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Key indicators

Single-crystal X-ray study  
T = 295 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
R factor = 0.038  
wR factor = 0.101  
Data-to-parameter ratio = 10.0

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

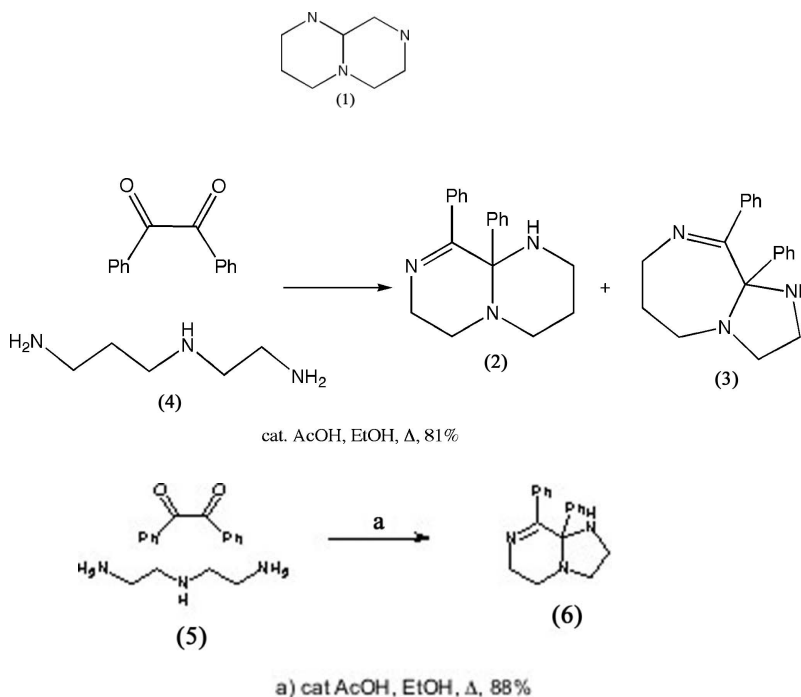
## 9,9a-Diphenyl-1,3,4,6,7,9a-hexahydro-2H-pyrazino[1,2-a]pyrimidine at 130 K

The stereochemistry of the title compound,  $\text{C}_{19}\text{H}_{21}\text{N}_3$ , has been confirmed by a single-crystal X-ray analysis. The bicyclic ring system adopts a *cis*-decalin-like conformation, which presumably minimizes steric repulsion involving the bridge-head phenyl substituent. The conformation of the amino group appears to be dictated by a nitrogen anomeric effect.

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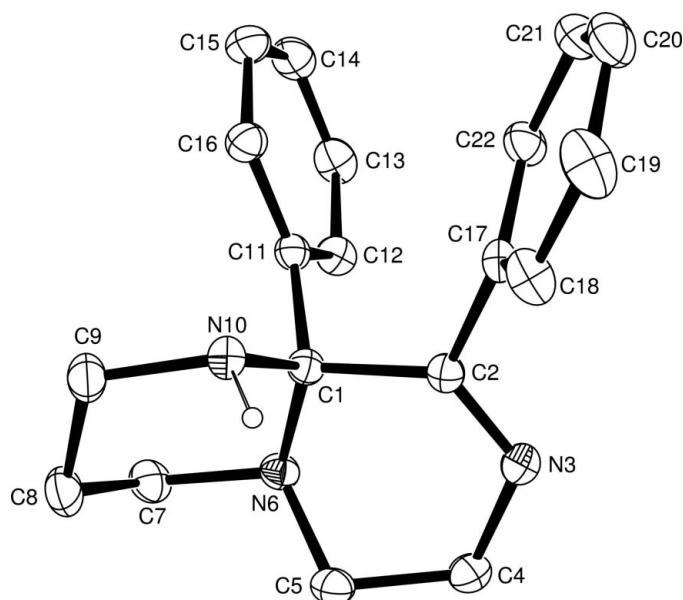
### Comment

Derivatives of 1,4,7-triazabicyclo[4.4.0]decane, (1), have attracted interest in recent years as substance P-binding inhibitors (Wong *et al.*, 1993) and anti-inflammatories (Stasiak *et al.*, 1999), as well as for their potential synthetic use in the selective protection of linear triamines (Okawara *et al.*, 1990).



Substituted derivatives of (1), such as the title compound, (2), are conveniently prepared by the acid-catalysed condensation of an  $\alpha$ -diketone with *N*-(2-aminoethyl)-1,3-propanediamine, (4) (see scheme). The related system, (6), is obtained by condensation of benzil with the dien, (5). In the case of the latter, only one bicyclic system may be generated. However, in the former case, two distinct bicyclic systems may reasonably be expected to form, namely the [4.4.0] system, (2), and the [5.3.0] structure, (3).

A single product is recovered in good yield from the reaction as a colourless crystalline solid. While this material has previously been identified as the [4.4.0] system, (2) (Okawara



**Figure 1**  
The molecular configuration and atom-numbering scheme for (2). Displacement ellipsoids are drawn at the 20% probability level. H atoms have been omitted.

*et al.*, 1990), spectroscopic evidence in support of this claim has not been published. Here, we report the crystal structure of (2) in combination with spectroscopic data which demonstrate that the bicyclo[4.4.0] structure does indeed form, and as a single diastereomer.

Crystals of (2) were grown from ethyl acetate and hexane. Selected bond distances, angles and dihedral angles for (2) are presented in Table 1, and a displacement ellipsoid plot is presented in Fig. 1.

The bicyclic ring system in (2) exists in a *cis*-decalin-like conformation, which is preferred to the alternative *trans*-decalin conformation (which is attainable by inversion at the bridgehead atom N6) due to the presence of the bulky phenyl substituent at C1. Interestingly, the H atom attached at N10, which was located in a difference map and refined satisfactorily without constraint, is axially oriented. This preferred axial orientation of atom H10 may have its origins in an anomeric interaction between the nitrogen lone pair on N10 and the C1–N6 bond (Alder *et al.*, 1999). However, the alternative equatorial conformation would be disfavoured on steric grounds, as H10 would clash with the H atom attached to C16.

There is a weak intermolecular hydrogen bond between atoms H10 and N3 [N10–H10 = 0.89 (1) Å, H10⋯N3<sup>i</sup> = 2.50 (2) Å, N10⋯N3<sup>i</sup> = 3.350 (2) Å and N10–H10⋯N3<sup>i</sup> = 159.1 (8)°; symmetry code: (i)  $-x + 2, \frac{1}{2} - y, \frac{1}{2} - z$ ].

## Experimental

A mixture of *N*-(2-aminoethyl)-1,3-propanediamine (5 ml, 46.3 mmol), benzil (9.73 g, 46.3 mmol), glacial acetic acid (0.5 ml) and ethanol (100 ml) was heated to reflux with stirring for 3 h, over which time a white precipitate formed. Volatiles were removed under reduced pressure and the residue was triturated with hexane and

dried. The crude product was recrystallized from ethyl acetate–hexane (1:1) to afford the title compound, (2), as large colourless blocks (yield 81%; m.p. 378–380 K). Elemental analysis, C<sub>19</sub>H<sub>21</sub>N<sub>3</sub> requires: C 78.3, H 7.3, N 14.4%; found: C 78.0, H 7.4, N 14.7%.

## Crystal data

C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>  
M<sub>r</sub> = 291.39  
Monoclinic, P2<sub>1</sub>/c  
a = 10.4099 (7) Å  
b = 8.2868 (6) Å  
c = 19.1371 (14) Å  
β = 103.483 (1)°  
V = 1605.4 (2) Å<sup>3</sup>

Z = 4  
D<sub>x</sub> = 1.206 Mg m<sup>-3</sup>  
Mo Kα radiation  
μ = 0.07 mm<sup>-1</sup>  
T = 295 (2) K  
Block, colourless  
0.50 × 0.40 × 0.30 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
φ and ω scans  
Absorption correction: none  
8199 measured reflections

2833 independent reflections  
2259 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.059  
θ<sub>max</sub> = 25.0°

## Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.039  
wR(F<sup>2</sup>) = 0.102  
S = 1.05  
2833 reflections  
284 parameters  
H atoms: see below

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0552P)<sup>2</sup>]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> = 0.002  
Δρ<sub>max</sub> = 0.16 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.14 e Å<sup>-3</sup>  
Extinction correction: SHELXL97 (Sheldrick, 1997)  
Extinction coefficient: 0.0091 (18)

**Table 1**

Selected geometric parameters (Å, °).

C1–N10	1.4662 (16)	C4–N3	1.4688 (18)
C1–N6	1.4748 (15)	C4–C5	1.496 (2)
C1–C11	1.5383 (16)	C5–N6	1.4551 (17)
C1–C2	1.5441 (16)	C7–C8	1.515 (2)
C2–N3	1.2703 (15)	C8–C9	1.516 (2)
C2–C17	1.4994 (17)	C9–N10	1.4708 (16)
N10–C1–N6	115.47 (10)	N3–C2–C1	126.38 (11)
N10–C1–C11	110.82 (10)	C17–C2–C1	116.90 (10)
N6–C1–C11	107.90 (9)	N3–C4–C5	112.94 (12)
N10–C1–C2	106.00 (9)	N6–C5–C4	107.84 (12)
N6–C1–C2	109.26 (9)	N6–C7–C8	113.46 (12)
C11–C1–C2	107.09 (9)	C7–C8–C9	109.55 (13)
N3–C2–C17	116.59 (10)	N10–C9–C8	113.31 (12)
N10–C1–C2–N3	117.10 (13)	C4–C5–N6–C1	-66.74 (14)
N6–C1–C2–N3	-7.93 (16)	C8–C7–N6–C5	71.06 (16)
C11–C1–C2–N3	-124.55 (12)	C8–C7–N6–C1	-54.19 (16)
N10–C1–C2–C17	-58.73 (13)	N10–C1–N6–C5	-76.69 (13)
N6–C1–C2–C17	176.23 (9)	C11–C1–N6–C5	158.74 (10)
C11–C1–C2–C17	59.62 (13)	C2–C1–N6–C5	42.64 (12)
N3–C4–C5–N6	54.85 (17)	N10–C1–N6–C7	49.52 (13)
N6–C7–C8–C9	54.90 (18)	C11–C1–N6–C7	-75.06 (12)
C7–C8–C9–N10	-50.40 (19)	C2–C1–N6–C7	168.85 (10)
N10–C1–C11–C16	17.31 (15)	N6–C1–N10–C9	-46.89 (15)
C1–C2–N3–C4	-2.66 (18)	C11–C1–N10–C9	76.15 (13)
C5–C4–N3–C2	-20.98 (19)	C2–C1–N10–C9	-168.01 (11)
C4–C5–N6–C7	168.15 (12)	C8–C9–N10–C1	47.26 (18)

The H atom attached to N10 was located by difference methods and its positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions, with C–H(aromatic) = 0.95 Å and C–H(aliphatic) = 0.99 Å, and they were treated as riding, with U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker 1999); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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