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*N*⁴,*N*⁶-Dimethyl-5-nitro-*N*⁴,*N*⁶-diphenylpyrimidine-4,6-diamine

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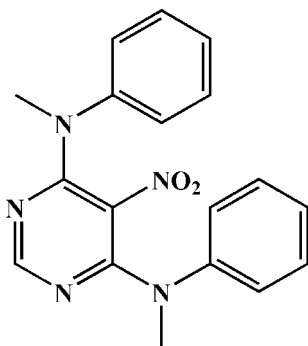
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 Key indicators: single-crystal X-ray study; *T* = 293 K; mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$; *R* factor = 0.074; *wR* factor = 0.146; data-to-parameter ratio = 16.9.

In the title compound, $\text{C}_{18}\text{H}_{17}\text{N}_5\text{O}_2$, the pyrimidine ring makes dihedral angles of 66.09 (12), 71.39 (13) and 56.7 (3)° with two phenyl rings and the nitro group, respectively. The dihedral angle between the two phenyl rings is 44.05 (14)°.

Related literature

For applications of pyrimidine diamines, see: Barillari *et al.* (2001); Che *et al.* (2008); Itoh *et al.* (2004); Koppel & Robins (1958); Shi *et al.* (2011).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{17}\text{N}_5\text{O}_2$	$V = 1689.8 (6) \text{ \AA}^3$
$M_r = 335.37$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.794 (2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 7.0019 (14) \text{ \AA}$	$T = 293 \text{ K}$
$c = 23.650 (6) \text{ \AA}$	$0.50 \times 0.12 \times 0.10 \text{ mm}$
$\beta = 109.02 (3)^\circ$	

Data collection

Rigaku R-Axis RAPID diffractometer	15784 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	3843 independent reflections
$T_{\min} = 0.956$, $T_{\max} = 0.991$	2018 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.108$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.074$	228 parameters
$wR(F^2) = 0.146$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
3843 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2768).

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supporting information

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N*⁴,*N*⁶-Dimethyl-5-nitro-*N*⁴,*N*⁶-diphenylpyrimidine-4,6-diamine*Fuqiang Shi, Li-Hong Zhu, Long Zhang and Ya-Feng Li****S1. Comment**

Pyrimidine diamines, important intermediate products (Koppel *et al.*, 1958; Itoh *et al.*, 2004; Che *et al.*, 2008; Shi *et al.*, 2011), exhibit a wide range of biological activities (Barillari *et al.*, 2001). Here, the crystal structure of *N*⁴,*N*⁶-dimethyl-5-nitro-*N*⁴,*N*⁶-diphenylpyrimidine-4,6-diamine is determined by X-ray single crystal diffraction.

In the structure of the title compound (Fig. 1), the dihedral angles between pyrimidyl and two phenyl rings and between two phenyl rings are 66.09 (12), 71.39 (13) and 44.05 (14)°, respectively.

S2. Experimental

4,6-Dichloro-5-nitro-pyrimidine (192 mg, 1 mmol), *N*-methylbenzenamine (0.33 mL, 3 mmol) and triethylamine (0.22 mL, 2 mmol) were dissolved in anhydrous THF (10 mL). The reaction mixture was stirred in reflux overnight. The product was concentrated in vacuo, diluted with water, and extracted with EtOAc. The organic phase was washed with 1mol/L HCl, brine, and dried over anhydrous MgSO₄. The crude product was purified by flash chromatography (elution with 15% EtOAc in petroleum ether) to give *N*⁴,*N*⁶-dimethyl-5-nitro-*N*⁴,*N*⁶-diphenylpyrimidine-4,6-diamine (yellow solid, 256 mg, 76.4%, 166.4-168.6 °C). ¹H NMR (CDCl₃, 400 Hz), δ: 8.46 (s, 1H), 7.23-7.19(m, 4H), 7.13-7.11(m, 2H), 7.02-6.99(m, 4H), 3.50 (s, 6H); ¹³C NMR (CDCl₃, 100 Hz), δ: 156.0, 155.7, 144.2, 129.2, 126.6, 125.1, 121.0, 42.0; ES-MS: 336.1 [(M + H⁺)].

S3. Refinement

All H atoms were located from difference Fourier maps. H atoms attached to C atoms were treated as riding [C—H = 0.93–0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

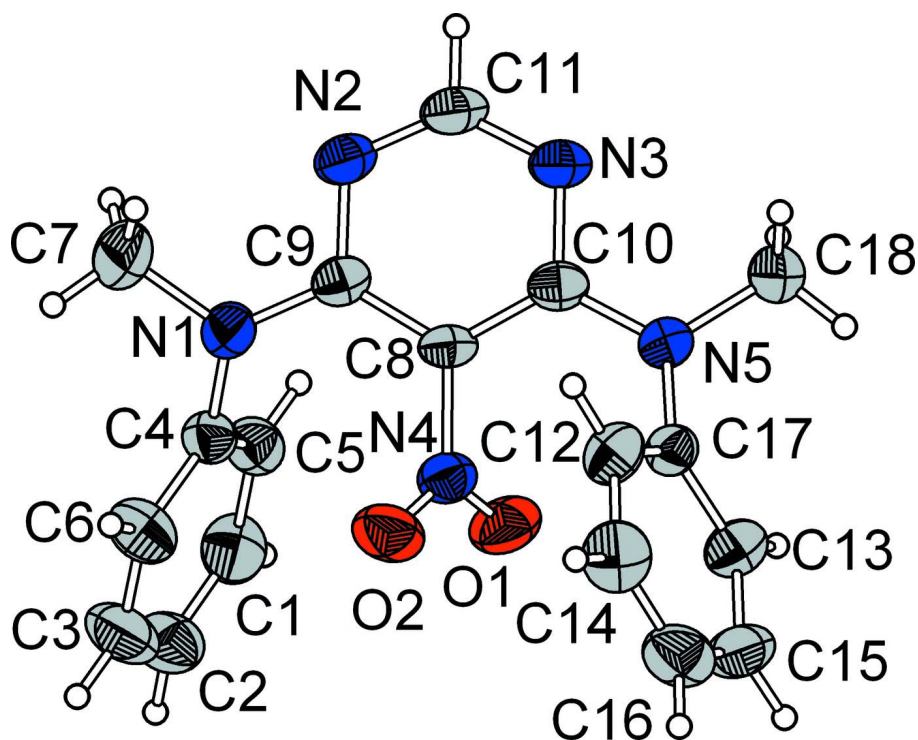


Figure 1

The molecular structure of the title compound, with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

*N*⁴,*N*⁶-Dimethyl-5-nitro-*N*⁴,*N*⁶- diphenylpyrimidine-4,6-diamine

Crystal data

C₁₈H₁₇N₅O₂

*M*_r = 335.37

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 10.794 (2) Å

b = 7.0019 (14) Å

c = 23.650 (6) Å

β = 109.02 (3)°

V = 1689.8 (6) Å³

Z = 4

F(000) = 704

*D*_x = 1.318 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 500 reflections

θ = 3.1–27.5°

μ = 0.09 mm⁻¹

T = 293 K

Block, colorless

0.50 × 0.12 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.00 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

*T*_{min} = 0.956, *T*_{max} = 0.991

15784 measured reflections

3843 independent reflections

2018 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.108

θ_{max} = 27.5°, θ_{min} = 3.1°

h = -14→13

k = -9→9

l = -30→30

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.074$ $wR(F^2) = 0.146$ $S = 1.05$

3843 reflections

228 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 0.0764P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$ *Special details*

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.84317 (18)	0.0703 (3)	0.35192 (9)	0.0577 (6)
O2	0.85674 (17)	0.2808 (3)	0.42079 (8)	0.0586 (6)
N1	0.5774 (2)	0.2175 (3)	0.41820 (9)	0.0435 (6)
N2	0.45045 (19)	0.3519 (3)	0.32882 (10)	0.0434 (6)
N3	0.52690 (19)	0.3954 (3)	0.24557 (9)	0.0412 (5)
N4	0.7997 (2)	0.2043 (3)	0.37282 (10)	0.0424 (6)
N5	0.74616 (19)	0.3627 (3)	0.25459 (9)	0.0393 (5)
C1	0.7275 (3)	-0.2635 (4)	0.44234 (13)	0.0553 (8)
H1	0.7216	-0.3782	0.4218	0.066*
C2	0.8135 (3)	-0.2471 (5)	0.49962 (14)	0.0639 (9)
H2	0.8663	-0.3498	0.5176	0.077*
C3	0.8210 (3)	-0.0796 (5)	0.53010 (13)	0.0678 (10)
H3	0.8784	-0.0692	0.5690	0.081*
C4	0.6587 (2)	0.0578 (4)	0.44551 (10)	0.0387 (6)
C5	0.6500 (3)	-0.1108 (4)	0.41512 (11)	0.0446 (7)
H5	0.5921	-0.1224	0.3763	0.054*
C6	0.7441 (3)	0.0745 (4)	0.50349 (12)	0.0562 (8)
H6	0.7496	0.1885	0.5243	0.067*
C7	0.4741 (3)	0.2699 (5)	0.44293 (13)	0.0705 (10)
H7A	0.4531	0.4028	0.4354	0.085*
H7B	0.5041	0.2470	0.4853	0.085*
H7C	0.3975	0.1943	0.4243	0.085*
C8	0.6703 (2)	0.2779 (3)	0.33805 (10)	0.0338 (6)
C9	0.5681 (2)	0.2799 (3)	0.36205 (11)	0.0362 (6)
C10	0.6494 (2)	0.3447 (3)	0.27970 (11)	0.0359 (6)

C11	0.4380 (2)	0.3965 (4)	0.27283 (13)	0.0456 (7)
H11	0.3545	0.4341	0.2493	0.055*
C12	0.8912 (3)	0.5770 (4)	0.32865 (12)	0.0461 (7)
H12	0.8181	0.6442	0.3303	0.055*
C13	0.9840 (3)	0.3278 (4)	0.28633 (12)	0.0474 (7)
H13	0.9742	0.2256	0.2601	0.057*
C14	1.0143 (3)	0.6310 (4)	0.36414 (13)	0.0573 (8)
H14	1.0246	0.7332	0.3904	0.069*
C15	1.1078 (3)	0.3861 (4)	0.32153 (13)	0.0573 (8)
H15	1.1815	0.3241	0.3184	0.069*
C16	1.1223 (3)	0.5339 (5)	0.36078 (13)	0.0604 (9)
H16	1.2056	0.5690	0.3853	0.072*
C17	0.8759 (2)	0.4228 (3)	0.29054 (10)	0.0365 (6)
C18	0.7094 (3)	0.3940 (4)	0.19040 (10)	0.0503 (7)
H18A	0.6509	0.2945	0.1697	0.060*
H18B	0.7865	0.3927	0.1786	0.060*
H18C	0.6664	0.5154	0.1805	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0466 (12)	0.0511 (12)	0.0785 (14)	0.0176 (10)	0.0247 (11)	0.0139 (11)
O2	0.0418 (11)	0.0717 (14)	0.0505 (11)	-0.0089 (10)	-0.0010 (9)	0.0050 (11)
N1	0.0423 (12)	0.0468 (13)	0.0451 (12)	0.0077 (11)	0.0194 (10)	0.0064 (11)
N2	0.0315 (12)	0.0430 (13)	0.0557 (14)	0.0047 (10)	0.0143 (10)	0.0090 (11)
N3	0.0313 (12)	0.0410 (12)	0.0469 (12)	0.0030 (10)	0.0066 (10)	0.0064 (10)
N4	0.0323 (12)	0.0434 (14)	0.0507 (14)	0.0013 (11)	0.0126 (11)	0.0124 (12)
N5	0.0314 (11)	0.0470 (13)	0.0389 (12)	0.0007 (10)	0.0108 (10)	0.0015 (10)
C1	0.065 (2)	0.0434 (16)	0.0620 (18)	0.0039 (15)	0.0270 (16)	0.0043 (15)
C2	0.059 (2)	0.064 (2)	0.066 (2)	0.0128 (17)	0.0162 (16)	0.0262 (18)
C3	0.058 (2)	0.084 (2)	0.0471 (17)	-0.0004 (19)	-0.0025 (15)	0.0157 (18)
C4	0.0346 (14)	0.0434 (15)	0.0364 (13)	-0.0024 (12)	0.0091 (11)	0.0021 (12)
C5	0.0439 (15)	0.0456 (17)	0.0420 (14)	-0.0041 (13)	0.0107 (12)	0.0034 (13)
C6	0.0603 (19)	0.0576 (19)	0.0424 (15)	-0.0027 (15)	0.0054 (14)	-0.0024 (14)
C7	0.069 (2)	0.092 (2)	0.0630 (19)	0.0289 (19)	0.0377 (17)	0.0118 (18)
C8	0.0234 (12)	0.0313 (13)	0.0417 (14)	0.0007 (10)	0.0037 (11)	0.0031 (11)
C9	0.0312 (13)	0.0316 (13)	0.0450 (14)	0.0009 (11)	0.0112 (12)	-0.0002 (12)
C10	0.0302 (13)	0.0311 (13)	0.0424 (14)	-0.0017 (11)	0.0063 (12)	-0.0019 (11)
C11	0.0287 (14)	0.0426 (16)	0.0610 (18)	0.0040 (12)	0.0087 (13)	0.0123 (14)
C12	0.0433 (16)	0.0426 (15)	0.0566 (16)	-0.0036 (13)	0.0219 (13)	-0.0039 (14)
C13	0.0416 (15)	0.0460 (16)	0.0568 (16)	0.0059 (13)	0.0188 (13)	-0.0010 (13)
C14	0.059 (2)	0.0513 (17)	0.0600 (18)	-0.0148 (16)	0.0176 (15)	-0.0084 (15)
C15	0.0347 (15)	0.064 (2)	0.073 (2)	0.0080 (15)	0.0174 (15)	0.0161 (17)
C16	0.0452 (18)	0.068 (2)	0.0580 (18)	-0.0170 (17)	0.0033 (15)	0.0101 (17)
C17	0.0321 (13)	0.0390 (14)	0.0393 (13)	-0.0003 (12)	0.0129 (11)	0.0038 (12)
C18	0.0465 (16)	0.0653 (19)	0.0403 (15)	0.0101 (15)	0.0157 (13)	0.0026 (14)

Geometric parameters (Å, °)

O1—N4	1.223 (3)	C5—H5	0.9300
O2—N4	1.224 (3)	C6—H6	0.9300
N1—C9	1.370 (3)	C7—H7A	0.9600
N1—C4	1.438 (3)	C7—H7B	0.9600
N1—C7	1.464 (3)	C7—H7C	0.9600
N2—C11	1.324 (3)	C8—C9	1.395 (3)
N2—C9	1.355 (3)	C8—C10	1.404 (3)
N3—C11	1.319 (3)	C11—H11	0.9300
N3—C10	1.353 (3)	C12—C14	1.374 (4)
N4—C8	1.464 (3)	C12—C17	1.382 (3)
N5—C10	1.366 (3)	C12—H12	0.9300
N5—C17	1.444 (3)	C13—C17	1.375 (4)
N5—C18	1.455 (3)	C13—C15	1.385 (4)
C1—C2	1.375 (4)	C13—H13	0.9300
C1—C5	1.381 (4)	C14—C16	1.374 (4)
C1—H1	0.9300	C14—H14	0.9300
C2—C3	1.365 (4)	C15—C16	1.365 (4)
C2—H2	0.9300	C15—H15	0.9300
C3—C6	1.382 (4)	C16—H16	0.9300
C3—H3	0.9300	C18—H18A	0.9600
C4—C5	1.369 (3)	C18—H18B	0.9600
C4—C6	1.386 (3)	C18—H18C	0.9600
C9—N1—C4	121.6 (2)	C9—C8—N4	120.7 (2)
C9—N1—C7	118.9 (2)	C10—C8—N4	119.2 (2)
C4—N1—C7	116.6 (2)	N2—C9—N1	116.1 (2)
C11—N2—C9	116.0 (2)	N2—C9—C8	118.9 (2)
C11—N3—C10	115.8 (2)	N1—C9—C8	125.0 (2)
O1—N4—O2	124.5 (2)	N3—C10—N5	117.0 (2)
O1—N4—C8	117.7 (2)	N3—C10—C8	119.1 (2)
O2—N4—C8	117.8 (2)	N5—C10—C8	123.9 (2)
C10—N5—C17	120.2 (2)	N3—C11—N2	129.4 (2)
C10—N5—C18	118.7 (2)	N3—C11—H11	115.3
C17—N5—C18	116.9 (2)	N2—C11—H11	115.3
C2—C1—C5	120.4 (3)	C14—C12—C17	120.0 (3)
C2—C1—H1	119.8	C14—C12—H12	120.0
C5—C1—H1	119.8	C17—C12—H12	120.0
C3—C2—C1	119.8 (3)	C17—C13—C15	119.3 (3)
C3—C2—H2	120.1	C17—C13—H13	120.4
C1—C2—H2	120.1	C15—C13—H13	120.4
C2—C3—C6	120.5 (3)	C16—C14—C12	119.9 (3)
C2—C3—H3	119.8	C16—C14—H14	120.0
C6—C3—H3	119.8	C12—C14—H14	120.0
C5—C4—C6	120.1 (2)	C16—C15—C13	120.5 (3)
C5—C4—N1	120.5 (2)	C16—C15—H15	119.8
C6—C4—N1	119.4 (2)	C13—C15—H15	119.8

C4—C5—C1	119.7 (2)	C15—C16—C14	120.2 (3)
C4—C5—H5	120.1	C15—C16—H16	119.9
C1—C5—H5	120.1	C14—C16—H16	119.9
C3—C6—C4	119.5 (3)	C13—C17—C12	120.1 (2)
C3—C6—H6	120.3	C13—C17—N5	120.0 (2)
C4—C6—H6	120.3	C12—C17—N5	119.9 (2)
N1—C7—H7A	109.5	N5—C18—H18A	109.5
N1—C7—H7B	109.5	N5—C18—H18B	109.5
H7A—C7—H7B	109.5	H18A—C18—H18B	109.5
N1—C7—H7C	109.5	N5—C18—H18C	109.5
H7A—C7—H7C	109.5	H18A—C18—H18C	109.5
H7B—C7—H7C	109.5	H18B—C18—H18C	109.5
C9—C8—C10	120.1 (2)		
