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2-Amino-1-[bis(*N*,*N*-dimethylamino)phosphoramido]benzimidazole

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Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.102
Data-to-parameter ratio = 23.3

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

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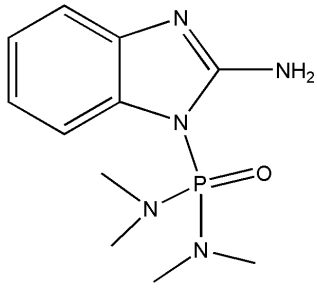
The crystal structure of the title compound, $C_{11}H_{18}N_5OP$, is stabilized by an intermolecular N—H···N-type hydrogen bond and another C—H···O interaction that is intramolecular. The N—H···N hydrogen bonding leads to inversion-related dimers.

Comment

Phosphorylation of benzimidazole has been extensively studied by Matevosyan and co-workers (Matevosyan *et al.* 1981, 1990; Matevosyan & Zalvin, 1998). These substrates are known for their activities as growth regulators, stability inductors for plants and antifungal agents (Zalvin *et al.*, 1999; Matevosyan & Zalvin, 1998; Anderson *et al.*, 2001). They are also used as intermediates in the Wittig–Horner reaction for the preparation of substituted olefins (Maier & Rist, 1987). Direct phosphorylation of benzimidazole can be accomplished by the reaction the sodium salt of 2-aminobenzimidazole derivative with chlorophosphoramide (Raouafi *et al.*, 2003). The structure determination of the title compound, (I), was undertaken as a part of our studies on phosphorylated benzimidazole derivatives.



(I)

The X-ray structure of (I) (Fig. 1), shows that the five-membered ring has an r.m.s. deviation of 0.004 Å, with the P atom lying 0.311 (2) Å outside this plane. The six-membered ring has an r.m.s deviation of 0.005 Å and makes an angle of 2.7 (9) ° with the five-membered ring.

The P—N4 [1.6317 (11) Å] and P—N5 [1.6352 (10) Å] bonds are shorter than the P—N1 bond [1.7124 (9) Å] (Table 1) which is close to standard non conjugated P—N bond length (1.73 Å; Allen *et al.*, 1987; Schulz *et al.*, 1999; Cruickshank, 1964; Yamamoto & Akiba, 2000). The three C—N bond lengths of the cyclic guanidine function are not equal; the C1—N3 and C1—N2 bond lengths are 1.3199 (14) Å and 1.3396 (14) Å, respectively, while the C1—N1 bond length is

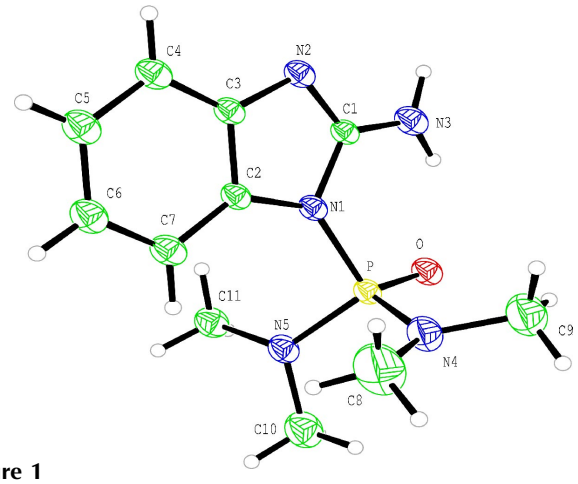


Figure 1
ORTEX (McArdle, 1995) plot of the title compound. Displacement ellipsoids are drawn at the 40% probability level. H atoms are drawn as small spheres of arbitrary radius.

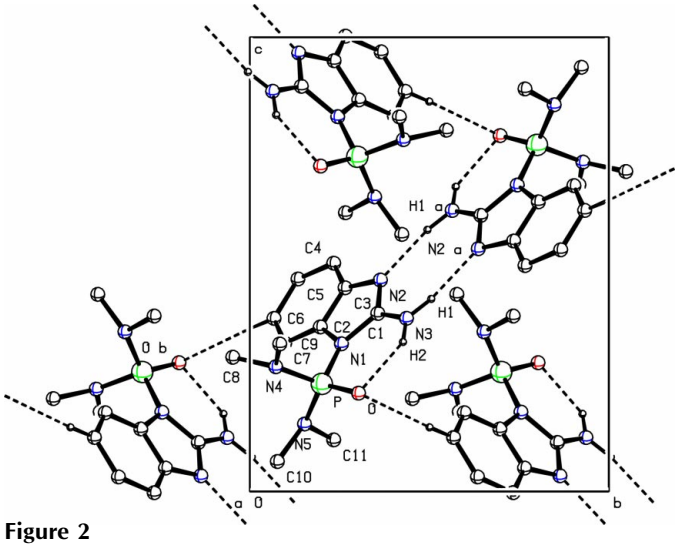


Figure 2
PLUTON view (Spek, 2001) of the unit-cell packing, with hydrogen bonds shown as dashed lines. H atoms not participating in hydrogen bonding have been omitted for clarity.

1.4140 (14) Å. These three bonds are shorter than a standard single C—N bond (1.47 Å; Hamada *et al.*, 1986) and longer than a pure non-conjugated C═N bond (1.27 Å; Häfelinger, 1970). This could be explained by conjugation of only two bonds (C1—N2 and C1—N3). Unlike the non-cyclic guanidine (Bishop *et al.*, 2003), the C1—N1 bond is not involved in this conjugation.

The packing reveals the presence of three intermolecular interactions (Table 2). The N3—H1···N2^{iii} hydrogen bond [symmetry code: (iii) $-x, -y, -z$] leads to inversion-related dimers (Fig. 2).

Experimental

The aminolysis of the product from the reaction of *N*-benzimidazol-2-yl imidate sodium salt and tetramethylchlorophosphoramide gives the corresponding compound, (I), in 90% yield. Compound (I) was recrystallized twice from tetrahydrofuran (m.p. = 472–473 K). The spectroscopic characterization was obtained from the analysis of IR, ^{1}H, ^{13}C and ^{31}P NMR spectra. IR ($CHCl_3$, cm^{-1}): ν_{NH} = 3489, ν_{NH} = 3331, δ_{NH} = 1633, ν_{PO} = 1251. ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 2.72 (*d*, 12H, N—CH_3, $^{3}J_{PH}$ = 11 Hz), 6.93–7.31 (*m*, 6H, 4 CH = C, 2N—H). ^{13}C NMR: 36.09, 36.15, 111.20, 115.29, 119.33, 122.54, 132.68, 143.46, 157.07. ^{31}P NMR: 15.21.

Crystal data

$C_{11}H_{18}N_5OP$
M_r = 267.27
Monoclinic, $P2_1/n$
a = 9.8997 (6) Å
b = 10.5514 (6) Å
c = 13.739 (1) Å
β = 103.613 (3)°
V = 1394.80 (15) Å^3
Z = 4
D_x = 1.273 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5780 reflections
θ = 2–30°
μ = 0.20 mm^{-1}
T = 133 (2) K
Prism, colourless
0.29 × 0.28 × 0.27 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω and φ scans
Absorption correction: none
28550 measured reflections
4081 independent reflections
3346 reflections with >2$\sigma(I)$
R_{int} = 0.036
θ_{max} = 30.0°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.102
S = 1.05
4081 reflections
175 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.3169P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P—N4	1.6317 (11)	N1—C1	1.4140 (14)
P—N5	1.6352 (10)	N1—C2	1.4242 (14)
P—N1	1.7124 (9)	N3—C1	1.3396 (14)
N4—P—N1	111.39 (5)	N2—C1—N3	123.99 (10)
N5—P—N1	101.86 (5)	N2—C1—N1	113.42 (10)
C1—N1—C2	104.65 (9)	N3—C1—N1	122.59 (10)
C2—N1—C1—N2	1.08 (13)	P—N1—C2—C7	−16.60 (19)
C2—N1—C1—N3	−179.07 (11)	P—N1—C2—C3	166.78 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O^{i}	0.95	2.56	3.4982 (15)	169
C9—H9*C*···O^{ii}	0.98	2.62	3.5932 (18)	175
N3—H1···N2^{iii}	0.925 (18)	2.024 (18)	2.9402 (14)	170.1 (15)

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $1-x, 1-y, 1-z$.

Methyl H atoms were identified in difference syntheses, idealized and then refined using rigid methyl groups [C—H 0.98 Å,H—C—H 109.5°; U_{iso}(H) = 1.2U_{eq}(C)] and allowed to rotate, but not to tip. H7 was included using a riding model, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). N—H H atoms were freely refined.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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