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5-(4-Bromophenyl)-3-phenyl-1-(3-phenyl-propyl)-1H-pyrazole

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Molecules of the title compound, $C_{24}H_{21}BrN_2$, are linked into chains by a single C—H···π(arene) hydrogen bond, but C—H···N hydrogen bonds and aromatic π–π stacking interactions are absent.
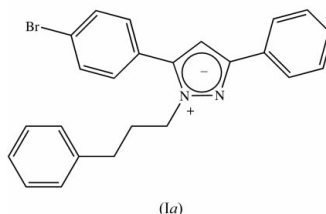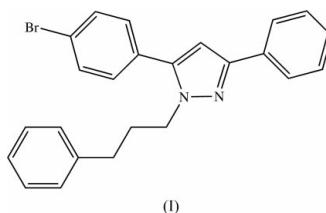
Comment

The title compound, (I), was obtained from the reaction of 1-(benzotriazol-1-ylmethyl)-5-bromophenyl-3-phenyl-1H-pyrazole with styrene in the presence of p-toluenesulfonic acid, as a by-product in the synthesis of fused tricyclic pyrazole systems using benzotriazole methodology (Abonia et al., 2001).

(I)

(Ia)

In the pyrazole ring of (I) (Fig. 1), the bond distances N1—N2 and C3—C4 (Table 1) are slightly less than the average values (1.366 and 1.410 Å; Allen et al., 1987) for bonds of these types. By contrast, bonds N2—C3 and C4—C5 are both longer than the mean values for such bonds (1.329 and 1.369 Å, respectively). These data therefore suggest some contribution to the overall molecular-electronic structure from the polar-
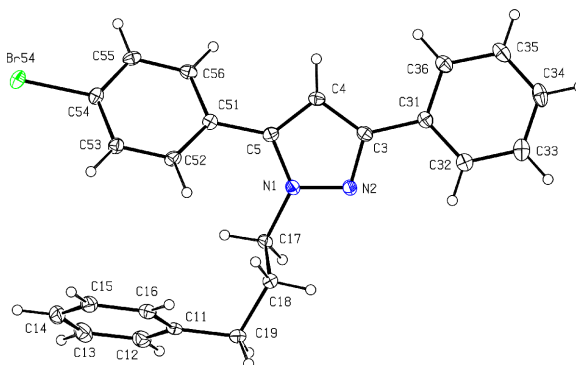

Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

ized and delocalized form (I*a*), in addition to the bond-localized form (I). On the other hand, the C5—N1 distance is at the upper quartile value for such bonds.

Although the sum of the interbond angles at each of atoms N1, C3 and C5 is 360.0° within experimental uncertainty, within each pair of exocyclic angles at these atoms, the individual values show significant differences, particularly those at N1 and C3 (Table 1). The dihedral angles between the pyrazole ring and the two pendent aryl rings at C3 and C5 are 15.3 (2) and 36.9 (2)°. The 3-phenylpropyl substituent at N1 does not adopt the usual chain-extended conformation but, instead, there is a synclinal torsion angle C17—C18—C19—C11 (Table 1).

The molecules of (I) are linked by a single C—H···π(arene) hydrogen bond (Table 2). Atom C18 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* H18*A*, to the ring C51–C56 in the molecule at (1 + x, y, z), so generating by translation a chain running parallel to the [100] direction (Fig. 2). This hydrogen bond may, in fact, be weakly reinforced by a C—H···π(pyrazole) interaction (Table 2), although the corresponding rather long H···$Cg2$ distance ($Cg2$ is the centroid of the N1/N2/C3–C5 ring) and small C—H···$Cg2$ angle preclude any very significant interaction: this may, indeed, simply be an adventitious contact. Despite the presence of the rather basic ring atom N2, there are no C—H···N hydrogen bonds present in (I) nor, despite the presence of three independent aryl rings, are there any aromatic π–π stacking interactions between the molecules. There are no Br···Br contact distances (Ramasubbu *et al.*, 1986) shorter than the sum of the van der Waals radii (Bondi, 1964; Nyburg & Faerman, 1985). Overall, the paucity of direction-specific intermolecular interactions is somewhat unexpected.

Experimental

5–Bromophenyl-3-phenyl-1*H*-pyrazole was converted into the intermediate 1-(benzotriazol-1-ylmethyl)-5-bromophenyl-3-phenyl-1*H*-pyrazole using the general method of Burckhalter *et al.* (1952). A mixture of this intermediate (0.25 g, 0.58 mmol), styrene (0.12 g, 1.15 mmol) and 4-toluenesulfonic acid (30 mg) was heated without solvent for 1 min. After cooling, the resulting paste was dissolved in ethyl acetate and the solution was washed with 5% aqueous NaOH solution followed by water. The organic solution was dried and evaporated to give an oily residue, which was separated by column chromatography on silica gel, using CHCl$_3$ as eluant. The fraction corresponding to the title compound (60 mg) was recrystallized from ethyl acetate–ethanol (1:9 v/v), yielding crystals suitable for single-crystal X-ray diffraction (10 mg, m.p. 353 K). IR (KBr disk, cm^{-1}): 3054, 2928, 2857, 1625, 1595, 1554, 1453, 1383, 760, 694. MS (70 eV): m/e (%) 418/416 (28/25), 314/312 (42/47), 313/311 (100/92).

Crystal data

C$_{24}$H$_{21}$BrN$_2$
M_r = 417.34
Orthorhombic, $Pbca$
a = 5.67550 (10) Å
b = 25.5102 (5) Å
c = 26.5536 (5) Å
V = 3844.51 (12) Å^3
Z = 8
D_x = 1.442 Mg m^{-3}

Mo Kα radiation
Cell parameters from 4410 reflections
θ = 3.1–27.5°
μ = 2.15 mm^{-1}
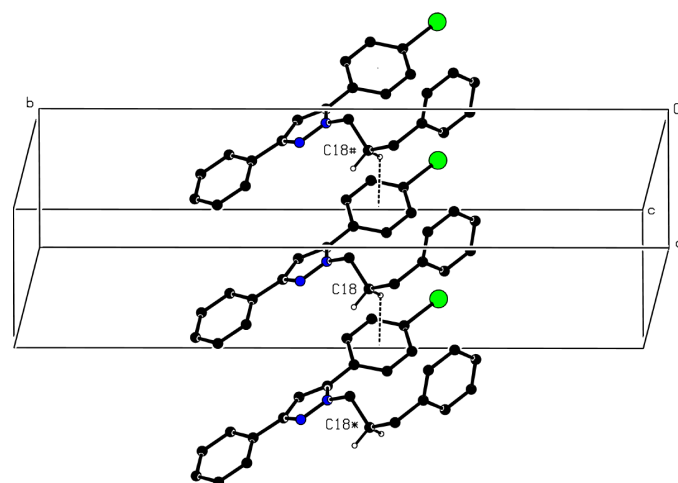T = 120 (2) K
Block, colourless
0.50 × 0.20 × 0.16 mm

Figure 2
Part of the crystal structure of (I), showing the formation of a [100] chain generated by C—H···π(arene) hydrogen bonds. For the sake of clarity, H atoms other than those bonded to C18 have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions (1 + x, y, z) and (x − 1, y, z), respectively.

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.575, T_{max} = 0.712
28 955 measured reflections
4410 independent reflections

3338 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 27.5°
h = −7 → 6
k = −32 → 33
l = −34 → 34

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.078
S = 1.04
4410 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 2.0921P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.350 (2)	C4—C5	1.384 (3)
N2—C3	1.336 (3)	C5—N1	1.365 (3)
C3—C4	1.404 (3)		
C5—N1—N2	112.43 (17)	C4—C5—N1	105.72 (18)
N2—N1—C17	116.49 (17)	N1—C5—C51	124.28 (18)
C5—N1—C17	131.01 (18)	C4—C5—C51	129.9 (2)
N2—C3—C4	110.84 (18)	N1—N2—C3	105.28 (17)
N2—C3—C31	118.76 (19)	C3—C4—C5	105.73 (19)
C4—C3—C31	130.38 (19)		
N2—N1—C17—C18	72.0 (2)	C17—C18—C19—C11	−70.4 (3)
N1—C17—C18—C19	176.02 (17)	C18—C19—C11—C12	115.9 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C18—H18A···$Cg1^i$	0.99	2.81	3.625 (2)	140
C56—H56···$Cg2^{ii}$	0.95	3.08	3.499 (2)	108

Symmetry codes: (i) 1 + x, y, z; (ii) x − 1, y, z.
Notes: $Cg1$ is the centroid of the C51–C56 ring; $Cg2$ is the centroid of the N1/N2/C3–C5 ring.

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All H atoms were located in difference maps, and subsequently treated as riding atoms, with C—H distances of 0.95 Å (aromatic and heteroaromatic) or 0.98 Å (CH_2), and with $U_{iso} = 1.2U_{eq}(C)$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 1995, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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