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5-(Biphenyl-4-yl)-3-(4-*tert*-butylphenyl)-1*H*-pyrazole

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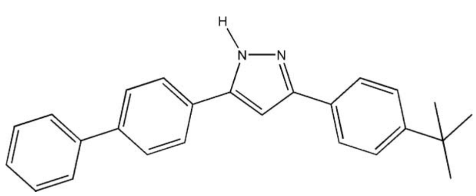
Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.004 Å; R factor = 0.060; wR factor = 0.184; data-to-parameter ratio = 14.3.

The molecules of the title compound, $C_{25}H_{24}N_2$, are connected by intermolecular N—H···N hydrogen bonds to form dimers. The crystal packing is stabilized by van der Waals forces.

Related literature

For related literature, see: Aggarwal *et al.* (2003); Claramunt *et al.* (2006); Hayter *et al.* (2006); Stephen & Swaminathan (2006).



Experimental

Crystal data

$C_{25}H_{24}N_2$
M_r = 352.46
Triclinic, $P\bar{1}$
a = 6.1119 (6) Å
b = 12.0498 (11) Å
c = 13.9657 (13) Å
α = 100.158 (2)°
β = 95.028 (2)°
γ = 103.283 (2)°
V = 976.47 (16) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 292 (2) K
0.30 × 0.16 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
6143 measured reflections
3570 independent reflections
2481 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.184
S = 1.10
3570 reflections
250 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N1^{i}	0.79 (3)	2.25 (3)	2.940 (3)	146 (3)

Symmetry code: (i) $-x, -y+1, -z$.

Data collection: *SMART* (Bruker, 1997); 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, 2001); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2023).

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supplementary materials

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5-(Biphenyl-4-yl)-3-(4-*tert*-butylphenyl)-1*H*-pyrazole

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Comment

Pyrazoles are an important class of heteroaromatic ring systems that find extensive use in the pharmaceutical industry (Aggarwal *et al.*, 2003; Stephen *et al.*, 2006), and have received much more interesting in what concerns the N—H···N hydrogen bonds network in their crystals (Claramunt *et al.*, 2006; Hayter *et al.*, 2006). In the crystal structure of the title compound (I) (Fig. 1), the molecules are connected by N—H···N intermolecular hydrogen bonds to form dimer, with the N···H hydrogen bonds distance of 2.25 (3) Å. The pyrazolyl ring makes dihedral angles of 9.18° and 11.60° with two benzene rings (C5—C10) and (C14—C19), respectively. The crystal packing is stabilized by van der Waals forces.

Experimental

Hydrazine monohydrate (3 ml) in ethol (10 ml) was added dropwise to a refluxing ethanol (30 ml) solution of the appropriate 1-(4-*tert*-butylphenyl)-3-(4-phenylphenyl) propane-1,3-dione (3.56 g). The solution was refluxed for 3 h and removed by evaporation, the residual solid was recrystallized from dilute ethanol solution to give the title compound (I) (yield 2.75 g, 78.1%, m.p. 495 K). Crystals suitable for X-ray diffraction were grown by slow evaporation of the CH_2Cl_2—EtOH (1:2) solutions at room temperature. Spectroscopic analysis, ^{1}H NMR ($CDCl_3$, 400 MHz): 1.34(s, 9H, $C(CH_3)_3$), 6.10(s, 1H, pyrazolyl N—H), 6.89(s, 1H, pyrazolyl C—H), 7.36–7.47(m, 5H, Ar—H), 7.58–7.62(m, 4H, Ar—H), 7.72(d, 2H, 8.4 Hz, Ar—H), 7.83(d, 2H, 8.4 Hz, Ar—H); analysis, calculated for $C_{25}H_{24}N_2$: C 85.19, H 6.86%, N 7.95%; found: C 85.25, H 6.85%; N 7.94%.

Refinement

The H atoms were included in the riding model approximation with C—H = 0.93 to 0.97 Å and with U_{iso}(H) = 1.2 (1.5 for methyl) U_{eq}(C).

Figures

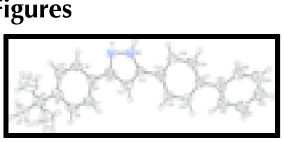


Fig. 1. View of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

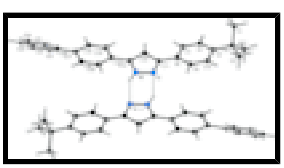


Fig. 2. Part of the crystal structure of (I). *ORTEP* view of the dimer formed by H-bonding of one independent molecule with its $-x$, $1 - y$, $-z$ symmetry counterpart. The dashed line indicates the intermolecular N—H···N hydrogen bonds.

3-(4-*tert*-Butylphenyl)-5-(biphenyl-4-yl)-1*H*-pyrazole

Crystal data

$C_{25}H_{24}N_2$	$Z = 2$
$M_r = 352.46$	$F_{000} = 376$
Triclinic, $P\overline{1}$	$D_x = 1.199$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 495 K
$a = 6.1119 (6)$ Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 12.0498 (11)$ Å	Cell parameters from 1534 reflections
$c = 13.9657 (13)$ Å	$\theta = 2.5–24.3°$
$\alpha = 100.158 (2)°$	$\mu = 0.07$ mm^{-1}
$\beta = 95.028 (2)°$	$T = 292 (2)$ K
$\gamma = 103.283 (2)°$	Block, colorless
$V = 976.47 (16)$ Å^3	0.30 × 0.16 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer	3570 independent reflections
Radiation source: fine-focus sealed tube	2481 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.023$
Detector resolution: 0 pixels mm^{-1}	$\theta_{max} = 25.5°$
$T = 292(2)$ K	$\theta_{min} = 1.5°$
φ and ω scans	$h = -7\rightarrow7$
Absorption correction: none	$k = -14\rightarrow14$
6143 measured reflections	$l = -16\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.060$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.184$	$w = 1/[\sigma^2(F_o^2) + (0.0796P)^2 + 0.2893P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
3570 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
250 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7158 (7)	0.3551 (3)	0.5414 (2)	0.0950 (13)
H1A	0.6643	0.4230	0.5656	0.142*
H1B	0.8564	0.3780	0.5158	0.142*
H1C	0.7382	0.3154	0.5939	0.142*
C2	0.6293 (6)	0.1697 (3)	0.4199 (3)	0.0783 (10)
H2A	0.6593	0.1307	0.4720	0.117*
H2B	0.7672	0.1962	0.3934	0.117*
H2C	0.5192	0.1167	0.3692	0.117*
C3	0.3255 (7)	0.2309 (5)	0.5034 (3)	0.123 (2)
H3A	0.2162	0.1751	0.4542	0.184*
H3B	0.2639	0.2955	0.5270	0.184*
H3C	0.3610	0.1950	0.5569	0.184*
C4	0.5378 (5)	0.2736 (2)	0.4597 (2)	0.0536 (7)
C5	0.4971 (4)	0.3378 (2)	0.37709 (18)	0.0449 (6)
C6	0.6779 (5)	0.4085 (3)	0.3445 (2)	0.0563 (8)
H6	0.8247	0.4156	0.3735	0.068*
C7	0.6464 (5)	0.4678 (3)	0.2712 (2)	0.0539 (7)
H7	0.7719	0.5138	0.2517	0.065*
C8	0.4300 (4)	0.4606 (2)	0.22552 (18)	0.0403 (6)
C9	0.2523 (4)	0.3885 (2)	0.25587 (19)	0.0477 (7)
H9	0.1057	0.3797	0.2258	0.057*
C10	0.2846 (4)	0.3289 (2)	0.3294 (2)	0.0506 (7)
H10	0.1590	0.2812	0.3474	0.061*
C11	0.3994 (4)	0.5269 (2)	0.14872 (18)	0.0404 (6)
C12	0.5617 (4)	0.6131 (2)	0.12097 (18)	0.0419 (6)
H12	0.7135	0.6406	0.1478	0.050*
C13	0.4531 (4)	0.6495 (2)	0.04618 (18)	0.0378 (6)
C14	0.5372 (4)	0.7374 (2)	−0.01143 (17)	0.0380 (6)
C15	0.7680 (4)	0.7856 (2)	−0.00671 (18)	0.0421 (6)
H15	0.8705	0.7620	0.0334	0.051*
C16	0.8468 (4)	0.8678 (2)	−0.06062 (19)	0.0438 (6)
H16	1.0024	0.8979	−0.0568	0.053*
C17	0.7011 (4)	0.9072 (2)	−0.12046 (18)	0.0395 (6)

C18	0.4706 (4)	0.8583 (2)	−0.1253 (2)	0.0520 (7)
H18	0.3685	0.8821	−0.1655	0.062*
C19	0.3893 (4)	0.7753 (2)	−0.0721 (2)	0.0488 (7)
H19	0.2338	0.7443	−0.0767	0.059*
C20	0.7866 (4)	0.9963 (2)	−0.17797 (18)	0.0420 (6)
C21	0.9742 (5)	0.9931 (3)	−0.2268 (2)	0.0577 (8)
H21	1.0473	0.9341	−0.2229	0.069*
C22	1.0547 (5)	1.0752 (3)	−0.2810 (2)	0.0663 (9)
H22	1.1799	1.0708	−0.3135	0.080*
C23	0.9497 (5)	1.1638 (3)	−0.2871 (2)	0.0647 (9)
H23	1.0037	1.2198	−0.3232	0.078*
C24	0.7637 (6)	1.1687 (3)	−0.2389 (2)	0.0623 (8)
H24	0.6926	1.2285	−0.2426	0.075*
C25	0.6814 (5)	1.0863 (2)	−0.1853 (2)	0.0495 (7)
H25	0.5549	1.0906	−0.1538	0.059*
N1	0.2007 (3)	0.51032 (18)	0.09379 (15)	0.0449 (5)
N2	0.2365 (4)	0.58635 (19)	0.03297 (17)	0.0442 (6)
H2	0.148 (5)	0.580 (2)	−0.014 (2)	0.053*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.147 (4)	0.081 (3)	0.055 (2)	0.033 (2)	−0.021 (2)	0.0170 (19)
C2	0.104 (3)	0.067 (2)	0.075 (2)	0.037 (2)	0.007 (2)	0.0256 (18)
C3	0.086 (3)	0.219 (5)	0.119 (4)	0.064 (3)	0.047 (3)	0.127 (4)
C4	0.0585 (18)	0.0610 (18)	0.0472 (16)	0.0205 (14)	0.0046 (13)	0.0204 (14)
C5	0.0501 (16)	0.0498 (15)	0.0380 (14)	0.0182 (12)	0.0046 (12)	0.0101 (12)
C6	0.0417 (16)	0.074 (2)	0.0564 (17)	0.0158 (14)	−0.0034 (13)	0.0252 (15)
C7	0.0397 (15)	0.0643 (18)	0.0602 (18)	0.0090 (13)	0.0027 (13)	0.0267 (15)
C8	0.0406 (14)	0.0394 (13)	0.0392 (14)	0.0105 (11)	0.0011 (11)	0.0054 (11)
C9	0.0365 (14)	0.0543 (16)	0.0512 (16)	0.0086 (12)	−0.0027 (12)	0.0159 (13)
C10	0.0421 (15)	0.0571 (17)	0.0547 (16)	0.0079 (12)	0.0075 (13)	0.0218 (14)
C11	0.0374 (14)	0.0404 (13)	0.0416 (14)	0.0100 (11)	−0.0011 (11)	0.0060 (11)
C12	0.0352 (13)	0.0421 (14)	0.0447 (15)	0.0063 (11)	−0.0036 (11)	0.0081 (11)
C13	0.0291 (13)	0.0393 (13)	0.0440 (14)	0.0081 (10)	0.0047 (10)	0.0063 (11)
C14	0.0384 (14)	0.0362 (13)	0.0385 (13)	0.0106 (10)	0.0025 (11)	0.0047 (11)
C15	0.0348 (13)	0.0431 (14)	0.0476 (15)	0.0098 (11)	−0.0045 (11)	0.0115 (12)
C16	0.0336 (13)	0.0421 (14)	0.0552 (16)	0.0070 (11)	0.0016 (12)	0.0143 (12)
C17	0.0391 (14)	0.0383 (13)	0.0413 (14)	0.0120 (11)	0.0032 (11)	0.0064 (11)
C18	0.0387 (15)	0.0654 (18)	0.0601 (18)	0.0186 (13)	0.0016 (13)	0.0291 (15)
C19	0.0307 (14)	0.0599 (17)	0.0591 (17)	0.0097 (12)	0.0034 (12)	0.0239 (14)
C20	0.0408 (14)	0.0431 (14)	0.0431 (14)	0.0119 (11)	0.0008 (11)	0.0119 (12)
C21	0.0525 (17)	0.0647 (18)	0.0658 (19)	0.0228 (14)	0.0088 (15)	0.0281 (16)
C22	0.0474 (17)	0.084 (2)	0.079 (2)	0.0188 (16)	0.0214 (16)	0.0391 (19)
C23	0.066 (2)	0.0635 (19)	0.068 (2)	0.0078 (16)	0.0062 (17)	0.0334 (16)
C24	0.077 (2)	0.0521 (17)	0.0641 (19)	0.0243 (15)	0.0033 (17)	0.0216 (15)
C25	0.0498 (16)	0.0502 (16)	0.0527 (16)	0.0184 (13)	0.0076 (13)	0.0132 (13)
N1	0.0370 (12)	0.0502 (13)	0.0485 (13)	0.0094 (10)	−0.0002 (10)	0.0174 (10)

N2	0.0321 (12)	0.0523 (13)	0.0471 (13)	0.0061 (10)	−0.0015 (9)	0.0164 (11)

Geometric parameters (Å, °)

C1—C4	1.532 (4)	C12—H12	0.9300
C1—H1A	0.9600	C13—N2	1.346 (3)
C1—H1B	0.9600	C13—C14	1.468 (3)
C1—H1C	0.9600	C14—C15	1.387 (3)
C2—C4	1.523 (4)	C14—C19	1.391 (3)
C2—H2A	0.9600	C15—C16	1.374 (3)
C2—H2B	0.9600	C15—H15	0.9300
C2—H2C	0.9600	C16—C17	1.386 (3)
C3—C4	1.505 (4)	C16—H16	0.9300
C3—H3A	0.9600	C17—C18	1.387 (3)
C3—H3B	0.9600	C17—C20	1.480 (3)
C3—H3C	0.9600	C18—C19	1.378 (4)
C4—C5	1.531 (3)	C18—H18	0.9300
C5—C10	1.379 (4)	C19—H19	0.9300
C5—C6	1.394 (4)	C20—C21	1.389 (4)
C6—C7	1.373 (4)	C20—C25	1.395 (3)
C6—H6	0.9300	C21—C22	1.378 (4)
C7—C8	1.395 (4)	C21—H21	0.9300
C7—H7	0.9300	C22—C23	1.377 (4)
C8—C9	1.375 (3)	C22—H22	0.9300
C8—C11	1.470 (3)	C23—C24	1.378 (4)
C9—C10	1.378 (3)	C23—H23	0.9300
C9—H9	0.9300	C24—C25	1.378 (4)
C10—H10	0.9300	C24—H24	0.9300
C11—N1	1.332 (3)	C25—H25	0.9300
C11—C12	1.396 (3)	N1—N2	1.350 (3)
C12—C13	1.378 (3)	N2—H2	0.79 (3)
C4—C1—H1A	109.5	C13—C12—H12	126.7
C4—C1—H1B	109.5	C11—C12—H12	126.7
H1A—C1—H1B	109.5	N2—C13—C12	105.5 (2)
C4—C1—H1C	109.5	N2—C13—C14	123.3 (2)
H1A—C1—H1C	109.5	C12—C13—C14	131.2 (2)
H1B—C1—H1C	109.5	C15—C14—C19	117.8 (2)
C4—C2—H2A	109.5	C15—C14—C13	120.8 (2)
C4—C2—H2B	109.5	C19—C14—C13	121.4 (2)
H2A—C2—H2B	109.5	C16—C15—C14	120.8 (2)
C4—C2—H2C	109.5	C16—C15—H15	119.6
H2A—C2—H2C	109.5	C14—C15—H15	119.6
H2B—C2—H2C	109.5	C15—C16—C17	121.9 (2)
C4—C3—H3A	109.5	C15—C16—H16	119.0
C4—C3—H3B	109.5	C17—C16—H16	119.0
H3A—C3—H3B	109.5	C16—C17—C18	117.1 (2)
C4—C3—H3C	109.5	C16—C17—C20	121.7 (2)
H3A—C3—H3C	109.5	C18—C17—C20	121.2 (2)
H3B—C3—H3C	109.5	C19—C18—C17	121.6 (2)

C3—C4—C2	108.8 (3)	C19—C18—H18	119.2
C3—C4—C5	112.5 (2)	C17—C18—H18	119.2
C2—C4—C5	109.4 (2)	C18—C19—C14	120.8 (2)
C3—C4—C1	108.4 (3)	C18—C19—H19	119.6
C2—C4—C1	108.1 (3)	C14—C19—H19	119.6
C5—C4—C1	109.5 (2)	C21—C20—C25	117.6 (2)
C10—C5—C6	115.8 (2)	C21—C20—C17	121.2 (2)
C10—C5—C4	123.2 (2)	C25—C20—C17	121.2 (2)
C6—C5—C4	120.9 (2)	C22—C21—C20	121.7 (3)
C7—C6—C5	122.2 (3)	C22—C21—H21	119.1
C7—C6—H6	118.9	C20—C21—H21	119.1
C5—C6—H6	118.9	C23—C22—C21	119.9 (3)
C6—C7—C8	121.3 (3)	C23—C22—H22	120.0
C6—C7—H7	119.4	C21—C22—H22	120.0
C8—C7—H7	119.4	C22—C23—C24	119.2 (3)
C9—C8—C7	116.4 (2)	C22—C23—H23	120.4
C9—C8—C11	123.1 (2)	C24—C23—H23	120.4
C7—C8—C11	120.5 (2)	C25—C24—C23	121.0 (3)
C8—C9—C10	122.1 (2)	C25—C24—H24	119.5
C8—C9—H9	119.0	C23—C24—H24	119.5
C10—C9—H9	119.0	C24—C25—C20	120.5 (3)
C9—C10—C5	122.1 (3)	C24—C25—H25	119.8
C9—C10—H10	119.0	C20—C25—H25	119.8
C5—C10—H10	119.0	C11—N1—N2	105.7 (2)
N1—C11—C12	109.7 (2)	C13—N2—N1	112.4 (2)
N1—C11—C8	122.4 (2)	C13—N2—H2	124 (2)
C12—C11—C8	127.9 (2)	N1—N2—H2	121 (2)
C13—C12—C11	106.6 (2)		

C3—C4—C5—C10	−17.5 (4)	C19—C14—C15—C16	−0.2 (4)
C2—C4—C5—C10	103.6 (3)	C13—C14—C15—C16	180.0 (2)
C1—C4—C5—C10	−138.2 (3)	C14—C15—C16—C17	0.9 (4)
C3—C4—C5—C6	163.6 (3)	C15—C16—C17—C18	−1.2 (4)
C2—C4—C5—C6	−75.3 (3)	C15—C16—C17—C20	179.6 (2)
C1—C4—C5—C6	42.9 (4)	C16—C17—C18—C19	0.9 (4)
C10—C5—C6—C7	1.5 (4)	C20—C17—C18—C19	−180.0 (3)
C4—C5—C6—C7	−179.5 (3)	C17—C18—C19—C14	−0.2 (4)
C5—C6—C7—C8	0.2 (5)	C15—C14—C19—C18	−0.2 (4)
C6—C7—C8—C9	−1.8 (4)	C13—C14—C19—C18	179.7 (2)
C6—C7—C8—C11	178.6 (3)	C16—C17—C20—C21	41.9 (4)
C7—C8—C9—C10	1.8 (4)	C18—C17—C20—C21	−137.3 (3)
C11—C8—C9—C10	−178.7 (2)	C16—C17—C20—C25	−138.3 (3)
C8—C9—C10—C5	0.0 (4)	C18—C17—C20—C25	42.5 (4)
C6—C5—C10—C9	−1.6 (4)	C25—C20—C21—C22	−0.2 (4)
C4—C5—C10—C9	179.4 (3)	C17—C20—C21—C22	179.6 (3)
C9—C8—C11—N1	−9.2 (4)	C20—C21—C22—C23	0.5 (5)
C7—C8—C11—N1	170.4 (2)	C21—C22—C23—C24	−0.4 (5)
C9—C8—C11—C12	171.1 (3)	C22—C23—C24—C25	−0.2 (5)
C7—C8—C11—C12	−9.4 (4)	C23—C24—C25—C20	0.6 (4)
N1—C11—C12—C13	0.2 (3)	C21—C20—C25—C24	−0.4 (4)

C8—C11—C12—C13	−180.0 (2)	C17—C20—C25—C24	179.8 (2)
C11—C12—C13—N2	0.4 (3)	C12—C11—N1—N2	−0.8 (3)
C11—C12—C13—C14	−179.9 (2)	C8—C11—N1—N2	179.4 (2)
N2—C13—C14—C15	−168.9 (2)	C12—C13—N2—N1	−1.0 (3)
C12—C13—C14—C15	11.4 (4)	C14—C13—N2—N1	179.3 (2)
N2—C13—C14—C19	11.3 (4)	C11—N1—N2—C13	1.2 (3)
C12—C13—C14—C19	−168.4 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1^{i}	0.79 (3)	2.25 (3)	2.940 (3)	146 (3)

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

Fig. 1

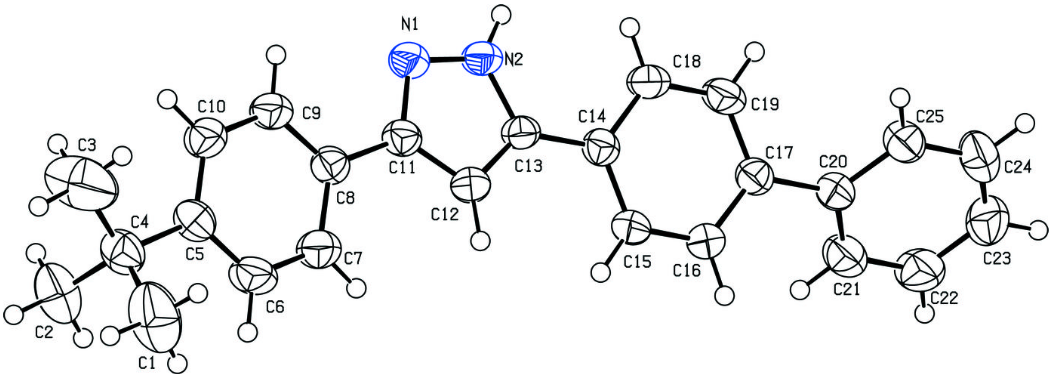
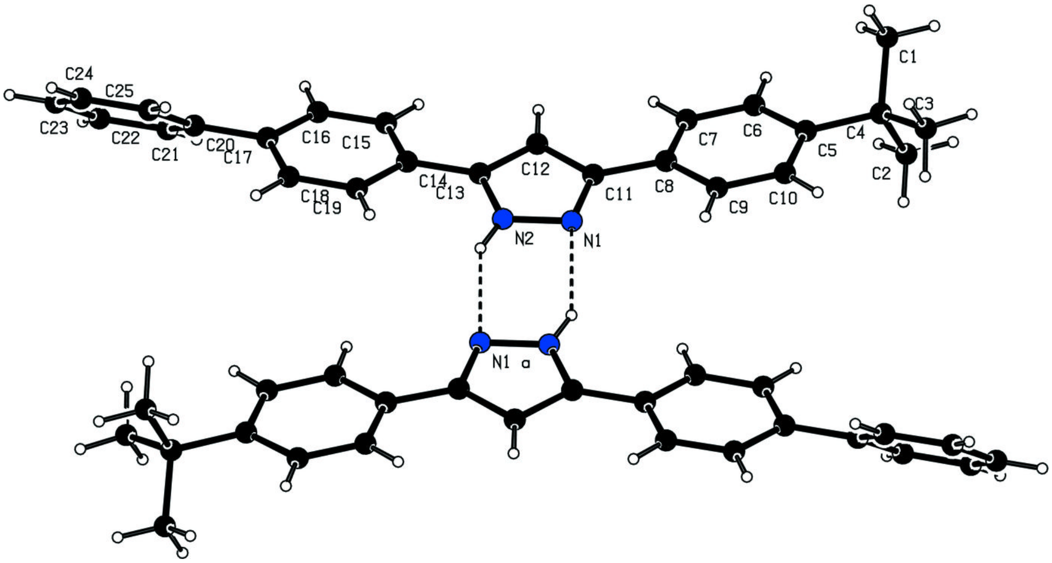

N1
N2
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25

Fig. 2


C24
C25
C23
C22
C21
C20
C17
C16
C15
C14
C13
C12
C11
C18
C19
N2
N1
C8
C7
C6
C9
C10
C5
C4
C1
C3
C2
N1 a