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1-Bromo-2,6-bis[(pyrazol-1-yl)-methyl]benzene

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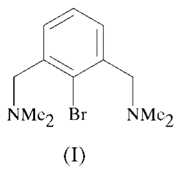
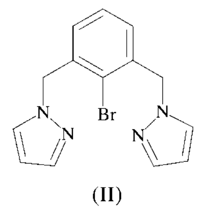
The title compound, $C_{14}H_{13}BrN_4$, has a planar central unit, $(C)_2C_6H_3Br$, the pendant pyrazole rings forming dihedral angles of 83.8 (3) and 89.3 (3)° with this plane. The pyrazole rings are oriented such that there is an approximate twofold axis coincident with the C—Br bond.

Comment

Aryl halides containing nitrogen donor groups are useful reagents for the synthesis of organometallic compounds with interesting stability, structural and reactivity properties (Canty & van Koten, 1995; Albrecht & van Koten, 2001). The most extensively explored reagent is 1-bromo-2,6-bis[(dimethylamino)methyl]benzene, 2,6-$(Me_2CH_2)_2C_6H_3Br$, (I), which gives a wide range of organometallic compounds, including square-planar palladium(II) and platinum(II) complexes, and octahedral platinum(IV) complexes. In these complexes, the $[N—C—N]^-$ ligand normally acts in a planar tridentate fashion, *e.g.* square-planar PtI[2,6-$(Me_2NCH_2)_2C_6H_3$-N,C,N] (Smeets *et al.*, 1987) and *mer*-$PtCl_3$[2,6-$(Me_2CH_2)_2C_6H_3$-N,C,N] (van Koten *et al.*, 1990). We have reported that the closely related reagent 1-bromo-2,6-bis[(pyrazol-1-yl)-methyl]benzene, (II), undergoes an oxidative addition reaction with $[PtMe_2(SEt_2)]_2$ to form *fac*-$PtBrMe_2$[2,6-$(pzCH_2)_2$-C_6H_3-N,C,N], a platinum(IV) complex with the $[N—C—N]^-$ group as a tripodal tridentate ligand (Canty *et al.*, 1990; Canty *et al.*, 2000). Additional interest in these ligand systems has arisen from the discovery that 2,6-(3,5-$Me_2pz)_2C_6H_3Br$ reacts with $[Pt(p\text{-Tol})_2(SEt_2)]_2$ (*p*-Tol is *p*-tolyl) to form PtBr[2,6-(3,5-$Me_2pz)_2C_6H_3$-N,C,N], rather than a Pt^{IV} complex, thus providing a new and facile route to Pt^{II} complexes containing $[N—C—N]^-$ ligands that coordinate *via* a planar rather than a tripodal mode. Nevertheless, the puckering of the five-membered chelate rings is such that the ligand as a whole is not planar, having symmetry degraded to quasi-2 rather than *m* (Canty *et al.*, 2000). This methodology has been extended to 2,6-$(Me_2pzCH_2)_2C_6H_3Br$, resulting in a wide range of applications, *e.g.* the synthesis of nanosize multimetallic catalysts (Dijkstra *et al.*, 2001). The precursor (II) is itself of interest, as the Br atom occupies the position of the coordinated metal atom in PtBr[2,6-(3,5-$Me_2pz)_2C_6H_3$-N,C,N] and the possibility exists of interaction of the position of the coordinated metal with the pyrazole N atom or CH components should the peripheral rings lie quasi-coplanar with the central ring. A structure determination of (II) (Fig. 1) was therefore undertaken in order to explore this point.



(I)



(II)

In the event, the structure was found to be otherwise. The asymmetric unit comprises a single molecule, devoid of crystallographic symmetry, the planes of the peripheral pyrazole rings lying quasi-normal to the central ring [the interplanar dihedral angles are 83.3 (3) and 89.3 (3)°]. In the central ring, the C2—C1—C6 angle is enlarged to greater than 120° at the expense of the pair of exocyclic angles. The capability of derivative ligands to coordinate in planar or tripodal tridentate modes is a consequence not only of the latitude available in terms of free rotation about the bonds to either side of atoms C*n*0 (*n* = 1 or 2) in the pendant groups but also of the capacity to adjust chelate bite in the six-membered rings by puckering of the rings, thus degrading the overall symmetry. In this mode in (II), pyrazole atoms N*n*2 may lie in proximity to

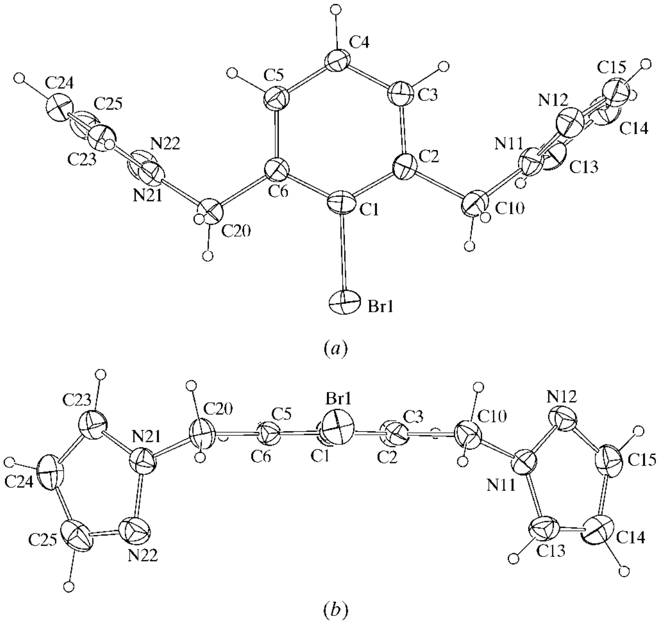


Figure 1
A molecule of (II) projected (*a*) normal to and (*b*) through the central aromatic plane. Anisotropic displacement ellipsoids are shown at the 50% probability level. H atoms, where shown, have arbitrary radii of 0.1 Å.

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the Br atom or, by virtue of the exocyclic asymmetry at atom N*n*1, to the CH*n*3 groups, directed away from it, as extremes. In the event, the C1—C2—C10—N11 and C1—C6—C20—N21 torsion angles are 157.7 (6) and −157.7 (6)°, and the C2—C10—N11—N12 and C6—C20—N21—N22 torsion angles of 91.5 (9) and 78.4 (8)°. The Br atom lies ~2.7 and 2.8 Å from methylene atoms H10*B* and H20*A*, respectively. The angles at atoms C10 and C20 [113.9 (6) and 113.5 (5)°] are appreciably greater than the tetrahedral values, perhaps a consequence of the repulsion between the faces of the pyrazole rings and atoms H3 and H5 (N11···H3 and N21—H5 = 2.5 Å). The exocyclic angles at atoms C2 and C6 (Table 1) are essentially equivalent.

Experimental

Colourless crystals of the title compound, prepared as reported by Canty *et al.* (2000), were crystallized from dichloromethane/petroleum and were found to be suitable for structural studies.

Crystal data

$C_{14}H_{13}BrN_4$
$M_r = 317.19$
Triclinic, $P\overline{1}$
$a = 10.758$ (6) Å
$b = 8.951$ (5) Å
$c = 8.425$ (5) Å
$\alpha = 111.24$ (4)°
$\beta = 100.94$ (4)°
$\gamma = 105.74$ (4)°
$V = 689.3$ (8) Å^3

$Z = 2$
$D_x = 1.528$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 12 reflections
$\theta = 12.2$–14.3°
$\mu = 2.97$ mm^{-1}
$T = 296$ (2) K
Plate, colourless
0.67 × 0.32 × 0.12 mm

Data collection

Syntex *P*21 diffractometer
2θ–ω scans
Absorption correction: Gaussian (*Xtal*3.5; Hall *et al.*, 1995)
$T_{min} = 0.41$, $T_{max} = 0.72$
2231 measured reflections
2231 independent reflections
1304 reflections with $I > 2.00\ \sigma(I)$

$\theta_{max} = 25.1°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -9 \rightarrow 9$
8 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.155$
$S = 1.10$
2231 reflections
172 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F^2) + 2.5F^2 + 0.002F^4]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.917 (7)		
Br1—C1—C2	117.6 (6)	C1—C6—C5	116.9 (5)
Br1—C1—C6	118.6 (4)	C1—C6—C20	121.3 (6)
C2—C1—C6	123.7 (6)	C5—C6—C20	121.8 (7)
C1—C2—C3	116.3 (7)	C2—C10—N11	113.9 (6)
C1—C2—C10	122.7 (6)	C6—C20—N21	113.5 (5)
C3—C2—C10	121.0 (5)		

H atoms were located from difference Fourier maps and placed at idealized positions (C—H = 0.95 Å), with U_{iso}(H) values of $1.25U_{eq}$(C), N- and C-atom positions being unambiguously assigned in the process.

Data collection: *Syntex P*2$_1$ *Software* (Syntex, 1974); cell refinement: *Syntex P*2$_1$ *Software*; data reduction: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1429). Services for accessing these data are described at the back of the journal.

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