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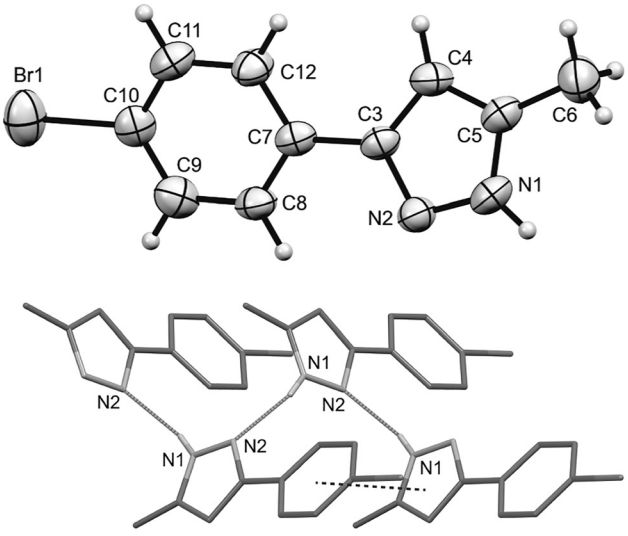
Crystal structure of 3-(4-bromophenyl)-5-methyl-1*H*-pyrazole, $C_{10}H_9BrN_2$



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Abstract

$C_{10}H_9BrN_2$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.9070(3) Å, b = 9.2731(7) Å, c = 17.5641(14) Å, V = 962.09(12) Å^3, Z = 4, $R_{gt}(F)$ = 0.0504, $wR_{ref}(F^2)$ = 0.0947, T = 293(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Pink prism
Size:	0.30 × 0.20 × 0.15 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	4.22 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	29.2°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4442, 2196, 0.039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1346
$N(param)_{refined}$:	119
Programs:	CrysAlis^{Pro} [1], Shelx [2], Mercury [3], Platon [4], WinGX/Ortep [5, 6]

1 Source of materials

3-(4-bromophenyl)-5-methyl-1*H*-pyrazole (L) was purchased from Sigma–Aldrich. 0.05 g L was dissolved in 5 ml of ethanol, slowly heated and left to crystallize. After 24 h clear light pink single crystals of the title compound were filtered and washed with ethanol.

2 Experimental details

The H atoms bonded to pyrazole and phenyl ring were placed at calculated positions and refined as riding atoms with U_{iso}(H) set to 1.2U_{eq} of the parent atom. The H atoms of the methyl group were positioned geometrically and allowed to rotate around the C–C bond to best fit the experimental electron density (HFIX 137 in the Shelx program suite [2]), with U_{iso}(H) set to 1.5U_{eq}(C).

3 Comment

Pyrazole and its derivatives have important pharmacological properties [7]. They bonds to metal atoms as monodentate or bridging bidentate ligands [8]. Strong affinity towards metals may lead to the formation of metal-organic frameworks [9]. N–H···N hydrogen bonding is prevalent interaction in the assembly of pyrazolyl molecules [10]. Their hydrogen bonding capacity may lead to the formation of extended molecular networks [11]. Substituents at the pyrazole ring give more possibilities for supramolecular arrangements. Between phenyl-pyrazole molecules

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.09722 (11)	0.42935 (9)	0.13546 (5)	0.0661 (3)
C3	0.3789 (9)	0.4409 (7)	0.3881 (3)	0.0370 (15)
C4	0.2283 (10)	0.5528 (8)	0.4041 (4)	0.0446 (17)
H2	0.2242	0.6436	0.3817	0.054*
C5	0.0874 (12)	0.5008 (8)	0.4598 (4)	0.0436 (17)
C6	−0.1065 (11)	0.5682 (8)	0.5008 (4)	0.0617 (19)
H6A	−0.2125	0.4947	0.5155	0.093*
H6B	−0.1801	0.6363	0.468	0.093*
H6C	−0.0519	0.6168	0.5454	0.093*
C7	0.5569 (9)	0.4369 (8)	0.3295 (4)	0.0366 (15)
C8	0.7295 (11)	0.3349 (7)	0.3291 (4)	0.0436 (17)
H8	0.737	0.2668	0.3679	0.052*
C9	0.8887 (11)	0.3331 (7)	0.2724 (4)	0.0515 (19)
H9	1.0037	0.2646	0.2729	0.062*
C10	0.8780 (9)	0.4331 (8)	0.2145 (4)	0.0426 (16)
C11	0.7109 (11)	0.5352 (8)	0.2132 (4)	0.048 (2)
H11	0.7037	0.6021	0.1737	0.057*
C12	0.5535 (10)	0.5377 (8)	0.2710 (4)	0.0465 (18)
H12	0.4423	0.6087	0.2709	0.056*
N1	0.1578 (9)	0.3659 (6)	0.4756 (3)	0.0472 (16)
H1	0.0966	0.3116	0.5095	0.057*
N2	0.3359 (8)	0.3253 (6)	0.4319 (3)	0.0416 (14)

stacking interactions are possible [12]. Addition of bromine to phenyl ring may lead to the halogen bonding [13]. Their variability in coordination modes extends their coordinative properties [14]. Phenol-pyrazole ligands influence the structural and magnetic properties of transition metal complexes [15, 16]. Brominated phenyl pyrazoles serve as ligands in the synthesis of molecular magnets [17, 18]. Steric effects of the phenol-pyrazoles, are important for the structural variability of the coordination compounds [19]. As a continuation of our work in the structural and supramolecular properties of the phenyl pyrazole molecules [20, 21], we are reporting the crystal and molecular structure of the 3-(4-bromophenyl)-5-methyl-1H-pyrazole. Bond lengths in the title molecule follow the pattern like in related bromophenyl-1*H*-pyrazole derivatives [22–24]. As in the crystal structure of [22], in the title molecule there are no Br···Br interactions. But, in the crystal structures of [23, 24] the Br···Br interaction of type I [25] is present, $\theta_1 = \theta_2 = 163°$ in Ref. [23] and $\theta_1 = \theta_2 = 156°$ in Ref. [24]. Molecules of the title compound are connected through the N1–H1···N2^i (the H···N distance is 2.24 Å, the N–H···N bond angle is 160°), (i = –1/2 + x, 1/2 – y, 1 – z). View along the *c* axis (lower part of the Figure) shows assembly of molecules into zigzag chain. Dotted black line depicts the closest phenole-pyrazole intermolecular distance. Centroids of the phenol and pyrazole rings from neighboring molecules are at a distance of 4.158(4) Å. Angle between the mean planes of the neighboring rings is 18.0(3)°. Such an arrangement of two cycles creates an opportunity for stacking interaction between their π-systems. Molecular chains are directed along the axis *a*. There are no significant inter-chain contacts. Br atom is not involved in significant intermolecular interactions.

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