3)
N8*A*—N7*A*—C17*A*—C18*A*	7.8 (7)	N8*B*—N7*B*—C17*B*—C22*B*	177.7 (4)
C6*A*—N7*A*—C17*A*—C18*A*	−177.3 (4)	C6*B*—N7*B*—C17*B*—C22*B*	33.3 (7)
N8*A*—N7*A*—C17*A*—C22*A*	−173.1 (4)	N8*B*—N7*B*—C17*B*—C18*B*	−4.1 (7)
C6*A*—N7*A*—C17*A*—C22*A*	1.9 (7)	C6*B*—N7*B*—C17*B*—C18*B*	−148.4 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2*A*—H2*A*···O01*A*	0.86	1.99	2.833 (5)	168
N2*B*—H2*B*···O01*A*	0.86	2.02	2.850 (5)	162
N4*B*—H4*B*···O01*B*^{i}	0.86	1.97	2.818 (5)	170
N4*A*—H4*A*···O1*B*^{ii}	0.86	1.97	2.821 (5)	170
O01*A*—H01*A*···O01*B*^{ii}	0.82	2.00	2.812 (5)	170
O01*B*—H01*B*···O3*A*	0.82	2.07	2.879 (5)	170

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

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_{iso}(H) = 1.2 U_{eq}(C). The highest peak in the Fourier difference map is 0.93 Å from atom H20*B*.

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**, o139–o141.
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.