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3′-Aminocyclohexanespiro-5′-hydantoin–phenylboronic acid (1/1)

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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.004 Å
R factor = 0.062
wR factor = 0.168
Data-to-parameter ratio = 22.7

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

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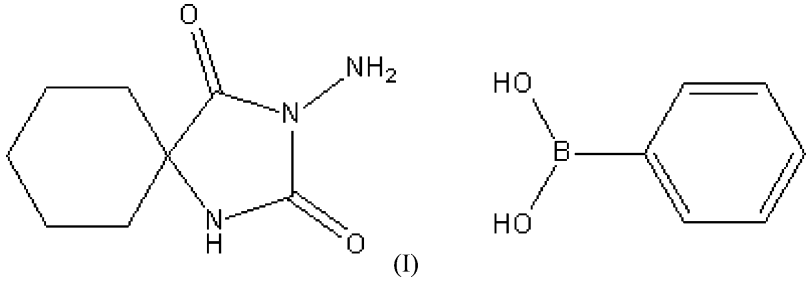
In the crystal structure of the title compound [systematic name: 3-amino-1,3-diazaspiro[4.5]decane-2,4-dione–phenylboronic acid (1/1)], $C_8H_{13}N_3O_2\cdot C_6H_7BO_2$, molecules are held together by O—H···O, N—H···O and C—H···O hydrogen bonds and by an N—H···π interaction.

Comment

Cycloalkanespirohydantoins are the subjects of extensive investigation due to their biological properties (Somsak *et al.*, 2005). Boronic acids, possessing a $-B(OH)_2$ functional group, have been used in areas such as molecular recognition, boron neutron capture therapy (BNCT) agents, inhibitors of proteases, sensors for carbohydrates and reagents in Suzuki cross-coupling reactions, *etc*. (Yang *et al.*, 2003). The title compound, (I), was obtained as a side product in attempts to link phenylboronic acid (PBA) and 3′-aminocyclohexanespiro-5′-hydantoin [SHN; systematic name: 1′-aminocyclohexanespiro-4′-imidazole-2′,5′(3′H,4′H)-dione]. It follows an effort to interact SHN and boric acid $B(OH)_3$, which gave a second polymorph of SHN (Shivachev *et al.*, 2005). In both cases, $B(OH)_3$ and PBA, we expected that the $-NH_2$ functional group of the SHN would be the reaction center, but the expected B—N interaction could not be achieved. Instead, SHN and PBA crystallized in a molecular complex, (I) (Fig. 1).



(I)

Structural parameters of the SHN and PBA molecules are comparable with those reported earlier (Shivachev *et al.*, 2005; Rettig & Trotter, 1977). The PBA hydroxyl groups are in a *syn* position similar to the PBA-4,4′-bipirydine complex (Pedireddi & SeethaLekshmi, 2004). The phenyl and hydantoin rings are essentially planar, with r.m.s. deviations of 0.004 (6) and 0.026 (4) Å, respectively; the angle between their mean planes is 22.23 (13)°. The cyclohexyl ring adopts a chair conformation.

The hydantoin and $-B(OH)_2$ units are largely responsible for the observed hydrogen bonding in the crystal structure (Table 2). Hydrogen bonding between SHN and PBA results in the formation of an SHA and PBA (1/1) unit. Two adjacent

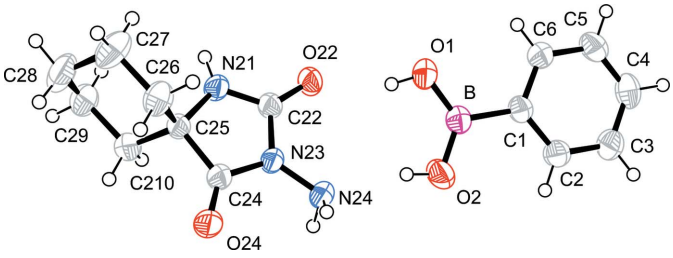


Figure 1
The molecular structure and the atom-numbering scheme of (I), showing 50% probability displacement ellipsoids.

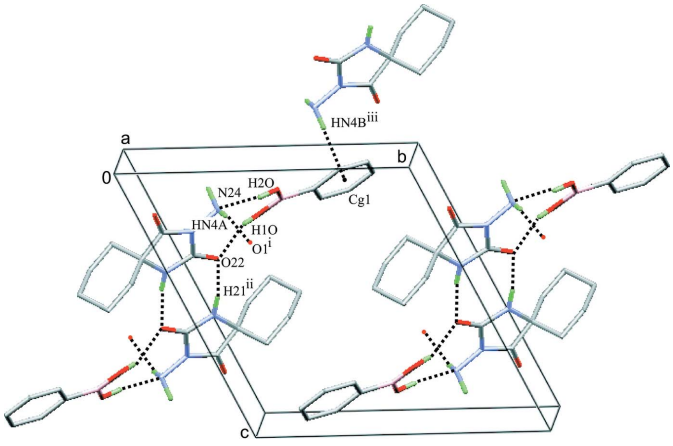


Figure 2
A view of the molecular packing in (I). Hydrogen bonds are represented by dotted lines. Symmetry codes (i), (ii) and (iii) are as given in Table 2.

units are linked through an N21—H21···O22^{ii} hydrogen bond (symmetry code as in Table 2), generating an SHA–PBA (2/2) unit, the main structural motif observed in (I); the hydrogen bonds form a centrosymmetric hydrogen-bonded ring with graph-set $R_2^2(8)$. The SHA–PBA (2/2) units are stacked along the *a* axis through an N24—H*N*4*A*···O1^{i} hydrogen bond (symmetry code as in Table 2). The crystal packing is additionally stabilized by weak N—H···π and C—H···O interactions, producing a pseudo-layer parallel to (011) (Fig. 2).

Experimental

3′-Aminocyclohexanespiro-5′-hydantoin was prepared according to Naydenova *et al.* (2002) and phenylboronic acid was obtained from Acros. The title compound, (I), was obtained by slow evaporation of a 50% ethanol–water solution (20 ml) of SHN (0.18 g) and PBA (0.12 g).

Crystal data

$C_8H_{13}N_3O_2{\cdot}C_6H_7BO_2$
M_r = 305.14
Triclinic, $P\overline{1}$
a = 6.0430 (10) Å
b = 12.0940 (11) Å
c = 12.3011 (12) Å
α = 62.514 (7)°
β = 89.291 (9)°
γ = 80.182 (8)°
V = 783.59 (17) Å^3
Z = 2
D_x = 1.293 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 290 (2) K
Prism, colorless
0.35 × 0.26 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4971 measured reflections
4568 independent reflections
2434 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 30.0°
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.168
S = 1.03
4568 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.1895P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—B	1.564 (3)	C25—N21	1.462 (2)
C22—O22	1.222 (2)	B—O2	1.352 (3)
C22—N23	1.398 (3)	B—O1	1.363 (3)
C24—O24	1.201 (2)	N23—N24	1.408 (2)
C24—N23	1.375 (3)		
O22—C22—N21	128.3 (2)	O2—B—C1	118.6 (2)
N21—C22—N23	106.73 (17)	O1—B—C1	118.4 (2)
O24—C24—C25	127.33 (19)	C24—N23—N24	125.17 (16)
N23—C24—C25	106.97 (17)		

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

*Cg*1 is the centroid of the phenyl ring of PBA.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O22	0.82	2.00	2.778 (2)	158
O2—H2*O*···N24	0.82	2.09	2.897 (2)	167
N24—H*N*4*A*···O1^{i}	0.96	2.18	3.120 (3)	165
N21—H21···O22^{ii}	0.86	2.20	3.037 (2)	166
C2—H2···O24^{iii}	0.93	2.55	3.222 (3)	130
N24—H*N*4*B*···*Cg*1^{iv}	0.94	2.51	3.346 (3)	147

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

The hydroxy and amino H atoms were located in a difference map and their positional parameters were fixed, with U_{iso}(H) = 1.5U_{eq}(O) and 1.2U_{eq}(N). Other H atoms were placed in idealized positions (cyclohexyl C—H = 0.97 Å, aromatic C—H = 0.93 Å and N—H = 0.86 Å) and were constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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